University of Bath

PHD

Novel C-organostannyl heterocycles

Waterfield, P. C.

Award date:
1988

Awarding institution:
University of Bath

Link to publication

General rights
Copyright and moral rights for the publications made accessible in the public portal are retained by the authors and/or other copyright owners and it is a condition of accessing publications that users recognise and abide by the legal requirements associated with these rights.

- Users may download and print one copy of any publication from the public portal for the purpose of private study or research.
- You may not further distribute the material or use it for any profit-making activity or commercial gain
- You may freely distribute the URL identifying the publication in the public portal ?

Take down policy
If you believe that this document breaches copyright please contact us providing details, and we will remove access to the work immediately and investigate your claim.

Download date: 13. May. 2019

NOVEL C-ORGANOSTANNYL HETEROCYCLES.

submitted by P.C. Waterfield
for the degree of Ph.D
of the University of Bath

1988

COPYRIGHT

"Attention is drawn to the fact that copyright of this thesis rests with its author. This copy of the thesis has been supplied on condition that anyone who consults it is understood to recognise that its copyright rests with its author and that no quotation from the thesis and no information derived from it may be published without prior written consent of the author."

'This thesis may be made available for consultation within the University Library and may be photocopied or lent to other libraries for the purposes of consultation'.

P. Waterfield

UMI Number: U499566

All rights reserved

INFORMATION TO ALL USERS
The quality of this reproduction is dependent upon the quality of the copy submitted.

In the unlikely event that the author did not send a complete manuscript
and there are missing pages, these will be noted. Also, if material had to be removed,
a note will indicate the deletion.

UMI U499566
Published by ProQuest LLC 2014. Copyright in the Dissertation held by the Author.
Microform Edition © ProQuest LLC.
All rights reserved. This work is protected against
unauthorized copying under Title 17, United States Code.

ProQuest LLC
789 East Eisenhower Parkway
P.O. Box 1346
Ann Arbor, MI 48106-1346

[illegible]
21 24 APR 1939
PHD.

5026627.

CONTENTS

Page

ABSTRACT 1

ACKNOWLEDGEMENTS 3

CHAPTER ONE The Chemistry and Biological Action of Organotin Compounds

1.1 Introduction 4

1.2 Synthetic Routes to Organotin Compounds 5

1.3 The Structures of Organotin Compounds 6

1.3.1 Four Coordinate Organotin Compounds 8

1.3.2 Five Coordinate Organotin Compounds 10

1.3.3 Six Coordinate Organotin Compounds 14

1.3.4 Seven Coordinate Organotin Compounds 18

1.4 Spectroscopy and Structural Identification of Organotin Compounds

1.4.1 Mossbauer Spectroscopy 20

1.4.2 N.M.R. Spectroscopy 26

1.4.3 Infra-red Spectroscopy of Organotins 34

1.4.4 Mass Spectroscopy of Organotins 34

1.5 Organotin Compounds as Biocides

1.5.1 Biological Activity 37

1.5.2 Mechanisms of Toxicity and Environmental Degradation 38

1.5.3 Environmental Chemistry 42

1.6 Heterocyclic Biocides 45

1.7 Organotin Biocides 46

CHAPTER TWO The Synthesis of Triorganostannyl-C-Bonded 1-Methylimidazole, Benzothiazole and Benzoxazole

2.1 Introduction 52
2.2 Synthesis 53
2.3 Spectroscopy
2.3.1 Infra-red Spectroscopy 56
2.3.2 Mass Spectroscopy 56
2.3.3 N.M.R. Spectroscopy 61
2.3.4 Mossbauer Spectroscopy 67
2.4 The Crystal Structure of 2-(Triphenyltin) Benzothiazole 72
2.5 Reaction Chemistry 75
2.6 Experimental 80

CHAPTER THREE The Synthesis and Characterisation of [2-(2'-pyridyl)ethyl]-, [2-(4'-pyridyl)ethyl)- and [2-(N-Pyrrolidin-2-one)ethyl]triphenyltin Compounds and their Derivatives

3.1 Introduction 88
3.2 Synthesis 90
3.3 Spectroscopy
3.3.1 Infra-red Spectroscopy 94
3.3.2 N.M.R. Spectroscopy 97
3.3.3 Mossbauer Spectroscopy 110
3.4 The Crystal and Molecular Structure of [2-(2'-pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate 114

3.5 Experimental 129

CHAPTER FOUR Synthesis of (Heterocyclic Thiomethyl) triphenyltin Compounds and their Derivatives

4.1 Introduction 135
4.2 Synthesis 137
4.3 Spectroscopy
4.3.1 Infra-red Spectroscopy 140
4.3.2 N.M.R. Spectroscopy 141
4.3.3 Mossbauer Spectroscopy 153
4.4 Experimental 156

CHAPTER FIVE The Synthesis and Characterisation of some *N*- and *C*-Organostannyl Tetrazoles

5.1 Introduction 160
5.2 Synthesis 162
5.3 Spectroscopy
5.3.1 Infra-red Spectroscopy 171
5.3.2 N.M.R Spectroscopy 173
5.3.3 Mossbauer Spectroscopy 186
5.4 The Crystal and Molecular Structure of 2,3,4,5-Tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene 189
5.5 Experimental 204

CHAPTER SIX An Investigation into the Thermal Dynamics of *N*-Trialkyltin-5-Substituted Tetrazole Compounds

6.1 Introduction 216
6.2 The Structures of *N*-Trialkyltin-5-Substituted Tetrazoles

6.2.1 Variable Concentration NMR Spectroscopy 219

6.2.2 Variable Temperature NMR Spectroscopy 222

6.3 The Thermal Behaviour of N-Tributyltin-5-alkyl Tetrazoles 232

6.4 The Thermal Cyclisation of 5-Organostannyl-2-Tributylstannyl-Tetrazoles 237

CONCLUSIONS 242

APPENDIX I Synthesis of Organotin Starting Materials 244

APPENDIX II Crystallographic parameters for compounds (6), (16) and (41) 246

APPENDIX III Instrument Details 256

REFERENCES 258

STRUCTURAL FORMULAE 276

List of abbreviations used in this work

ox	8-oxyquinoline anion
py	pyridine
tbp	trigonal bypyramidal
pbp	pentagonal bypyramidal
Ph	phenyl
Bu	butyl
Et	ethyl
Me	methyl
D.M.S.O.	dimethyl sulphoxide
acac	acetyl acetonate anion
H.M.P.A.	hexamethylphosphoric acid
Bzt	benzothiazole
1-MI	1-methylimidazole
Box	benzoxazole
TMS	tetramethylsilane
ppm	parts per million
Het	heterocycle
THF	tetrahydrofuran
Hz	hertz
K	kelvin
ax	axial
eq	equatorial
pymd	pyrimidyl
I.S.	isomer shift

abbreviations continued,

Q.S.	quadrupole split
P.M.T.	pentamethylene tetrazole

Abstract

Several novel organotin compounds containing potentially biologically active heterocyclic ligands have been synthesised and characterised using standard spectroscopic techniques. The structures of three of the compounds have been determined by X-ray crystallography. One particular class of compound has been closely scrutinised by variable temperature nmr.

The structures of trimethylstannyl-, tributylstannyl- and triphenylstannyl- derivatives of 1-methylimidazole, benzothiazole and benzoxazole were critically examined and found to be tetrahedral compounds as expected. The X-ray diffraction study of 2-(triphenylstannyl)-benzothiazole has shown it to have a slightly distorted tetrahedral structure, and this has helped to rationalise the small, but measurable ΔEq values found for these tetraorganotin compounds in the Mossbauer experiments. The reaction chemistry of these air and moisture sensitive compounds was also explored.

Two classes of very similar compounds were synthesised in which the organotin moiety was separated from the heterocyclic group by either a $-CH_2CH_2-$ or a $-CH_2S-$ chain. This was found to effectively stop the hydrolysis of the organotin from the heterocycle and to direct the site of halogenation to a Sn-Ph bond. The structures of these compounds were shown by various techniques to be intramolecularly chelated structures, and this is shown by the X-ray structure of [2-(2'-pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate.

During work re-examining the structures and synthetic utility of 2-trialkylstannyl-tetrazoles it was found that these compounds display a unusual dynamic behaviour, and through a study of this behaviour, several examples of an interesting new type of compound were synthesised, that in which a tin atom forms an integral part of a bi-heterocyclic ring system. The structures of these compounds were characterised by standard techniques and were found to be polymeric and this is confirmed by the X-ray structure of 2,3,4,5-tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene. The mechanisms whereby these compounds were synthesised were closely examined and several alternatives have been described.

ACKNOWLEDGEMENTS

I would like to particularly thank Dr. K.C. Molloy for his friendship, advice and great help during the course of this work. I would also like to thank Dr. M.F. Mahon for carrying out the crystallographic analyses reported here, Dr. S. Blunden and Dr. R. Hill for collecting the variable temperature ^{119}Sn n.m.r. data, Mr. D. Woods for collecting the majority of the ^{1}H, ^{13}C and ^{119}Sn n.m.r. data and Mr. A. Carver for the C.H.N. analyses, thanks are also due to the chemistry technical staff at Bath University, I.T.R.I and S.E.R.C. for funding the work.

I would finally like to thank my parents for their continued support and financial assistance.

CHAPTER 1

THE CHEMISTRY AND BIOLOGICAL ACTION OF ORGANOTIN COMPOUNDS

1.1 Introduction

An organotin compound is defined by the presence of at least one direct tin-carbon bond in the molecule. Tin, a main group IV metal, has two available oxidation states and it is possible to prepare both organotin(II) and organotin(IV) species. The tin(IV) compounds are considerably more stable than those of tin(II) and because of this the tetravalent state compounds dominate the field of organotin chemistry. Tetravalent organotin compounds can be convieniently classified into four groups: mono-, di-, tri- and tetraorganotins. A wide variety of organic ligands can be attached to the tin through σ bonds and the number and nature of the organic groups dramatically affects the properties of the compound particularly in its biological role.

Organic groups may bind to divalent tin(II) species through sigma or pi bonds. However, these compounds are generally extremely reactive or short lived and have until recently, not been extensively studied.

The readers attention is drawn to the several books [1-3] and review articles [4-5] for a discussion on general tin chemistry in greater detail than can be entered into here. Periodic surveys on aspects of tin chemistry are also available [6]

Since 1950 the production of organotin compounds has increased by 1000%, to an estimated 40,000 tonnes per year. The industrial applications are quite diverse ranging from P.V.C. stabilizers, glass coatings, esterification catalysts, wood preservatives, antifouling paints, agrochemicals and various anti-bacterial agents.

This thesis describes the preparation and chemistry of several novel, possibly biocidal, triorganotin compounds in which tin is C-bonded to a heterocycle and also later examines the structures of related compounds in which tin is part of the heterocycle. As an introduction the general synthetic and structural aspects of organotin chemistry are reviewed.

1.2 Synthetic Routes to Organotin Compounds

Tin(IV) chloride is a relatively cheap, colourless liquid that is used as a starting material for nearly all organotin compounds. It is very reactive towards nucleophiles and hence most organometallic reagents such as organolithiums, Grignards and alkyl aluminiums. These reagents, most commonly the Grignards, are used commercially to prepare the appropriate tetraorganotin (Eq.1) although Wurtz coupling (Eq.2) and alkyl aluminiums (Eq.3) have also been used:

$$SnCl_4 + 4RMgX \rightarrow R_4Sn + 4MgClX \qquad (1)$$

$$SnCl_4 + 8Na + 4RCl \rightarrow R_4Sn + 8NaCl \qquad (2)$$

$$3SnCl_4 + 4R_3Al + 4R'_2O \rightarrow 3R_4Sn + 4AlCl_3.R'_2O \qquad (3)$$

Tin-carbon bond formation can also be effected by hydrostannylation of alkenes and alkynes, acidolysis of stannylamines and treatment of organotin halides with other organometallics e.g. ICH_2ZnI.

Mono-, di- and triorganotin halides can be synthesised from the tetraorganotin and stannic chloride using Kocheshkov's comproportionation reactions (Equations 4-6).

By mixing the appropriate stoichiometric quantities of materials together at high temperatures (approx 200°C) the desired organotin halide can be realised. The halides can then be converted to a wide variety of compounds by nucleophilic displacement of halogen. A summary of the main reactions of organotin halides are listed, (Scheme 1).

$$3SnX_4 + R_4Sn \rightarrow 4RSnX_3 \qquad (4)$$

$$SnX_4 + R_4Sn \rightarrow 2R_2SnX_2 \qquad (5)$$

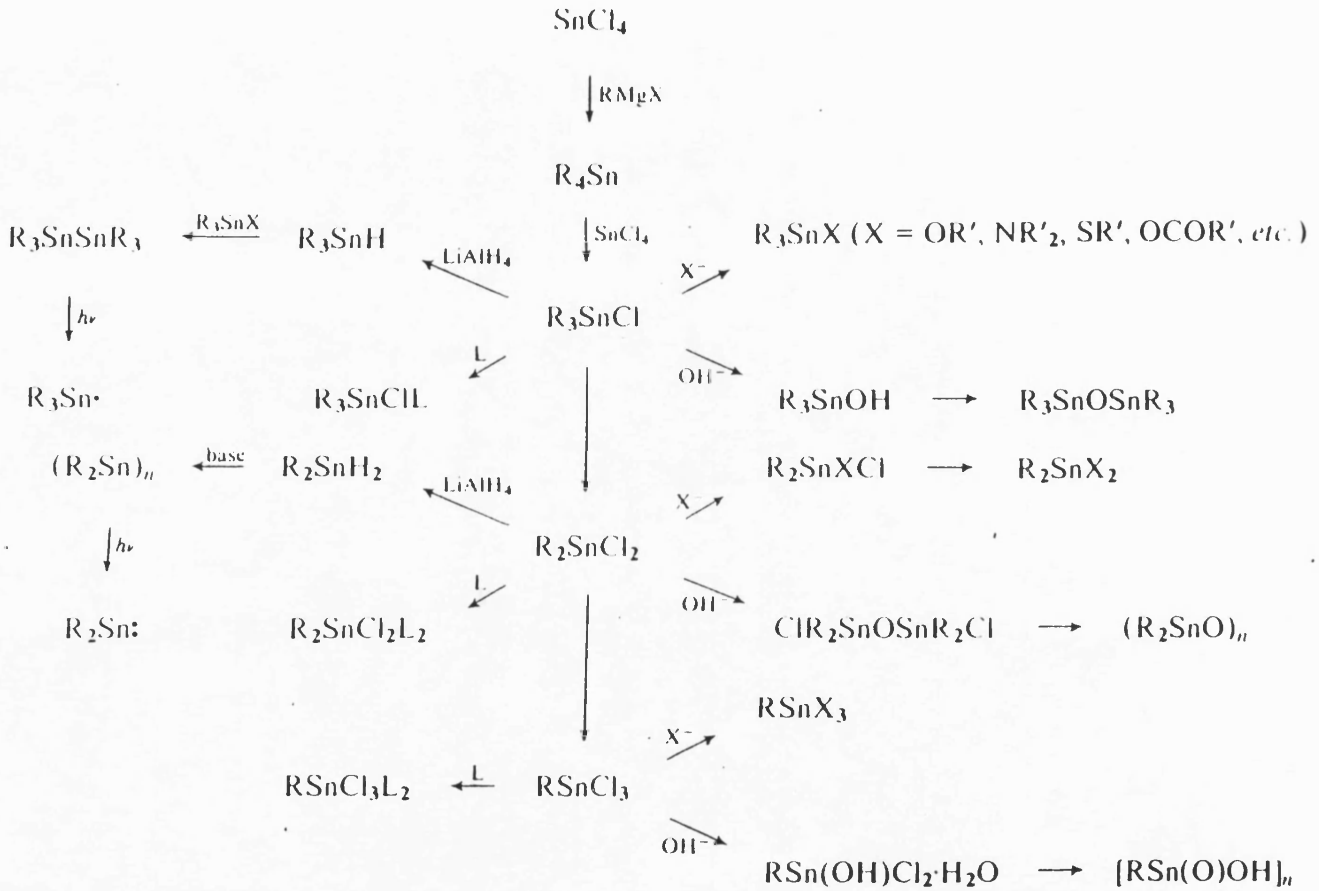
$$SnX_4 + 3R_4Sn \rightarrow 4R_3SnX \qquad (6)$$

1.3 The Structure of Organotin Compounds

In 1963 Hulme [7] demonstrated crystallographically the 5-coordinate nature of the mono pyridine adduct of trimethyltin chloride. Prior to this it was assumed that most organotin(IV) compounds were regular tetrahedral molecules with 4-coordinate tin.

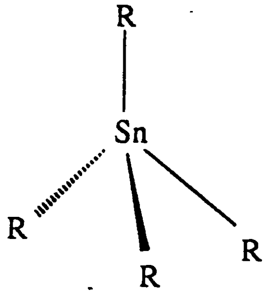
It has now been shown that organotin(IV) compounds can exhibit 4-, 5- 6- and 7-coordination and these structural types are reviewed below. Organotin(II) compounds are also known to show 2- and 3-coordination e.g. the 2 coordinate molecule, $\{(Me_3Si)_2CH\}_2Sn$ [8] but unless the R groups are π-bonded cyclopentadienyl ligands or are strongly sterically hindering, the monomeric stannylenes exist as only short-lived intermediates.

There are several reviews of X-ray crystal structures of tin compounds available [9,10] and new structures are being published continually.

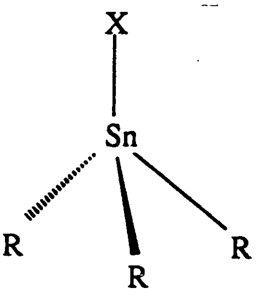


Scheme 1

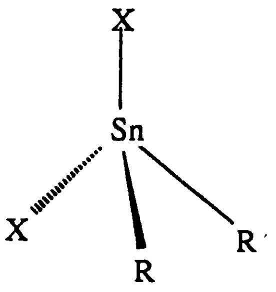
1.3.1 Four Coordinate Organotin Compounds



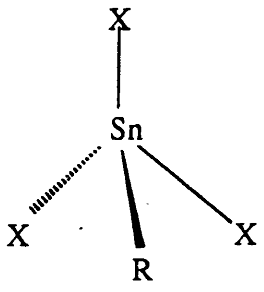
(I)



(II)

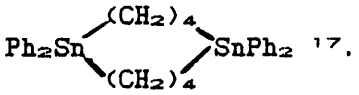


(III)



(IV)

4-Coordinated organotin(IV) compounds are always tetrahedral and there are a large number of reported $\mathrm{R_4Sn}$ structures which demonstrate this, e.g. $\mathrm{Sn(C_6F_5)_4}$ [11], $\mathrm{Sn(C_6H_4Me\text{-}4)_4}$ [12], $\mathrm{Sn(2\text{-}thienyl)_4}$ [13] and more recently $\mathrm{Sn(CPh{=}CMe_2)_4}$ [14]. Unsymmetric compounds $\mathrm{R_3SnR'}$ have also been reported e.g. $\mathrm{Ph_3SnCH_2I}$ [15], $\mathrm{Ph_3SnC_7H_7}$ [16] and



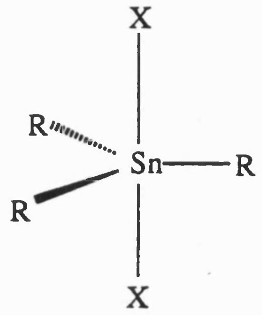
$\mathrm{Ph_2Sn{<}^{(CH_2)_4}_{(CH_2)_4}{>}SnPh_2}$ [17].

Tetraorganotins do not generally expand their coordination number because they are poor electron pair acceptors. If one organic group is replaced by an electronegative substituent, X, the Lewis acidity of the tin atom increases and this enhances the possibility that tin will increase its coordination number. If the R groups are bulky and/or the X group is not too electronegative (e.g. I, Br vs. Cl, S vs. O) the tetrahedral architecture can be retained, e.g. $\mathrm{[(Me_3Si)_2CH]_3SnCl}$ [18] and $\mathrm{Ph_3SnSC_6H_4\text{-}Bu^t\text{-}4}$ [19].

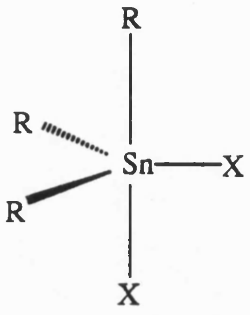
If bulky organic ligands or low electronegative X groups are used, 4-coordinated $\mathrm{R_2SnX_2}$ compounds can be prepared, e.g., the dimeric $\mathrm{[{}^tBu_2SnSe]_2}$ [20] and the cyclic trimer $\mathrm{(Me_2SnS)_3}$ [21].

There are very little structural data regarding 4-coordinate tetrahedral $RSnX_3$ compounds. The adamantane cage-like structure of $(MeSnS_{3/2})_4$ [22] has the tin in a 4-coordinate, near-tetrahedral environment and a recent X-ray diffraction study [23] of the structure of CH_3SnI_3 has shown it to be comprised of discrete, non-interacting monomers which show an almost ideal tetrahedral geometry, in which the <C-Sn-I is 116.1° and the average <I-Sn-I is 105.92°.

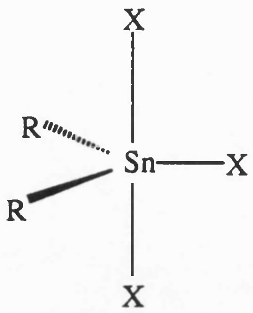
1.3.2 Five Coordinated Organotin Compounds



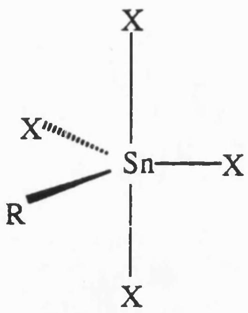
(V)



(VI)



(VII)



(VIII)

5-Coordinated organotin compounds appear to be mainly trigonal bypyrimidal (tbp) in shape, however Ng *et al.* have recently published an example of square pyramidal (SP) geometry [24,25]. Tribenzyl-(2-thiolpyridine-N-oxide)tin(IV) achieves this geometry via the Berry interconversion mechanism (Fig 1).

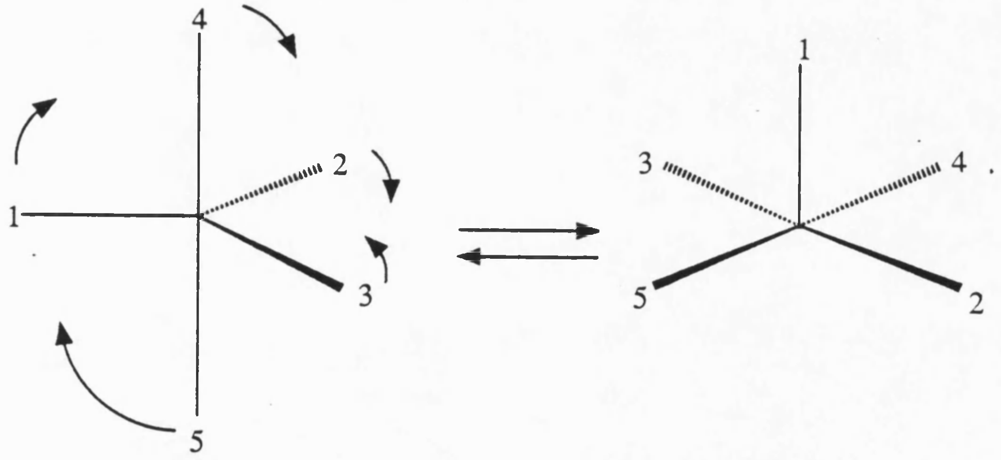
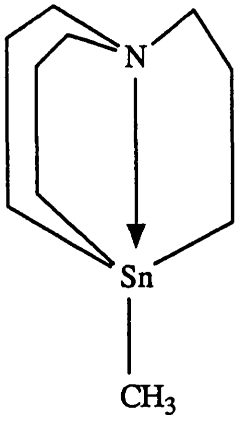

4
2
1
3
5
1
3
4
5
2

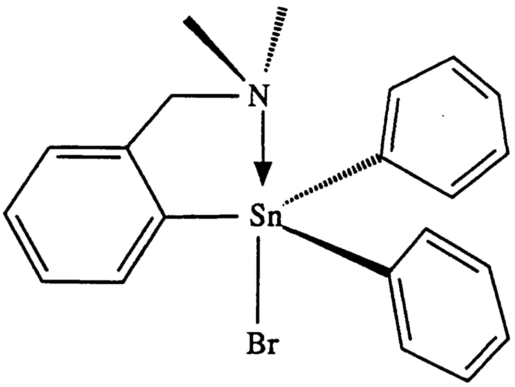
Figure 1.

Generally tetraorganotin species do not show expanded coordination, but trimethyl(trifluoromethyl)tin forms a 1:1 (tbp) adduct with HMPA triamide [26] and $MeSn(CH_2CH_2CH_2)_3N$ has been shown crystallographically [27] to also have this geometry but with the methyl group forced into the axial position (IX).

R_3SnX_2 species can show two possible isomeric forms, (V) and (VI). The trans-isomer (V) is the most common, this usually occurs as the result of either bridging interactions, e.g. Me_3SnCN [28] (giving rise to polymeric structures) or anionic species e.g. $R_3SnCl_2^-$ (R=Me, Bu, Ph). Neutral monomeric forms of the trans-isomer do exist and these include $Me_3SnCl.py$ [7] and (3-thienyl)$_3$SnBr.Ph$_3$PO [29]. An interesting form of this isomer is shown by the chelation effect of an equatorial organic ligand with a donor atom substituent located 3 or 4 carbon atoms away from the tin-ligand bond, e.g. C,N-[2{(dimethylamino)methyl}phenyl]-diphenyltin bromide [30] structure (X). The most electronegative atoms are in the axial positions. The structure is not entirely regular and deviations from ideal trans-tbp geometry generate a <N-Sn-Br of 171°.



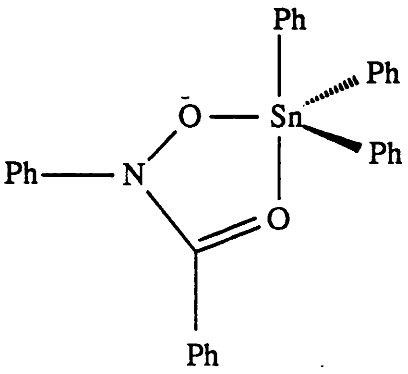
(IX)



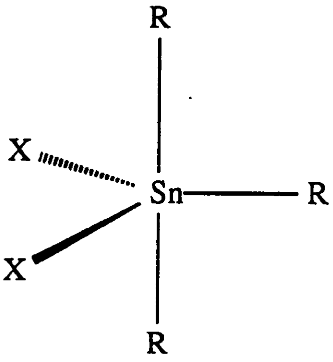
(X)

Bidentate ligands are capable of forming infinite polymer chains. The degree of linearity of the polymer will vary according to the nature of the bridging ligand. Classification of the various polymer types has been given [31] and it has been shown that small bridging groups such as -CN give rise to almost linear polymers e.g. Me_3SnCN [28], whilst larger bridging groups such as $-O_2SMe$ produce helical structures.

The cis-analogues, (VI), invariably arise from intramolecular chelation effects. This is exemplified by (N-benzoyl-N-phenylhydroxylamine)triphenyltin [32], (XI). Due to ring strain there is a significant deviation from ideal trans-tbp geometry. The trans C-Sn-O angle is 157.2° and the axial Sn-O interaction is longer at 2.308 Å than the equatorial Sn-O bond at 2.091 Å [32]. It can be seen that the donor atoms are always at an axial and equatorial site. There has been a report [33] of an organotin compound with meridional R_3SnX_2 geometry, (XII) however this has not been confirmed by X-ray diffraction studies and the issue is still very much in doubt.



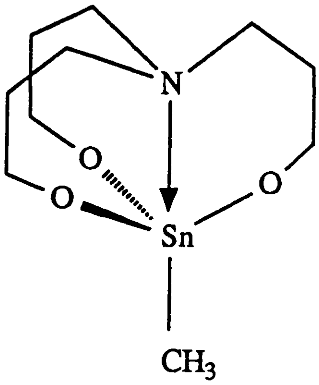
(XI)



(XII)

The diorganotin compounds, R_2SnX_2, that have been demonstrated to exhibit tbp geometries, (VII) are relatively scarce, primarily due to the increased Lewis acidity at tin and the more usual concurrent expansion of coordination to 6. Some examples of 5-coordination do exist, e.g. $Me_2SnCl_3^-$ [34] and [N-(2-hydroxyphenyl)-salicyladimine]dimethyltin [35]. In both cases the methyl groups occupy equatorial sites.

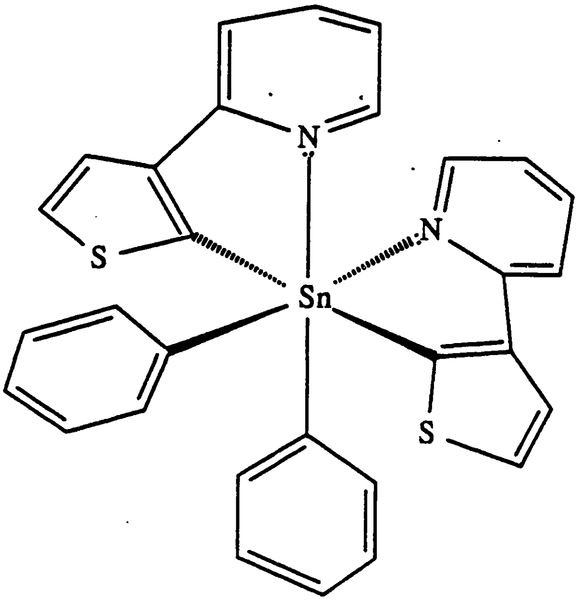
Very few 5-coordinate monoorganotin, species $RSnX_4$ (VIII) have been reported. The one example of note is $(Ph_4As)^+(MeSnCl_4)^-$ [36] in which the methyl group occupies an equatorial site. The structures of monoorganostannatranes have been shown to have tbp geometries [37] but with the organic group forced into an axial site (XIII).



(XIII)

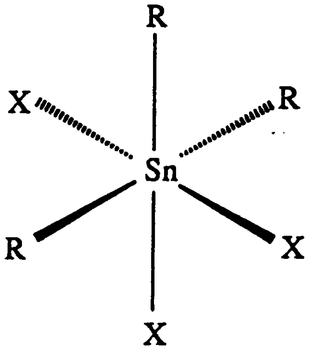
1.3.3 Six Coordinated Organotin Compounds

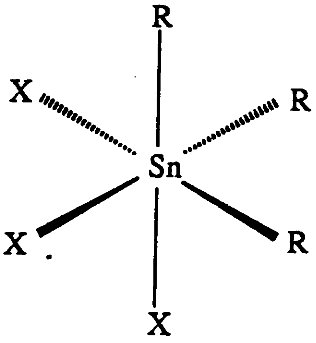
Tetraorganotins generally have a low Lewis acidity and consequently are reluctant to expand their coordination number. There is a unique example of a 6-coordinate tetraorganotin recently confirmed by X-ray diffraction studies, bis[3-(2-pyridyl)-2-thienyl-C,N]diphenyltin [38] (XIV) which shows a cis configuration of the more electronegative donor nitrogen atoms. 6-Coordinate triorganotin compounds are equally rare but two compounds have been recently reported [39,40] with both mer and fac, (XV) and (XVI) geometries.



(XIV)

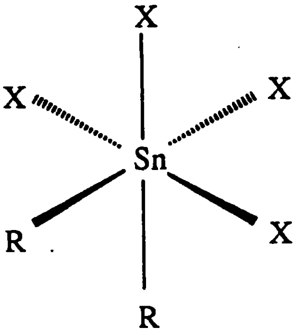
The fac compound is formed using the tridentate tris-(pyrazolyl)borate ligand [40] and the mer isomer occurs in the coordination polymer $Ph_3SnO_2CH_3$ [39]. However, in the latter case it must be noted that one Sn-O bond is abnormally long (Sn-O : 3.206 Å), and the structure is not retained in solution.

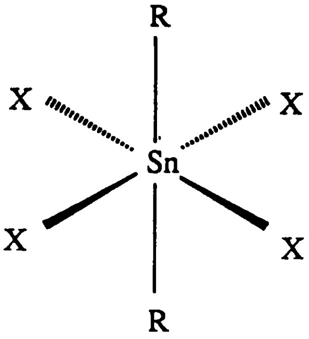




(XV) (XVI)

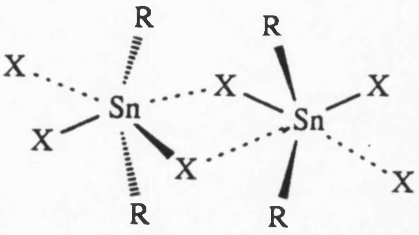
Diorganotin ,R_2SnX_2, compounds will readily increase the coordination number to 6 and isomeric forms have been identified, (XVII) and (XVIII).





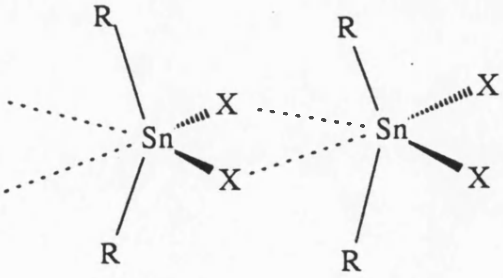
(XVII) (XVIII)

The diorganotin dihalides and pseudohalides have a strong tendency to form intermolecular polymeric species. The structure of the most regular, dimethyltin difluoride was reported in 1966 [41] and was shown to consist of infinite two dimensional sheets of regularly spaced coplanar tin and fluorine, with the methyl groups above and below the plane. The structures of the polymeric dihalides vary considerably with the organic group and the halogen or pseudohalide involved in the bridging. The structures for dimethyltin dichloride [42], diethyltin dichloride [43] and dibromide [43] are very similar. The arrangement of groups around the tin atom now describe an irregular octahedral trans-R_2SnX_2 geometry with coplanar chlorines and bridging chlorines pairs (XIX).



(XIX)

Diethyltin diiodide [43], dimethyltin diisothiocyanate [44] and bis(chloromethyl)tin dichloride [45] form a different type of structure in which the chlorine atoms bridge in a chelating fashion, (XX).

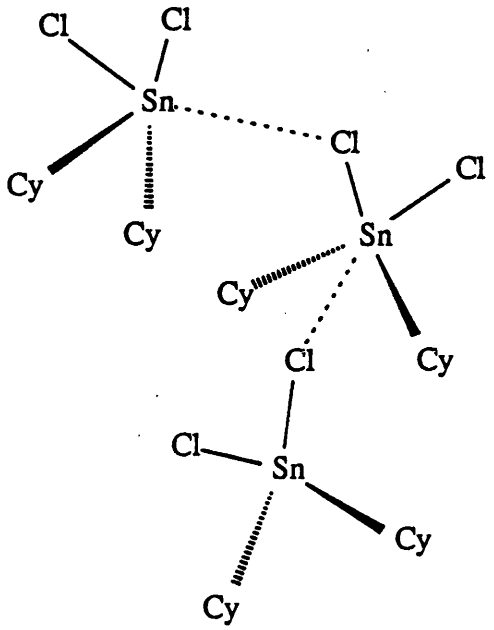


(XX)

Green and Bryan reported [46] the structure of diphenyltin dichloride as a distorted tetrahedron and although the C-Sn-C angle opens to 127°, the evidence for long range additional Sn.....Cl interactions is very weak. This fine balance between which geometry an R_2SnX_2 compound adopts has been highlighted by Molloy and Tagliavini [47]. The crystal structure of dicyclohexyltin dichloride was established independently by the two groups [48,49] and two different modifications were found. Molloy *et al.* found a 6-coordinate structure similar to (XX), whereas Tagliavini *et al.* described their structure as 'tetrahedral' with long monochlorine bridged interactions, Sn--Cl, 3.54Å, (XXI).

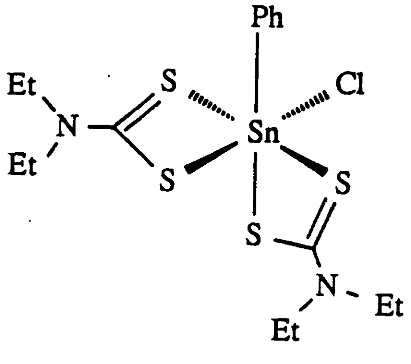
The variation in the differing structures of diorganotin dichlorides is primarily the result of varying Lewis acidities on the tin atom, but a secondary effect is the steric interactions of the organic ligands, indeed as in the previous case, the balance is so fine that minor differences in the crystallisation can be enough to change the structure.

Diorganotins may also produce discrete 6-coordinate monomers by chelating with bidentate ligands. When two bidentate ligands are present the trans-isomer appears to be the favoured configuration. There are many reported examples e.g. $Me_2Sn(acac)_2$ [50], $(H_2NCOCH_2CH_2)_2SnCl_2$ [51] and $\{CH_2(COOEt)CH(COOEt)\}_2SnBr_2$ [52]. Most of these structures have distorted octahedral geometries and in the latter compound the C-Sn-C angle is 148°, significantly away from the ideal trans angle of 180°. Again, the distortions are produced by ligand repulsions and differences in donor atom strength e.g. bidentate ligands such as $-SCSNMe_2$ will display different Sn-S bond lengths. There are reported examples of the cis-isomer and these include $Me_2Sn(ox)_2$ [53] and $Ph_2Sn(SCSNEt_2)_2$ [54]. The structure of the latter compound is quite distorted and the C-Sn-C bond angle is forced open to 101.4°, 11.4° away from the ideal cis angle.

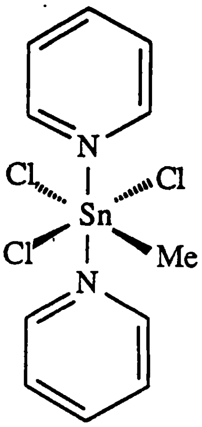

Cl
Cl
Sn
Cy
Cy
Cl
Cl
Sn
Cy
Cy
Cl
Cl
Sn
Cy
Cy

(XXI)

Monoorganotin compounds are strongly Lewis acidic and will readily form 6-coordinate structures e.g. chloromonophenyltin bis(N,N-diethyldithiocarbamate) [55] with a cis arrangement of chelating groups, (XXII), or a trans arrangement e.g. $MeSnCl_3.2py$ [56], (XXIII).


Ph
Et
S
Cl
N
Sn
Et
S
S
S
N
Et
Et

(XXII)

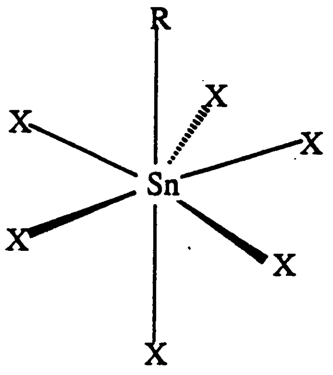

N
Cl
Cl
Sn
Cl
Me
N

(XXIII)

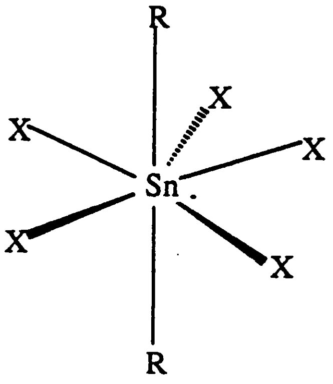
1.3.4 Seven-coordinated organotin compounds

Organotin species can form 7-coordinate structures of two distinct compositions, both of which exhibit pentagonal bypyramidal (pbp) geometry (XXIV) and (XXV).

An example of the $RSnX_6$ form is given by $MeSn(NO_3)_3$ [57]. The methyl group occupies one axial site and oxygen atoms occupy the other and 5 equatorial sites to give a distorted pentagonal bypyramidal configuration. An example of a diorganotin forming a R_2SnX_5 form was reported [58] by Pelizzi *et al.* 2,6-Diacetylpyridine bis(2-aminobenzoylhydrazone)diphenyltin forms a distorted, pentagonal bypyramidal trans arrangement. The two phenyl rings on the tin lie above and below the plane and each tin atom is coplanar with three equatorial nitrogens and two oxygens.



(XXIV)



(XXV)

1.4. Spectroscopy and Structural Identification of Organotins

The wealth of information that can be extracted from single crystal X-ray diffraction studies has provided the organotin chemist with sufficient data to catalogue the structures of hundreds of organotins. However simple X-ray diffraction does have its limitations, for example, i) many organotins are liquids at room temperature and ii) many organotins do not form suitable single crystals.

The general techniques of U.V.[2], I.R.[2, 59] and mass spectroscopy can provide information on the natures of the groups present, ^{1}H and ^{13}C n.m.r. can provide information on ligand structure. The presence and oxidation state of tin can be determined using E.S.C.A [60].

The elucidation of the structures of organotin compounds has been considerably improved with the relatively new techniques of ^{119m}Sn Mossbauer spectroscopy (since 1960) and ^{119}Sn n.m.r (1960) and even more recently cross polarized magic angle spinning (CP-MAS) solid state ^{119}Sn n.m.r., the published results of which are still relatively scarce [61-65]. These relatively new techniques are discussed in greater depth below.

1.4.1. Mossbauer Spectroscopy

The Mossbauer effect was first observed for tin in 1960 [66]. Since then several general reviews [67-71] and many books [72-75] dealing with theoretical and chemical applications of the Mossbauer phenomena have been published.

The Mossbauer effect is the emission and resonant absorption of γ-rays in certain elements without loss of energy due to recoil of the nucleus. The effect is observed for tin when the source, the metastable ^{119m}Sn isotope emits a 23.875 KeV γ-ray and excites a ^{119}Sn atom from ground to the first excited state. The exciting γ-radiation is highly monochromatic but the range of γ energies can be modulated using the Doppler effect by mounting the source on a movable support. The isomer shift (δ) is the energy difference between the nuclear transition in the absorber nucleus and that of the source (for tin usually SnO_2 or $BaSnO_3$). The energy differences are such that velocities of a few mmsec^{-1} are usually enough to match the transitions.

The Mossbauer effect is very sensitive to quite small changes of electron density around the absorber nuclei. These changes, due to differing chemical environments, are primarily the result of changes in the electron density of the valence 5s orbitals which have a finite chance of existing at the nucleus. The isomer shift parameter, δ can be classically computed and the following relationship has been proposed:-

$$\delta = K\{|\psi_{5s}(0)_{a}|^2 - |\psi_{5s}(0)_{s}|^2\}.\delta R/R \qquad (7)$$

where K is a constant for a given isotope, $\psi_{5s}(0)_{a}$ is the Schrodinger wavefunction for the absorber's 5s orbital, $\psi_{5s}(0)_{s}$ is the wavefunction for the source's 5s orbital and $\delta R/R$ is the change in atomic radii from excited to ground state.

δ Is related to the 5s electron density of the absorber and hence it is a probe to the oxidation state of the metal. It is not unexpected then that Sn(II), Sn(IV) and Sn(0) fall into characteristic regions of a total velocity range -0.61 to +4.69 $\mathrm{mmsec^{-1}}$ (with respect to SnO_2 at 0.00 $\mathrm{mmsec^{-1}}$). It is now generally accepted [70] that the Sn(II) compounds appear above +2.10 $\mathrm{mmsec^{-1}}$.

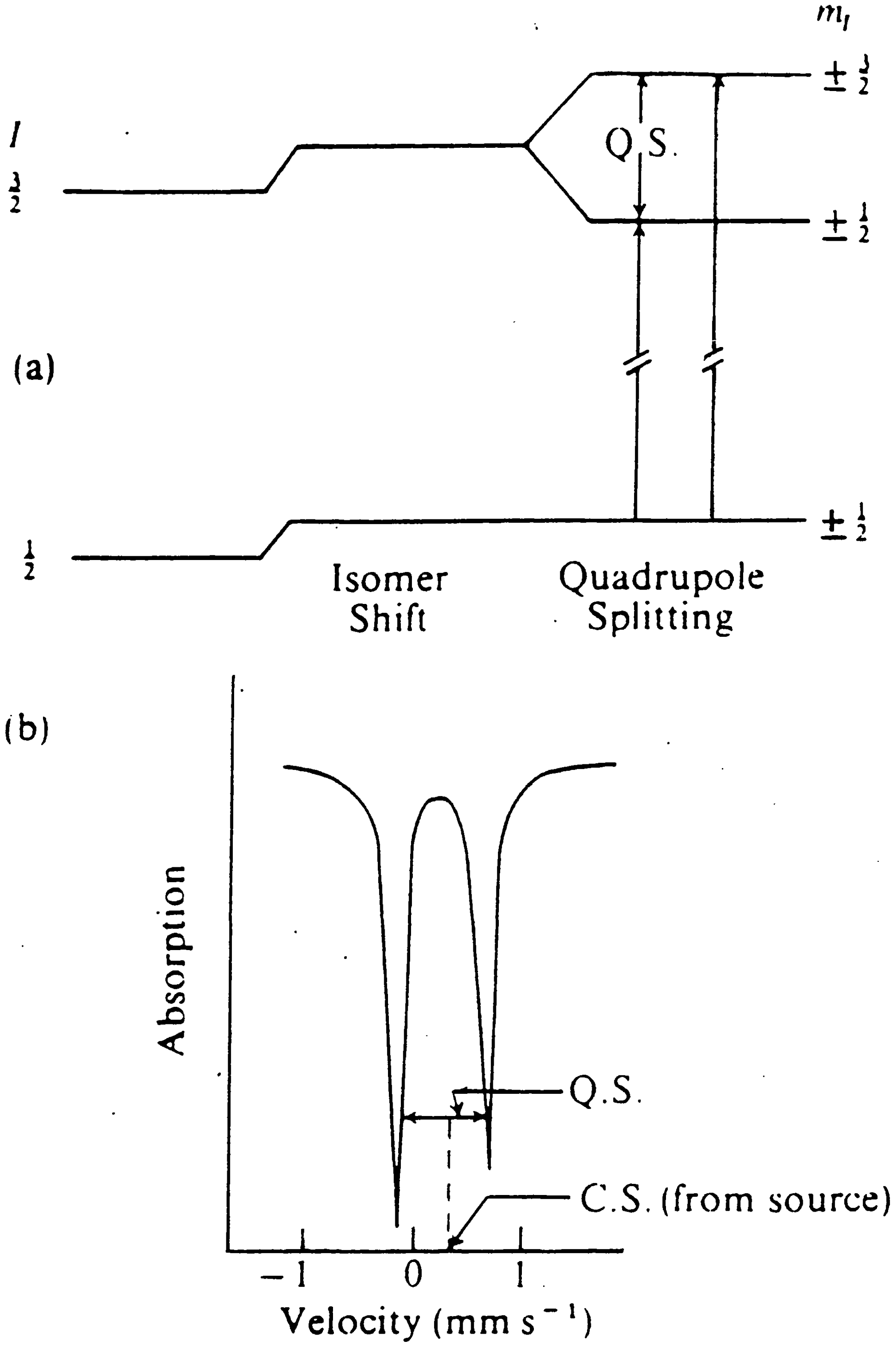
Tetravalent, 4-cordinate tin generally bonds through hybrid sp^3 orbitals. With greater numbers of ligands there is an reduction of the 5s-electron density at the tin nucleus and a concomittant drop in the isomer shift is observed. The effect is seen in the series [69]:- $SnBr_4$ δ=1.14 $\mathrm{mmsec^{-1}}$, $SnBr_5^-$ δ=0.99 $\mathrm{mmsec^{-1}}$ and $SnBr_6^{2-}$ δ=0.90 $\mathrm{mmsec^{-1}}$.

The isomer shift is also affected by the electronegativity of the groups attached to the tin atom. If the polarity of the bond is such that 5s electron density is reduced at tin the δ value will be reduced. As the Mullikan electronegativity of the halide increases it is generally held that δ is reduced, e.g. for the series [57]:- Ph_3SnI δ=1.41 $\mathrm{mmsec^{-1}}$, Ph_3SnBr δ=1.40 $\mathrm{mmsec^{-1}}$ and Ph_3SnCl δ=1.37 $\mathrm{mmsec^{-1}}$. The electron withdrawing properties of an R group also affect the δ value in a similar way. This is exemplified by the series [76]:- Bu_4Sn δ=1.35 $\mathrm{mmsec^{-1}}$, Et_4Sn δ=1.30 $\mathrm{mmsec^{-1}}$, Me_4Sn δ=1.20 $\mathrm{mmsec^{-1}}$ and Ph_4Sn δ=1.15 $\mathrm{mmsec^{-1}}$. The δ value decreases as the organic ligand becomes more electron withdrawing. For a given coordination number the stereochemistry of the compound is another factor to influence the isomer shift. Cis-isomers usually have lower δ values than trans-isomers and this is probably due to a higher % of s-character in the Sn-C bonds of the latter [77].

Quadrupole splitting (ΔEq) occurs when an electric field gradient (e.f.g.) is generated at the nucleus, as a result of a non-cubic arrangement of valence electrons. The effect of the e.f.g. is to partially relieve the degeneracy of the I=3/2 energy levels and a characteristic two-line spectrum is obtained (Fig 2). ΔEq is the resultant energy difference of the two transitions and δ is the centroid of the two peaks relative to the source.

The magnitude of the quadrupole splitting parameter is much more sensitive to the nature, number and stereochemistry of the surrounding ligands than δ. The point-charge model [78] seeks to calculate the theoretical ΔEq values from ideal geometries. On this basis, for molecules involving two ligands R and X, the model predicts definite ranges for certain geometries. Regular tetrahedral R_3SnX and R_2SnX_2 compounds give ΔEq values in the range 1.00-2.40 $mmsec^{-1}$. 5-coordinate trans R_3SnX_2 compounds give ΔEq values in the range 3.00-4.00 $mmsec^{-1}$, whilst the cis isomers give values in the range 1.70-2.40 $mmsec^{-1}$. The octahedral R_2SnX_4 compounds can be either cis or trans and regardless of the nature of X. The former gives ΔEq values around 2.00 $mmsec^{-1}$ and the latter around 4.00 $mmsec^{-1}$. The experimental data are in excellent agreement with the model [79]. The model also suggests that 5-coordinate R_3SnX_2 structures should give slightly lower δ values than trans-R_2SnX_4, and this too is in agreement with the data.

The ΔEq parameter is a useful aid in determining the geometry around R_2SnX_4 isomers. Bancroft [80] observed that in these systems ΔEq is generated predominantly by the organic ligand. With this consideration the ΔEq parameter and the <C-Sn-C angle have been related:-


m_I
I
$\frac{3}{2}$
$\pm\frac{3}{2}$
Q.S.
$\pm\frac{1}{2}$
(a)
$\frac{1}{2}$
$\pm\frac{1}{2}$
Isomer Shift
Quadrupole Splitting
(b)
Absorption
Q.S.
C.S. (from source)
−1
0
1
Velocity (mm s⁻¹)

(a) Nuclear energy levels, the isomer shift, and quadrupole splitting for Igr=1/2, Iex=3/2

(b) Resultant Mossbauer spectrum.

Figure 2.

$$|\Delta Eq| = 4\{R\}(1-3\sin^2\theta\cos^2\theta)^{1/2} \qquad (8)$$

where {R} is the partial quadrupole split for R and <C-Sn-C =(180-2θ)°. The ΔEq values smoothly increase as <C-Sn-C increases. Good agreement is found for a wide range of <C-Sn-C (110.7°-180°) [31].

Information regarding the structure and distribution of molecules in the solid can be extracted from a variable-temperature Mossbauer experiment. The recoil-free fraction (f) of Mossbauer events is dependent on the amplitude of thermal motion of the ^{119}Sn nucleus, and is related to the area under the spectral peaks (A_T):-

$$A_T \propto f = \exp(-E_\gamma\langle x^2\rangle/hc) \qquad (9)$$

where E_γ is the energy of the γ-ray and $\langle x^2\rangle$ is the mean square vibrational amplitude of the tin atom. Thus a plot of $\ln(A_T/A_{77K})$, (normalised for comparison) vs. T (temp/K) will result in a straight line of negative slope. The more tightly bound the tin atoms, the more gentle the slope. Discrete, monomeric compounds tend to have slopes ca -1.8x10^{-2} K^{-1} and polymers (e.g Sn(II)O) have slopes ca -0.2x10^{-2} K^{-1} Various classes of polymers have been identified [32] and correlated with their variable temperature Mossbauer characteristics.

1.4.2. N.M.R. Spectroscopy

Organotin compounds may contain such nuclei as; ^{1}H, ^{13}C, ^{19}F, ^{29}Si, ^{31}P in addition to ^{119}Sn, all of which have nuclear spins of I=1/2 and have reasonable abundances. Therefore high resolution n.m.r. is an ideal tool to study the structures of organotins and it is becoming increasingly common to quote the ^{119}Sn chemical shift and related coupling constants in the literature. Tin has ten naturally occurring isotopes of which 3 have nuclear spin I=1/2: ^{119}Sn (8.58%), ^{117}Sn (7.57%) and ^{115}Sn (0.34%). ^{119}Sn resonances are usually quoted due to the slightly higher abundances and the greater magnetic receptivity. The field has become the subject of several reviews [83-85,86] and books [87,88].

The ^{119}Sn chemical shift range covers some 3000 ppm and are quoted relative to Me_4Sn (Fig 3). There are several major principles that relate the structure of the organotin with the experimentally determined n.m.r. spectral parameters, and these are briefly reviewed below.

As the electron donating ability of the R group increases, the tin atom becomes progressively more shielded and the ^{119}Sn chemical shift (δ) value moves to lower frequencies, (Table 1). The δ values for the Ph derivatives appear anomalous, since the greater electron withdrawing properties of the Ph group should give less shielding, hence a positive δ value, however this effect is masked by the increased polarizability of the Ph group. Other unsaturated R groups e.g. alkenyl, allyl and vinyl cause similar effects.

In a series of compounds, R_3SnX, the ^{119}Sn δ value should move to

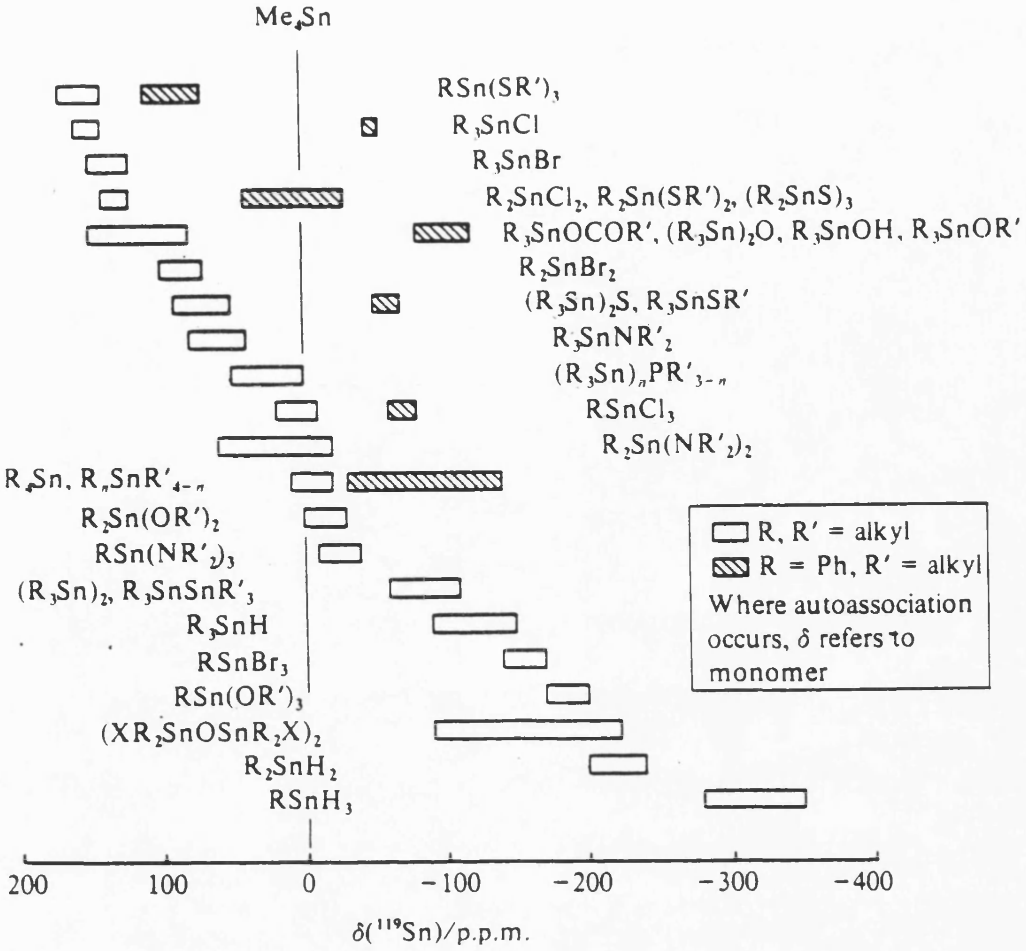


Figure 3: 119Sn nmr chemical shifts of organotin compounds in non-coordinating solvents

Table 1: The Variation of δ(^{119}Sn)/ppm with R group

R	RSnCl$_3$	R$_2$SnCl$_2$	R$_3$SnCl
Me	+20	+141	+164
Et	+6.5	+126	+155
^{n}Bu	+6.0	+122	+141
^{t}Bu	-	+52	-
Ph	-63	-32	-43

higher frequencies with increased inductive withdrawing power of X [89]. This effect is illustrated by a series of monomeric Me_3SnX compounds, where δ is plotted against the Pauling electronegativity of X [90] (Fig 4). Cheremisin *et al.*[91] disagree and argue that with the organotin halide derivatives the dominating factor influencing the $\delta(^{119}Sn)$ values is the bulk or polarizability of the halogen and that electronegativities play only a minor role.

Several workers [89,92,93] have reported that 5-, 6- and 7-coordinate organotin species show ^{119}Sn signals which occur at much lower frequencies than the 4-coordinate derivatives. For systems with similar R groups, δ is reduced by approximately 150 ppm. per step [93] on going from 4- to 5- to 6- coordination and δ is reduced by a further 100 ppm. for 7-fold coordination. It is speculated that this is primarily caused by π-bonding effects and occupancy of tin 5d orbitals. Examples of 4-, 5-, 6- and 7- coordinate diphenyltin compounds are given in Table 2. Hunter and Reeves have shown [89] that the dilution of trimethyltin halides in non-polar solvents has only a slight effect on the $\delta(^{119}Sn)$ values and this indicates that a) no coordinating interaction occurs with the solvent and b) the trimethyltin halides do not self-associate in solution. Polar coordinating solvents e.g. acetone, dimethyl sulphoxide and pyridine can produce large decreases in the $\delta(^{119}Sn)$ value by complexing with the Lewis acidic tin centre to form enhanced coordination adducts, and this effect is dependent on the concentration, (Table 3).

If an organotin species has strong intermolecular forces a chemical shift-concentration study will reveal dramatic increases in the $\delta(^{119}Sn)$ value as the concentration decreases. McFarlane and Wood [94]

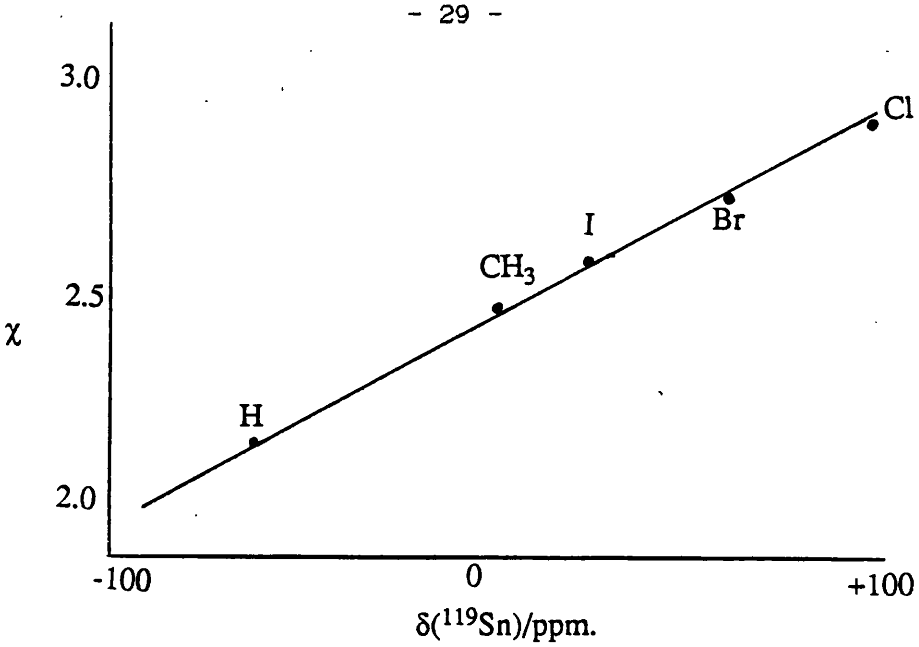


Figure 4: Dependance of ^{119}Sn chemical shifts upon the Pauling electronegativity χ of substituents for some Me_3SnX compounds

Table 2: Effect of coordination number on the ^{119}Sn chemical shift.

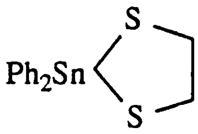
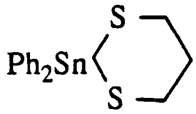
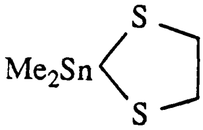
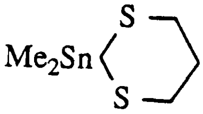
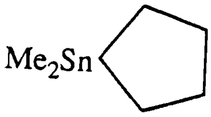
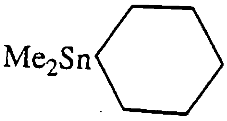
Compound	Coordination No.	$\delta(^{119}Sn)/ppm$	Ref.
Ph_4Sn	4	-128.1	85
Ph_3SnH	4	-164.5	85
Bis[3-(2-Pyridyl)-2-thienyl-C,N]$Ph_2Sn(IV)$	5	-245.5	38
$Ph_3SnCl.Py$	5	-203.5	85
$Ph_3SnI.DMSO$	5	-228.5	85
$Ph_2(Cl)ox$	5	-245.0	85
$Ph_2Sn(ox)_2$	6	-397.0	85
$Ph_2Sn(acac)_2$	6	-514.0	95
$PhSn(mdtc)_3$ [a]	7	-659.0	96

[a] mdtc=N,N'-dimethyldithiocarbamate.

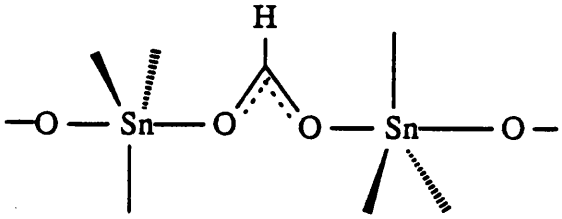
Table 3: Values of $\delta(^{119}Sn)$ for Me_3SnCl in a variety of solvents

Solvent System	$\delta(^{119}Sn)$/ppm
3% in Ph-H	+164.2
5M in CCl_4	+160.0
5% in CS_2	+152.7
3% in MeCN	+92.7
1:1.3M Me_3SnCl:Py	+36.5
1:4.5M Me_3SnCl:Py	-0.45
1:12.7M Me_3SnCl:Py	-9.52

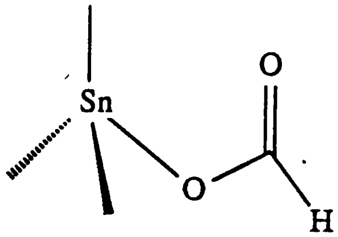
Table 4: Variation of $\delta(^{119}Sn)$ with ring size

Compound	$\delta(^{119}Sn)$/ppm
	+78
	+28.5
	+190
	+149
	+53
	-42.5

have shown that a 3M solution of trimethyltin formate in deuterochloroform forms a 5-coordinate oligomeric or polymeric species (XXVI) $\delta(^{119}Sn)=2.5$ ppm., however if the concentration is reduced to 0.05M the organotin forms discrete 4-coordinate monomeric units (XXVII) $\delta(^{119}Sn)= +152$ ppm.



(XXVI)



(XXVII)

The (CP-MAS)-^{119}Sn solid state n.m.r data on several self-associating organotin carboxylates, thiophosphates and dioxastannolanes have been recently recorded [51,52] and are at great variance with the solution state data. With the former two types of compound the change on dissolution is from 5-coordinate polymers to discrete 4-coordinate monomers and the latter from a 6-coordinate polymer to a 5-coordinate dimer.

It has been reported that when the tin atom is incorporated into a 5- or 6-membered ring system, the ^{119}Sn nuclear shielding is markedly dependent upon ring size (Table 4). The higher frequency shifts for the 5-membered ring compounds are due to a deformation in the <X-Sn-X (X=-S- or $-CH_2-$) from the tetrahedral angle [97], i.e. a "ring-strain" effect.

1-, 2-, 3- and 4-Bond spin-spin coupling constants have been measured for tin against a wide variety of spin I=1/2 nuclei [98]. The two most important with regard to stereochemical information are $^2J(^{119}Sn, ^1H)$ and $^1J(^{119}Sn, ^{13}C)$. Studies relating the coupling constants and the <C-Sn-C bond angles in methyltin compounds [98,99] have been made. The bond angles are calculated from empirical equations (10) and (11) and provide information on coordination number, the amount of s-character in the tin-carbon bonds and stereochemistry about the tin . It is apparent that as the <Me-Sn-Me increases the coupling constants also increase (Table 5).

$$\theta(\mathrm{deg}) = 0.0161*[^2J(^{119}Sn, ^1H)]^2 - 1.32*[^2J(^{119}Sn, ^1H)] + 133.4 \qquad (10)$$

$$[^1J(^{119}Sn, ^{13}C)] = 11.4*\theta - 875 \qquad (11)$$

For a given methyltin, the results from both equations generally agree to within +/- 4°. Holeček *et al.* [100] have given the chemical shifts and coupling constant ranges for various 4- and 5-coordinate triphenyltin compounds. The chemical shifts and the coupling constants $^1J(^{119}Sn, ^{13}C)$ for 4-coordinate compounds are in the range -40 to -120 ppm. and 550-660 Hz. respectively. The $\delta(^{119}Sn)$ values for 5-coordinate (tbp) compounds are in the ranges -180 to -260 ppm. The trans-tbp compounds have $[^1J]$ values in the range 750-850 Hz. and the cis-tbp compounds have coupling constants in the range 600-660 Hz.

Table 5: Effect of <Me-Sn-Me on $^{1}J(^{119}Sn, ^{13}C)$ and $^{2}J(^{119}Sn, ^{1}H)$ [a]

Compound	<Me-Sn-Me	$^{1}J(^{119}Sn, ^{13}C)$ [b]	$^{2}J(^{119}Sn, ^{1}H)$ [b]	Geometry
Me_4Sn	109.5	336.3	54.7	(I)
Me_3SnCl	110.1	379.7	58.1	(II)
$Me_3SnCl.Py$	118.2	472.0	67.0	(V)
Me_2SnCl_2	117.9	469.4	69.0	(III)
Me_2SnBr_2	115.5	442.6	67.0	(III)
$Me_2SnCl_2.2L$ [c]	165.3	1009.0	113.0	(XVIII)

[a] Non-coordinating solvent unless specified otherwise.

[b] Hz.

[c] $L=Me_2SO$.

1.4.3. Infra-red Spectroscopy of Organotins

Although not yet a strictly quantitative technique, infra-red spectroscopy is a useful tool for fingerprinting previously unknown compounds and several reviews of i.r. data have been published [59,101,102]. In addition to the identification of compounds, infra-red spectroscopy can also yield valuable structural information. Due to symmetry considerations, tetrahedral trimethyltin and dimethyltin halides (except F) exhibit two bands near 500 cm^{-1} and 550 cm^{-1} and have been assigned to the symmetric and antisymmetric Sn-CH$_3$ stretching vibrations [103]. It has been noted that some trimethyltin compounds, e.g. Me$_3$SnF and various carboxylates, only show one band around 550 cm^{-1} and the absence of the second band would indicate coplanar tin and methyl groups. Lewis acidic organotins may form adducts with a suitable donor solvent, e.g. DMSO and H$_2$O. Solution state infra-red analysis of the number of Sn-CH$_3$ stretches can shed light on the acceptor properties of the methyltin, and prove the coplanarity of the tin and the methyl groups. The X-ray crystal structure has confirmed this for Me$_3$SnCl.py [7]. Attempts have been made to distinguish various Sn-X stretches where X is a wide range of groups. Several known Sn-X stretches are summarised in Table 6.

1.4.4. Mass spectroscopy of organotins.

Tin occurs in one of ten isotopes (112-124 atomic weight) and the fragmentation patterns of tin containing species are very distinctive. Chambers and co-workers [109] have summarized most of the common fragmentation modes of the organotins, (Eq's 12-14).

Table 6

Assignments of Infra-red Vibrations Involving Sn-X Groups

Compound	Assignment	Frequency (cm^{-1})	Ref
Me_3SnH	Sn-H str.	1843	104
Bu_3SnH	Sn-H str.	1820	104
Ph_3SnH	Sn-H str.	1825	105
Me_3SnCl	Sn-Cl str.	315 and 336	106
Me_3SnBr	Sn-Br str.	219	106
Ph_3SnCl	Sn-Cl str.	327	107
$(Ph_3Sn)_2O$	Sn-O-Sn str.	777	108

Bond cleavage: $[Sn-R]^{\cdot +} \rightarrow [Sn]^{+} + R^{\cdot}$ (12)

The odd electron parent-ion, usually low in abundance, expels an $R^{\cdot}$ radical to yield an even electron tin species. Elimination of a further R radical to give an odd-electron ion is not a favoured reaction, elimination of a neutral alkane to give another even-electron ion being more favourable.

Alkene elimination: $>Sn-CH_2-CH_3]^{+} \rightarrow >Sn-H]^{+} + C_2H_4$ (13)

This process is observed for even-electron ions and it is common for compounds which possess a β-methylene group, e.g. butyl, propyl and cyclohexyl ligands. Aryltins do not show this fragmentation mode. An alkene is eliminated with proton transfer to yield another even-electron ion.

Elimination of a neutral molecule: $Ph_3Sn]^{+} \rightarrow Ph_2 + [Ph-Sn]^{+}$ (14)

This process occurs for predominantly even-electron ions, although in tetraphenyltin both odd- and even-electron species expel biphenyl as a product.

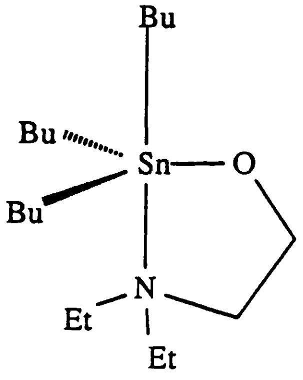
Jamieson and co-workers [110] have reported the mass spectral fragmentation reactions of several organotin pesticides including Ph_3SnOH, $Ph_3SnOCOCH_3$ and $Bu_3SnOCOCH_3$. The peaks found most commonly for organotins are the even-electron ions R_2SnX^{+}, R_3Sn^{+}, RSn^{+} and SnX^{+}.

1.5 Organotin Compounds as Biocides

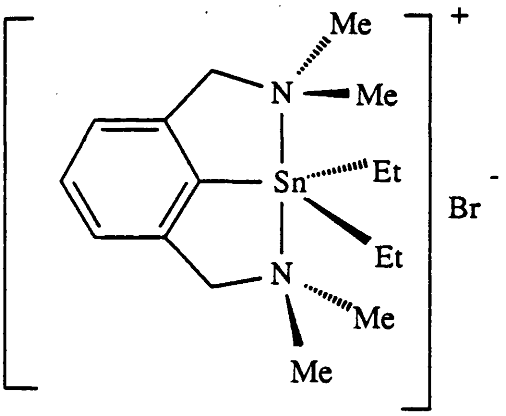
The biocidal activity of organotins was first commented upon in 1929 by Hartman *et al.* [111]. However no systematic survey was carried out until 1954 when van der Kerk explored the *in vitro* fungicidal and antibacterial properties of organotin compounds [112].

1.5.1 Biological Activity

The biological properties of triorganotin compounds are now well established. The compounds show a marked species dependence according to the nature of the R group used, (Table 7). In general the nature of the X group appears to be relatively unimportant [113], however coordinately saturated triorganotins, e.g. XXVIII and XXIX show much lower activites [114,115].



(XXVIII)



(XXIX)

It is speculated [114] that this is due to the reduced tendancy of these compounds to attack the active sites of an organism's protein.

Several commercial organotin biocides are based on tri-n-alkyltin acetates and activity/structure curves can be drawn for various species, (Fig 5). With longer alkyl chains, e.g. Octyl, the triorganotin compounds, (R_3SnX), are essentially non-toxic to all species.

Diorganotin, R_2SnX_2, compounds have received limited commercial explotation as biocides, although dibutyltin dilaurate is used as an effective anthelmintic (de-wormer) for treating poultry. Diorganotin species are currently being tested as anti-tumour agents. It has been shown [116] that the presence of cis halogens is essential for activity, therefore octahedral adducts of diorganotin dihalides and bidentate ligands have been screened. The nature of the toxic action is more dependent on the X group than with the R_3SnX compounds.

Monoorganotins do not appear to have any important toxic action towards mammals [117], but they show the typical pattern of decreasing toxicity with chain length, with the maximum again falling at monoethyltin derivatives.

1.5.2. Mechanisms of Toxicity and Environmental Degradation.

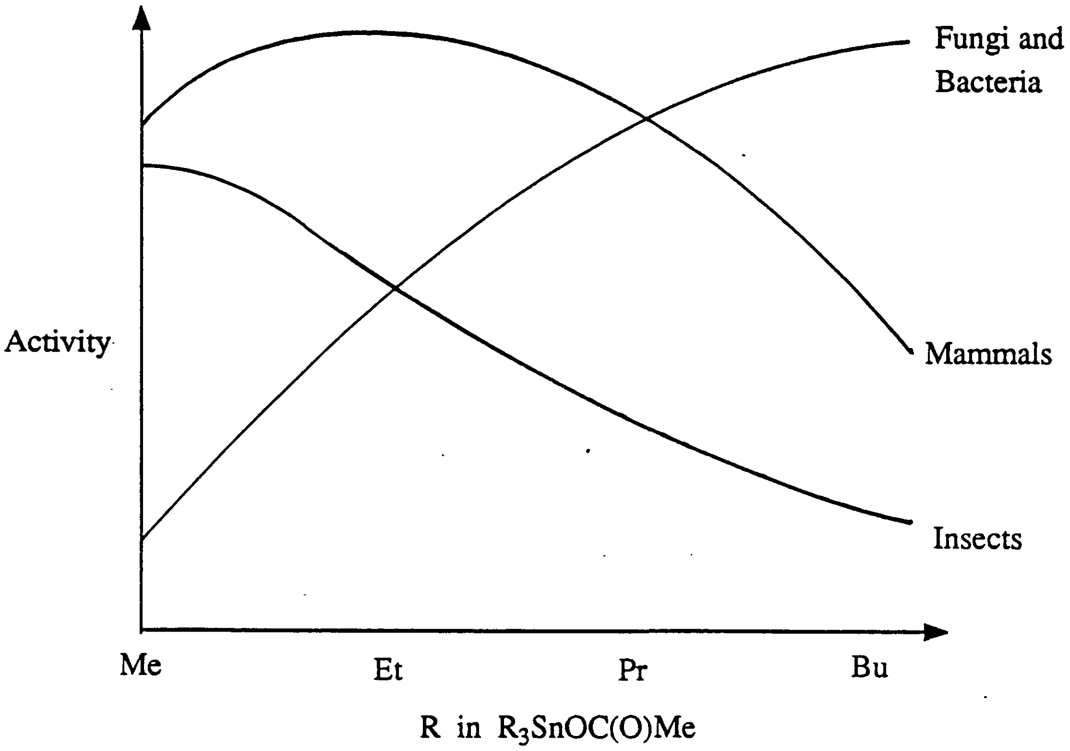
Tetraorganotin compounds are relatively inert biologically. However studies by Caujolle *et al.* [118] have revealed that R_4Sn compounds are rapidly converted *in vivo*, by the liver [119], to triorganotins which are toxic.

Aldridge [120] established that dialkyltin and trialkyltin compounds inhibit oxgen uptake in tissues or mitochondria. The biological action of dialkyltin compounds is different from trialkyltins. The toxicity of the former is due to the dialkyltin reacting with two adjacent thiol groups on specific enzymes, such as lipoic acid or lipoyl dehydrogenase, thus blocking the oxidation of α-keto acids [120]. The more toxic lower dialkyltin halides are Lewis acidic and the probable reaction pathway of biological action involves the formation of an

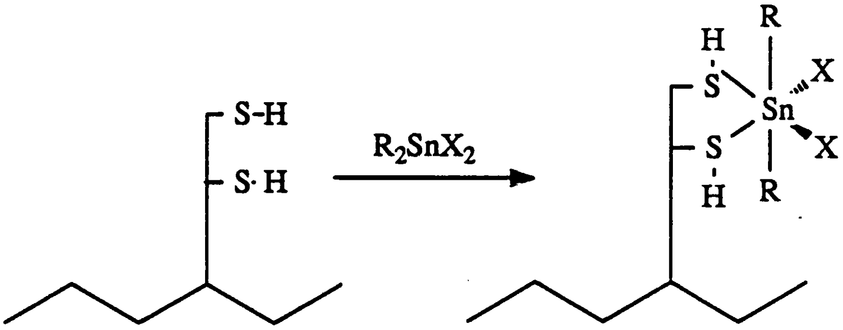
Table 7:

Species	R in most active R_3SnX compound
Insects and Mammals	Me
Mammals	Et
Gram-negative bacteria	Pr
Gram-positive bacteria, fish ,fungi and molluscs	^{n}Bu
Fish, fungi and molluscs	Ph
Mites	Cy, Neophyl

Fig 5.

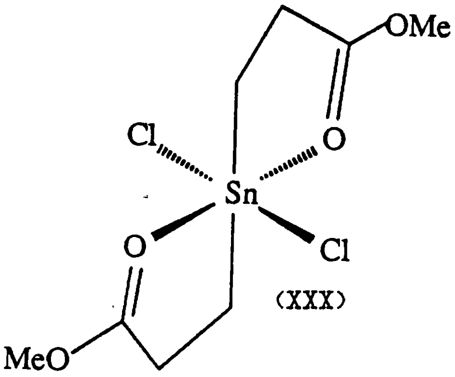


an octahedral trans $R_2SnX_2(SH-)_2$ type species or a tetrahedral species, (Scheme 2).



Scheme 2.

The Lewis acidity of the tin is the prime factor influencing the binding strength of the dithiol adduct and is dictated by the electronegativity of the X groups. Reduction in electronegativity [2] or utilisation of R groups that coordinately saturate the tin [2], (XXX), renders the dialkyltins essentially non-toxic.



(XXX)

The biochemical mode of action of the triorganotin compounds is the disruption of mitochondrial function. These are small intra-cellular particles which contain a complex system of enzymes important to oxidative metabolism [122]. The disruption manifests itself in three different ways:

a) Interaction with the basic energy conservation system involved in ATP synthesis [120].

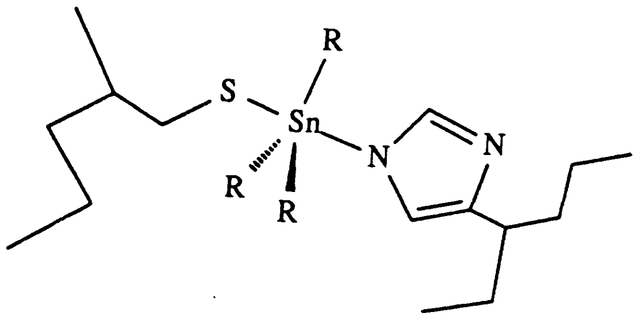
b) An interaction with mitochondrial membranes causing swelling and disruption [123].

c) The interference of a Cl^-/OH^- ion-gradient maintained by the mitochondrial membrane [124].

The processes of b) and c) are related and due to the ionophoric action of triorganotins mediating an exchange of SCN^-, I^-, Br^-, Cl^- or F^- for hydroxide ions and the optimal pH for certain enzyme reactions is altered. Inhibition of ATP synthesis, process a), is dependent on the effectiveness of the triorganotin to bind to certain sites on the mitochondrial proteins. Two sites with high and low affinity have been found [125] and several attempts have been made to identify the amino acids involved with the binding of organotins to the proteins.

The results of binding of Et_3Sn derivatives to cat haemoglobin originally suggested to Elliot *et al.* [126] that the coordination sphere about tin was R_3SnN_2, the two donor ligands being imidazole nitrogens from a pair of histidine residues, however more recent evidence has suggested that both cysteine and histidine residues bind to tin [127,128]. The original Mossbauer experiments using Et_3Sn- derivatives bound to cat haemoglobinon, performed by Elliot [129] and Farrow *et al.*

[129] found that the ΔEq value were generally less than 2.3 mmsec^{-1} and this value led the workers to propose a cis-R_3SnNS arrangement. Recently Barbieri has shown that from a point-charge approach the predicted ΔEq for a trans-R_3SnNS species is only *ca* 2.13 mmsec^{-1} [130], and this seems to indicate that the trans geometry (XXXI)is correct.



(XXXI)

1.5.3 Environmental Chemistry.

It is desirable for toxic biocides to be ultimately degraded into non-toxic inert substances. The tin-carbon bond is susceptible to slow environmental hydrolysis leading eventually to non-toxic SnO_2. Since tonnes of organotin(IV) compounds are used in many natural environments it is important to understand the degradation mechanisms and ultimate speciation of these biocides.

The photochemical breakdown of triphenyltin compounds to inorganic tin, via diphenyl- and monophenyltin derivatives has been extensively studied [131-133] and Chapman [132] *et al.* have studied the microbiological conversion of triphenyltin acetate to inorganic tin oxides in soil and report the half-life of triphenyltin acetate to be 140 days.

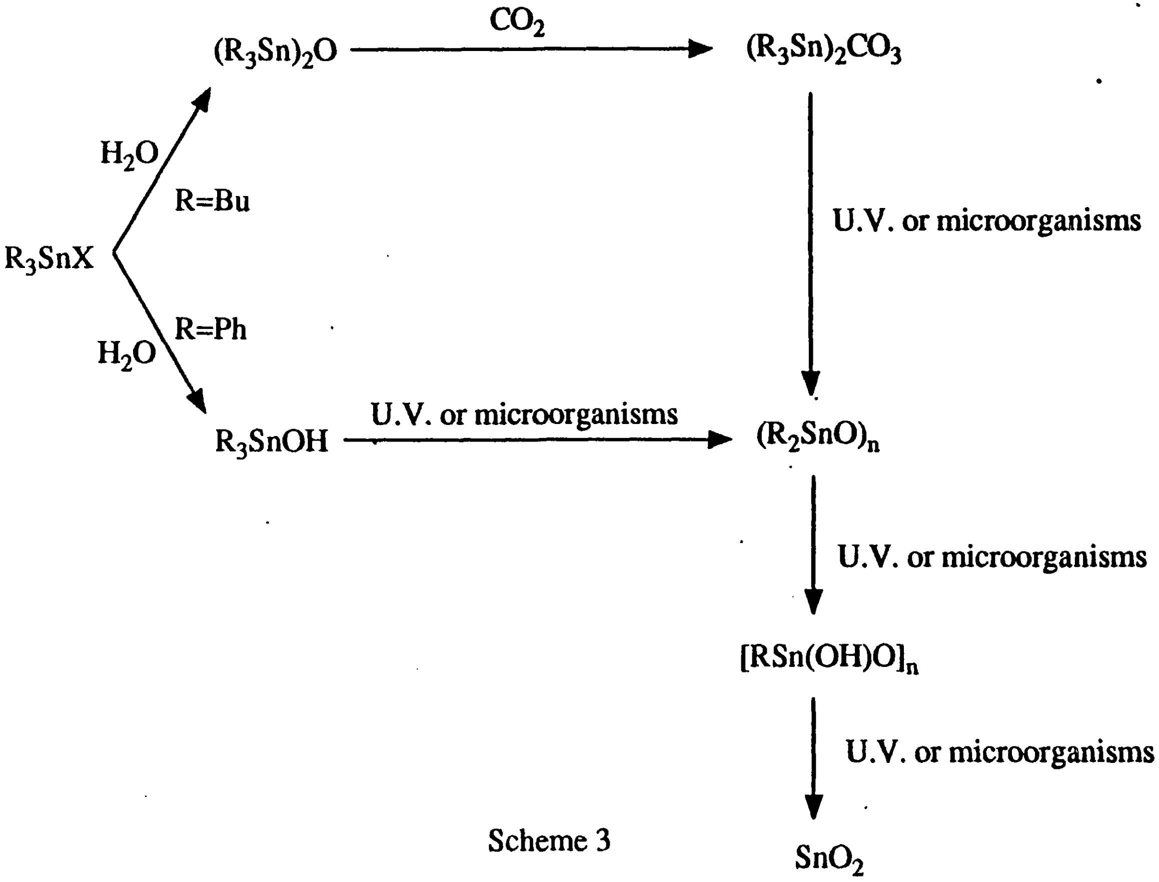
Various mechanisms have been proposed for the degradation of bis(tributyltin)oxide involving U.V. radiation [134], atmospheric (and trapped) CO_2 [135] and water [136]. The half-life of bis(tributyltin)oxide in pond water has been measured as 16 days. Sheldon [137] has proposed a general degradation scheme for the environmental breakdown of tributyl- and triphenyltin biocides to non-toxic inorganic tin, (Scheme 3).

It has been shown by Wood [138] that biomethylation of inorganic tin(II) residues can occur under very specialised conditions with a Co^{3+} catalyst and a methylation agent. Brinkman *et al.* [139] have shown that certain *Pseudomonas* bacteria are capable of biomethylation of $SnCl_4$ to dimethyltin species under laboratory conditions. Chau *et al.* [140] reported on a series of various inorganic tin(II) salts which were incubated in lake sediments which led to methyltin cations, although the more toxic trimethyltin species were only observed at nanogram levels. Although there is still uncertainty in the mechanisms of biomethylation of inorganic tin salts, it is generally accepted that trimethyltin salts may be readily converted to Me_4Sn. The process occurs via a sulphide intermediate [141] ,(Scheme 4).

$$2Me_3Sn^+ + S^{2-} \rightarrow (Me_3Sn)_2S$$

$$3(Me_3Sn)_2S + \text{light} \rightarrow 3Me_4Sn + \text{cyclo-}(Me_2SnS)_3$$

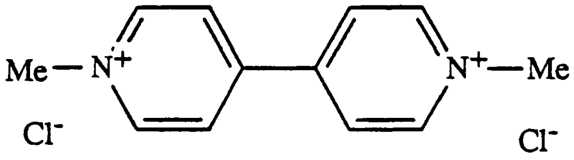
Scheme 4.


$(R_3Sn)_2O$
CO_2
$(R_3Sn)_2CO_3$
H_2O
R=Bu
R_3SnX
R=Ph
H_2O
U.V. or microorganisms
R_3SnOH
U.V. or microorganisms
$(R_2SnO)_n$
U.V. or microorganisms
$[RSn(OH)O]_n$
U.V. or microorganisms
SnO_2

Scheme 3

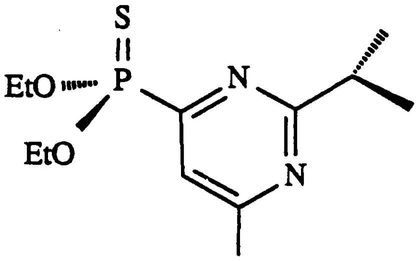
1.6 Heterocyclic Biocides

"Biocide" is the general term for the whole spectrum of chemical substances used to kill or control destructive organisms and the range covers, insecticides, nematicides (de-wormers), piscicides (fish control), herbicides, fungicides, bactericides and others. At a fundamental level, a toxic chemical is one that is capable of disrupting the biochemical homeostasis of a biological system. The mutagenic and carcinogenic activities of some simple heterocycles compared to simple aromatics have been compiled [142] and it is clear that no clear structure/activity relationship can be derived. However studies have established certain substituents, sub-structures or atoms which do seem to confer biological toxicity on a molecule. For example quaternary nitrogen competes with acetylcholine for nerve receptors, the most extreme response being paralysis or death caused by tubocurarine, a large polycyclic compound, and paraquat, (XXXII).



(XXXII)

The first heterocyclic insecticide, "Diazinon" (XXXIII), was made available in 1952 and is used in the home, garden and farmyard.



(XXXIII)

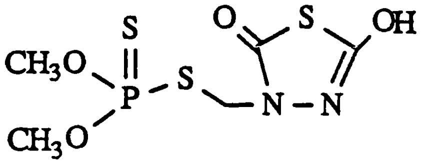
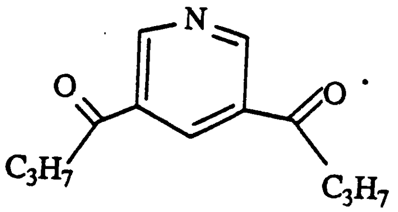
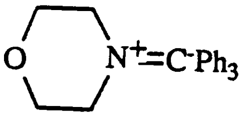
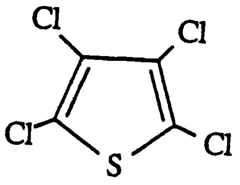
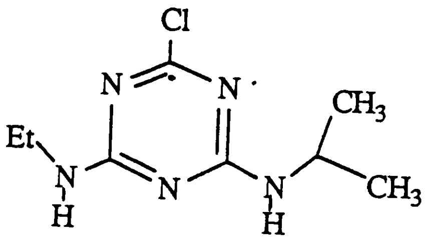
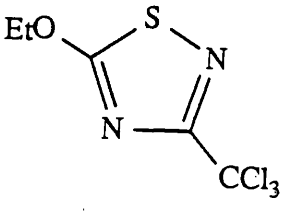
Since then many heterocyclic compounds have been used as commercial biocides, Table 8. It would be unsuitable to list them all here, but further details may be obtained from standard reference works [143,144]. A few examples have been studied in detail. Furan [145] derivatives show toxicity to Clara cells in mammalian lung tissue, pyrazole is toxic to both mice and rats causing necrosis of the liver [146], 3-aminotriazole is a non-selective herbicide and imidazole, benzoxazole and benzothiazole [147] have been shown to inhibit the enzymatic action of cytochrome P-450.

1.7 Organotin Biocides

There are currently six, commercially available, triorganotin biocides for agricultural use and several tributyltin wood preservative and anti-fouling paint formulations, (Table 9). The main advantages of the organotin agrochemicals is said to be their low phytotoxicity and general lack of toxicity towards non-target organisms.

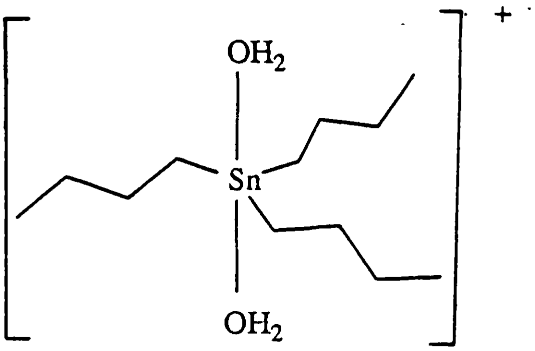
Organisms which develop resistance to biocides can be more effectively controlled with binary mixtures. Organotin compounds combined with various commercial heterocyclic biocides perform better than either of the two separate components [150-152].

Table 8: Selected commercial heterocyclic biocides

Compound	Trade name	Biocidal use
	Supracide™	Insecticide
	MGK™	Insect repellant
	Frescon™	Molluscicide
	Penphene™	Nematicide
	Atrazine™	Herbicide
	Terrazole™	Fungicide

Other related areas in which non-commercial organotins compounds are showing potential are: mosquito larvicides, snail control and chemotherapy.

It is cost effective and environmentally preferable for any commercial biocide to be water soluble, and for this reason aqueous solutions of tributyltin alkylsulphonate compounds have been studied [153]. It has been shown that triorganotin derivatives dissolved in polar solvents may exhibit enhanced coordination and the activity of a species is linked to its geometry. The existance of the hydrated trialkyltin cation has been recognised in aqueous solution [154] and Davies *et al.* [155] have reported the crystal structure of the trans-tbp unit of $[Bu_3Sn(OH_2)_2]^+$ (XXXIV).



(XXXIV)

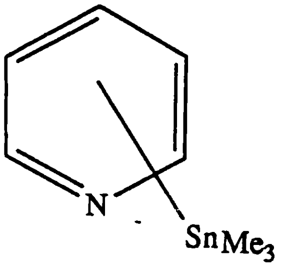
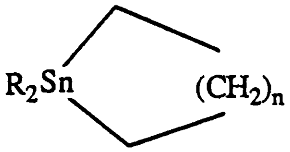
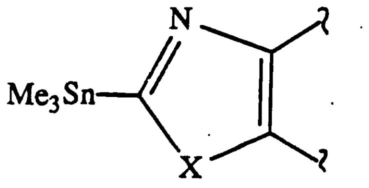
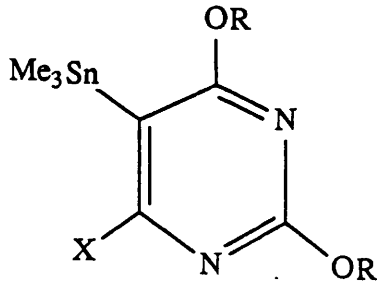
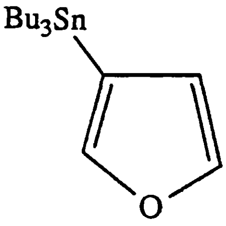
There are many reported [156] examples of organotin N-, O- or S- bonded heterocyclic compounds including imidazoles, aziridines, pyridines, quinolines, tetrazoles [157] and triazoles [158], however there are still relatively few carbon bonded derivatives and even fewer X-ray crystal structures. A selection of C-Organostannyl heterocycles are displayed in Table 10.

Table 9: Biocidal uses of R_3SnX compounds *

Compound	Application
$Ph_3SnOCOCH_3$	Fungicide
Ph_3SnOH	Fungicide
Ph_3SnCl	Molluscicide
Cy_3SnOH	Miticide
$\{[PhMe_2CCH_2]_3Sn\}_2O$	Miticide
Cy_3Sn-1,2,4-triazole	Miticide
$(Bu_3Sn)_2O$	Wood preservative, fungicide and molluscicide
$Bu_3SnOCOCH_3$	Molluscicide

* Further details are available [148,149]

Table 10: A Selection of C-Organotin Heterocycles

Compound	Comments	Ref.
	Patented as a herbicide	159
	Patented as a herbicide, fungicide and insecticide	160
	X=S, O, NMe	161-2
	R=Me, CH_2Ph X=Cl, H	163
	Precursor to 3-lithio- furan	164
$Ph_3PO.SnBr(C_4H_3S)_3$	Crystal structure	165

The primary aim of this project is to prepare a selection of novel *C*-organostannyl heterocyclic compounds that might show a significant enhancement in biocidal activity over current commercial organotin products. The secondary aim is to explore new aspects of organotin chemistry.

CHAPTER 2.

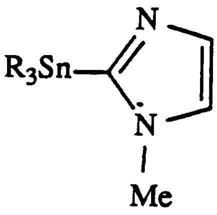
THE SYNTHESIS OF TRIORGANOSTANNYL-C-BONDED 1-METHYLIMIDAZOLE, BENZOTHIAZOLE AND BENZOXAZOLE.

2.1. Introduction

Heterocyclic compounds are very widely distributed in nature and are essential to life since they play a vital role in the metabolism of all living cells. There has been considerable interest in the biological and pharmacological properties of the imidazole group. The applications are diverse, including such uses as fungicides [166], anthelmintics [167], antibacterials [168] and radiotherapy [169]. Certain benzothiazole derivatives also show a wide range of biological action [167] and are found in fungicidal [168,169] and anthelmintic [167] preparations. Benzothiazole derivatives also act as bacterial mutagens [167] and reduce the activity of certain enzymes [170]. The oxazole nucleus and its benzo- derivatives are rarely found in nature, except for a few alkaloids. However there are several reported uses as anti-inflammatory and analgesic pharmaceuticals [171], antibacterial agents [172], antiviral drugs [172] and fungicides [168].

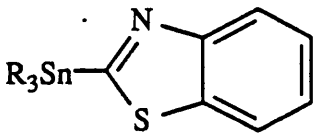
The three heterocycles selected here all show some degree of fungicidal activity and the mode of action is well documented [173]. Fungicides are often comprised of groups of nitrogen containing heterocycles that block the biosynthesis of ergosterol which is essential to the development of fungal cell membranes. By coordinating to the iron present in the cytochrome P-450, they inhibit the oxidative demethylation of a biosynthetic precursor, lanosterol.

In this chapter the synthesis, full spectral characterisation and reaction chemistry of various C-triorganostannyl 1-methylimidazole, benzothiazole and benzoxazole compounds, (1-7), are described. A small number of these types of compounds have been previously reported[161-164,174,175] but studies have been confined to synthesis and only basic characterisation.



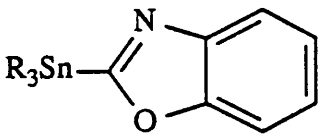
(1) (2) (3)

R=Me, Bu, Ph



(4) (5) (6)

R=Me, Bu, Ph



(7)

R= Ph.

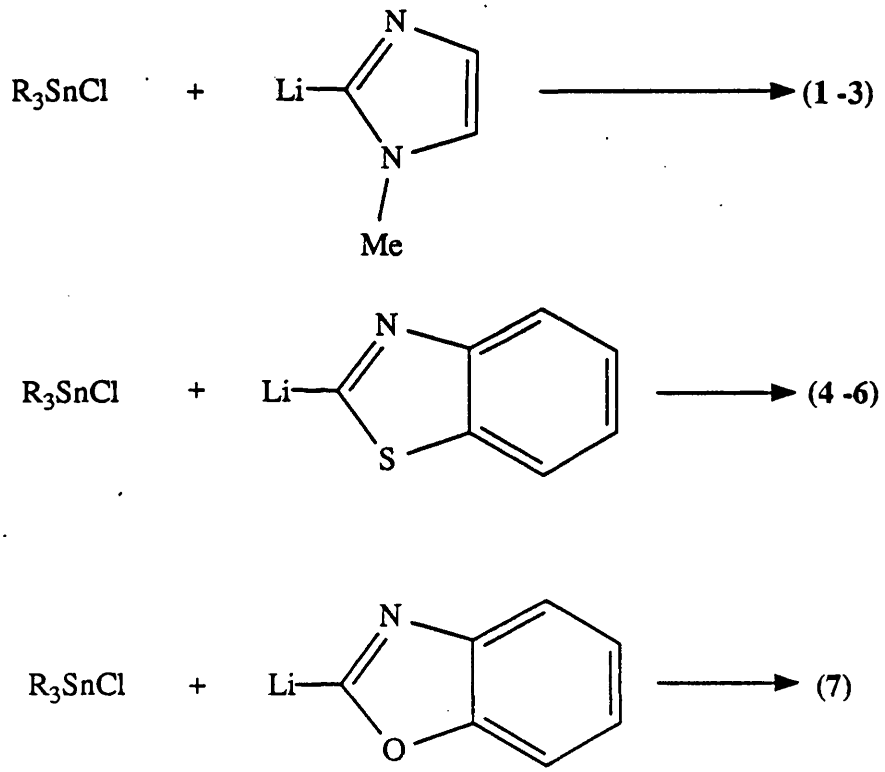
2.2. Synthesis

Using standard, dry, anerobic conditions, 1-methylimidazole, benzothiazole and benzoxazole were lithiated at the number 2 positions (see scheme 5) with n-butyllithium in diethyl ether or tetrahydrofuran (THF). Solutions of the 2-lithio-heterocycle were not stable at ambient temperatures, hence 2-lithio-1-methylimidazole was prepared at -10°C, 2-lithio-benzothiazole at -78°C and 2-lithio-benzoxazole at -115°C. The appearance of a yellow or milky precipitate indicated that anion formation was complete.

The appropriate triorganotin chloride was then added dropwise to quench the 2-lithio-heterocycle suspension and the solution was allowed to slowly warm to room temperature (Scheme 5).

The insoluble inorganic by-products were filtered off under nitrogen using a Schlenk-Stick.

The trimethyl- and tributylstannyl- derivatives were purified by distillation *in vacuo* to yield air and moisture sensitive colourless oils. The triphenylstannyl- derivatives were recrystallised in air from 60-80° petroleum (the 1-methylimidazole derivative was recrystallised under nitrogen.), to yield white, air stable crystalline materials. The analytical data are presented in Table 11.



Scheme 5.

Table 11:

Physical and Analytical Data for 2-Triorganotin-Heterocycles [a]

Compound	Mp/Bp °C	C% [b]	H%	N%
Me_3Sn-1-MI	84-6°C/0.5mm	33.34(34.33)	5.51(5.76)	10.78(11.44)
Bu_3Sn-1-MI [c]	145-6°C/0.5mm	49.17(51.78)	8.07(8.69)	6.11(7.54)
Ph_3Sn-1-MI	89-90°C	60.60(61.21)	4.56(4.67)	6.00(6.49)
Me_3Sn-Bzt	96-8°C/0.8mm	41.60(40.30)	4.40(4.39)	5.40(4.47)
Bu_3Sn-Bzt	179°C/1.0mm	52.50(53.79)	7.31(7.36)	3.28(3.30)
Ph_3Sn-Bzt	118°C	62.20(62.01)	3.88(3.95)	2.71(2.89)
Ph_3Sn-Box	87-8°C	63.90(64.10)	4.00(4.10)	2.80(3.00)

[a] 1-MI: 1-methylimidazole, Bzt: benzothiazole, Box: benzoxazole

[b] Analysis: Found(Calc)

[c] Although care was taken to present the sample for analysis under N_2 no special precautions were used during analysis to protect the sample from atmospheric moisture.

2.3. Spectroscopy

2.3.1. Infra-red spectroscopy.

The infra-red data are presented on Tables 12 and 13. Although there are several bands that are attributable to the R_3Sn- moiety, the bands associated with the heterocycles are often difficult to assign. The assignment of bands due to ring-skeletal and ring-hydrogen stretches have arisen from deuteration studies [176]. The observations of the two $(Sn\text{-}C)_{asym}$ and $(Sn\text{-}C)_{sym}$ stretching modes with the trimethylstannyl- compounds suggests that both have tetrahedral symmetry, indicative of 4-coordination. The triphenylstannyl- derivatives all show the characteristic (Sn-Ph) stretching band at 1065 cm^{-1}.

2.3.2. Mass Spectroscopy

Mass spectral data obtained under E.I. conditions (70 eV) are given on Table 14. Molecular parent ion peaks are found in all cases. It is observed that the even-electron ions appear to be the most abundant and this is typical for organotin compounds. This is apparent for two reasons: i) that even-electron ions have more inherrent stability relative to the odd-electron species and consequently last longer and ii) even-electron ions are degraded to produce a neutral fragment and another even-electron ion, whilst odd-electron ions lose odd-electron neutral fragments to yield a further even-electron ion, (Scheme 6). The heterocycles can degrade to produce neutral $CH_2{=}CH_2$, HCN, CS and CO molecules.

Table 12. Infra-red data [a] for bands assigned to the heterocycle [b]

Compound	$\nu(C\text{-}H)_{arom}$	$\nu(C\text{-}H)_{alk}$	Ring-Skel.	(C-H) def [c]	(C-H) def[d]
1-MIH	3315 s	2960 s	1490 m	1240 vs	920, 830 s
2-Me_3Sn-1-MI	3315 m	2960 w	1510 w	1235 w	915 m
2-Bu_3Sn-1-MI	3100 w	obsc.	1505 m	1235 vw	910 m
2-Ph_3Sn-1-MI	3115 vw	obsc.	1505 w	1240 m	940 m
BztH	3080 s	-	-	977 w	860 sh
2-Me_3Sn-Bzt	3075 m	-	-	935 w	865 sh
2-Bu_3Sn-Bzt	3060 w	-	-	960 m	865 sh
2-Ph_3Sn-Bzt	3050 w	-	-	980 vw	765 s
BoxH	3100 s	-	-	920 m	880 s
2-Ph_3Sn-Box	3100 vw	-	-	915 m	900 m

[a] Cm^{-1}

[b] 1-MI refers to 1-methylimidazole, Bzt refers to benzothiazole, Box refers to benzoxazole

[c] In plane.

[d] Out of plane.

Table 13. Infra-red data [a] for bands assigned to the R_3Sn-moiety [b,c].

Compound	4000-1600 region	1600-800 region	800-200 region
2-Me$_3$Sn-1-MI	2940 s ν(C-H)$_{alk}$	1190 m δ(C-H)	780 s (CH$_3$-rock)
			540 s ν(SnC)$_{asym}$
			520 m ν(SnC)$_{sym}$
2-Bu$_3$Sn-1-MI	2960-2850 s $_{alk}$	1460, 1070 s	-
2-Ph$_3$Sn-1-MI	3050 m ν(C-H)$_{arom}$	1480, 1065 s	702 s (C-H) def.
2-Me$_3$Sn-Bzt	3000-2925 m $_{alk}$	1450, 1020 m	775 s (CH$_3$-rock)
			540 s ν(SnC)$_{asym}$
			520 s ν(SnC)$_{sym}$
2-Bu$_3$Sn-Bzt	2950-2859 s $_{alk}$	1460, 1070 s	-
2-Ph$_3$Sn-Bzt	3050 w ν(C-H)$_{arom}$	1430, 1065 s	735, 700 s (C-H)
2-Ph$_3$Sn-Box	3055 w ν(C-H)$_{arom}$	1430, 1070 s	730, 700 s (C-H)

[a] Cm^{-1}

[b] abbreviations: s....Strong, m....Medium, w....Weak, vw....very weak.

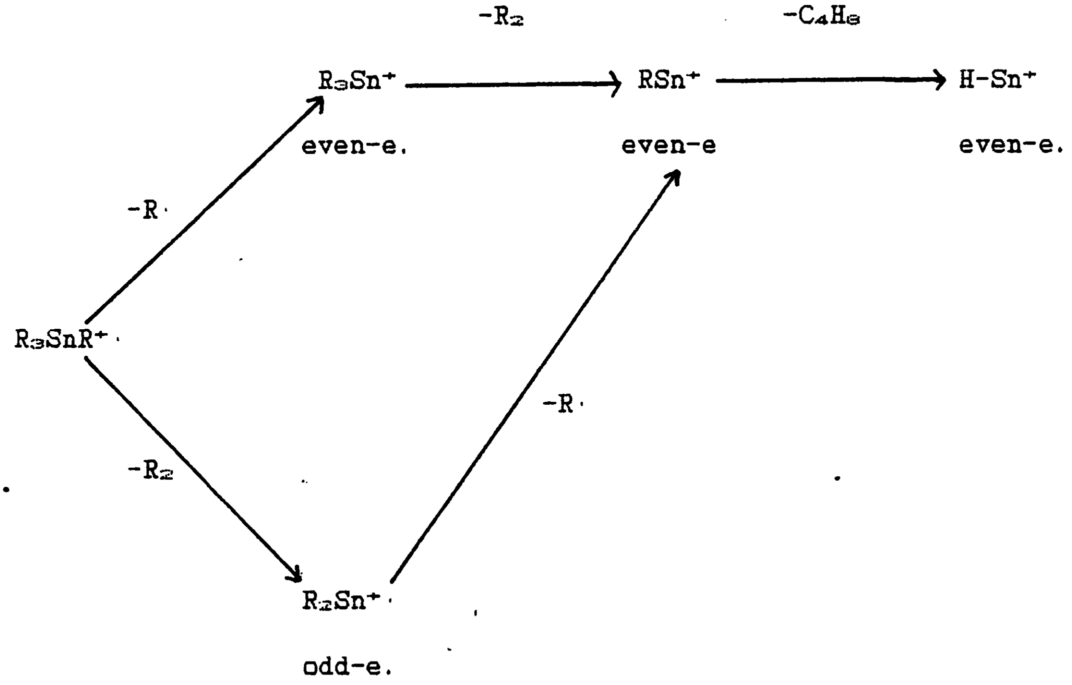
[c] Air sensitive oil samples were prepared under dry nitrogen. Solids were prepared as KBr discs and oils as liquid films on KBr discs.

Table 14. Fragments found in 70EV electron ionisation mass spectra of organotin derivatives of 1-MI and Bzt [a,b]

Compound	$R_3SnL^{+\cdot}$	R_2SnL^{+}	$RSnL^{+\cdot}$	SnL^{+}	R_3Sn^{+}	$R_2Sn^{+\cdot}$	RSn^{+}
2-Me_3Sn-1-MI							
m/e	246	231	216	201	165	150	135
% abund.	33	88	9	100	38	18	43
2-Bu_3Sn-1-MI							
m/e	372	314	-	201	291	234	177
% abund.	31	30	-	17	98	40	29
2-Ph_3Sn-1-MI							
m/e	432	355	278	201	351	-	197
% abund.	7	17	27	19	19	-	60
2-Me_3Sn-Bzt							
m/e	299	284	269	254	165	150	135
% abund.	42	55	8	10	36	14	88
2-Bu_3Sn-Bzt							
m/e	426	368	311	254	291	234	177
% abund.	58	36	9	14	28	10	15
2-Ph_3Sn-Bzt							
m/e	485	408	331	254	351	-	197
% abund.	68	49	19	12	66	-	97

[a] 1-MI: 1-Methylimidazole, Bzt: benzothiazole

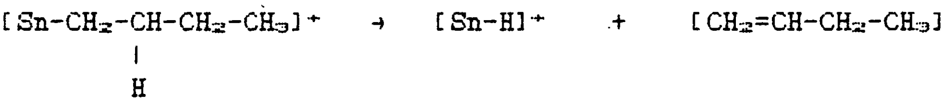
[b] Based upon ^{120}Sn isotope.


-R₂
-C₄H₈
R₃Sn⁺
RSn⁺
H-Sn⁺
even-e.
even-e
even-e.
-R·
R₃SnR⁺·
-R·
-R₂
R₂Sn⁺·
odd-e.

Scheme 6.

The fragmentation modes of a typical R_4Sn compound

All tetraorganotin compounds show a significant amount of $Sn^{+\cdot}$ in the spectra, however $[Sn\text{-}H]^+$ is only ever seen for the tributyltin-derivatives. This even-electron ion is the result of alkene elimination, (Equation 15).



$$[Sn\text{-}CH_2\text{-}\underset{\substack{|\\H}}{CH}\text{-}CH_2\text{-}CH_3]^+ \rightarrow [Sn\text{-}H]^+ + [CH_2{=}CH\text{-}CH_2\text{-}CH_3] \qquad (15)$$

It is clear that only compounds with a β-hydrogen can follow this decomposition pathway. This includes the butyltin compounds.

The biphenyl radical m/e 154 and [Ph-Sn] m/e 197 are both observed with strong abundances in the triphenylstannyl- derivatives. This suggests the following degradation pathway, (Equation 16).

$$[Ph_3Sn]^+ \rightarrow [Ph\text{-}Ph] + [Ph\text{-}Sn]^+ \qquad (16)$$

Previous studies [177,178] have assigned the fragments produced during the E.I. degradation of 1-methylimidazole and benzothiazole, and similar fragments have been noted with the 2-triorganotin-derivatives, e.g. [azirine, $C_2H_2N]^+$, $[Ph\text{-}N]^+$, $[Ph\text{-}S]^+$. etc.

2.3.3. N.M.R.

The ^1H nmr data are presented in Table 15. The disappearance of the C(2) proton resonance in the metallated heterocycle confirms this to be the site of attack. Lockhart and Manders have recently shown [93] that $^2J[^{119}Sn, ^1H]$ and θ, the Me-Sn-Me bond angle(s), are related by a smooth curve described by equation (10), and data for most di- or trimethyltin (IV) compounds lie within 4° of this empirical line. Tetracoordinated trimethyltin(IV) compounds generally have $^2J(^{119}Sn, ^1H)$ values of <59 Hz. The $^2J(^{119}Sn, ^1H)$ values obtained for the trimethyltin derivatives, **(1)** and **(4)**, are 57.6 Hz and 56.6 Hz respectively and give calculated bond angles of 110.8° and 110.3° respectively and the results are indicative of tetrahedral, 4-coordinate architecture at tin.

Table 15:

^{1}H N.M.R. Studies of 2-R$_3$Sn-C-bonded 1-methylimidazole, benzothiazole and benzoxazole [a]

R$_3$Sn-imidazoles:

R	δ(N-CH$_3$) [b]	δ(C$^{(4)}$H) [b]	δ(C$^{(5)}$H) [b]	δ(R) [b]	J^2(Sn,H) [c]
1-MIH[d]	3.70 (s,3H)	7.08 (d,1H)	6.88 (d,1H)	-	-
Me	3.41 (s,3H)	6.89 (d,1H)	6.72 (d,1H)	0.14 (s,9H)	54.8, 57.6
Bu	3.60 (s,3H)	7.12 (d,1H)	6.92 (d,1H)	0.6-0.7 (m,27H)	-
Ph	3.51 (s,3H)	6.99 (d,1H)	6.77 (d,1H)	7.8-7.2 (m,15H)	-

R$_3$Sn-benzothiazoles:

R	δ(R group) [b]	δ(Benzothiazole group) [b]	J^2($^{117/119}$Sn-H) [c]
BztH	-	8.05-6.80 (m,4H),H(2)=8.65	-
Me	0.63 (s,9H)	8.30-7.25 (m,4H)	55.0,56.6
Bu	1.57-0.73 (m,27H)	7.82-7.80 (d,1H) 7.33-7.20 (m,2H) 8.08-8.05 (d,2H)	-
Ph	7.51-7.36 (m,15H)	7.96-7.93 (d,1H) 7.51-7.36 (m,2H) 8.26-8.23 (d,1H)	

Table 15 continued,

R_3Sn-benzoxazole:

R	δ(R group) [b]	δ(benzoxazole group) [b]
BoxH	-	7.67-7.80 (m,4H), H(2)=7.46 (s,1H)
Ph	8.10-7.40 (m,15H)	8.09-7.42 (m,4H)

[a] Relative to TMS,

[b] ppm.

[c] Hz.

[d] H(2)= 7.47 ppm.

The chemical shift and coupling constant data for the trimethyltin compounds are in close agreement with that obtained by Jutzi and Gilge [162] (57.6 Hz. and 57.6 Hz. respectively) and are also consistent with similar C-trimethylstannyl heterocyclic compounds reported by the same author.

The ^{13}C n.m.r. data are given in Table 16. Typical 4-coordinate organotin compounds of the type R_4Sn have $^1J[^{119}Sn, ^{13}C]$ values between 300 and 340 Hz. [179] . The $[^1J]$ values for the trimethyltin derivatives, (1) and (4), are 359.1 Hz. and 356.2 Hz. respectively. The second equation developed by Lockhart, Manders and Zuckerman [39], relating $^1J[^{119}Sn, ^{13}C]$ with θ, equation (11), yields <C-Sn-C bond angles of 108.2° and 108.0° for the above two compounds. This is internally consistent with the ^1H n.m.r. data above and the quoted 4° error, again suggesting tetrahedral geometry about tin.

Holecek and Lycka [180] have suggested a similar empirical approach for the estimation of the C-Sn-C bond angles for n-butyltin compounds, Equation 17.

$$[^1J(^{119}Sn, ^{13}C)] = (9.99 \pm 0.73)*\theta - (746 \pm 100) \qquad (17)$$

Substituting in the experimental $^1J(^{119}Sn, ^{13}C)$ values for the tributyltin derivatives (2) and (5), the bond angles are calculated to be 110.9° and 111.1° respectively, indicating no structural changes from the trimethyltin- compounds. The coupling constants associated with the triphenyltin- compounds are consistent with other

Table 16

^{13}C n.m.r studies on 2-R_3Sn-C-bonded imidazole, benzothiazole and benzoxazole [a,b,c]

R_3Sn-1-Methylimidazoles:

R	δ(C2)	δ(C4)	δ(C5)	δ(C6)	δ(R)	J^1(Sn-C)
1-MeIH	138.70	130.20	121.0	34.20	-	-
Me	152.83	129.92	121.64	33.78	Me_3: -9.39	359.1
Bu	154.00	130.70	121.90	34.28	α : 10.12	362.3
					β : 26.97	-
					γ : 28.77	20.2
					δ : 13.37	-
Ph	150.90	129.23	121.87	33.87	*i* : 140.90	-
					o : 136.66	39.60
					m : 128.77	52.96
					p : 129.66	11.12

R_3Sn-benzothiazoles:

R	δ(C2)	δ(C3a)	δ(C4)	δ(C5)	δ(C6)	δ(C7)	δ(C7a)	δ(R)
BztH	155.2	153.2	123.1	125.9	125.2	122.1	133.7	-
Me [d]	155.6	149.7	123.1	125.4	124.3	121.2	136.2	Me:-9.5
Bu [a]	155.9	153.5	122.6	125.1	124.1	121.6	136.1	α: 11.0
								β :27.0
								γ :28.7
								δ :13.5

Table 16 continued,

Ph	156.1	140.5	123.4	125.6	124.9	121.4	136.4	*i*: 139.5 *o*: 137.1 m: 128.8 p: 129.7

R$_3$Sn-benzoxazole:

R	δ(C2)	δ(C3a)	δ(C4)	δ(C5)	δ(C6)	δ(C7)	δ(7a)	δ(R)
BoxH	152.6	140.1	120.5	125.4	124.4	110.8	150.0	-
Ph	173.7	141.1	120.0	124.9	123.8	110.5	152.0	*i*: 140.4 *o*: 136.9 *m*: 128.8 *p*: 129.7

[a] All spectra were recorded as CDCl$_3$ solutions at 298K and relative to TMS,

[b] : ppm.

[c] : Hz.

[d] : $^1J(^{119}Sn,^{13}C)$: 356.2 Hz.

[e] : $^1J(^{119}Sn,^{13}C)$: 364.2 Hz.

4-coordinate triaryltins.

The ^{119}Sn n.m.r results are presented in Table 17. Tetraorganotin compounds, R_4Sn, show weak acceptor properties and do not form adducts with coordinating solvents, however to reduce any possibility of minor interactions, the non-coordinating solvent $CDCl_3$ was used.

When unsaturated groups are attached to tin, there is a marked shift of the tin resonance to higher fields as the degree of polarizability, hence shielding, increases. The ^{119}Sn chemical shift values presented here are consistent with a 4-coordinate, near tetrahedral geometry arounds the tin. The ^{119}Sn chemical shift data for the similar systems, R_3SnPh, where R=Me, Bu and Ph, are given for comparison. Five and six coordinate structures would be expected to have chemical shifts appearing at lower frequencies e.g. bis[3-(2-pyridyl)-2-thienyl-C,N]diphenyltin(IV), δ= -245.5, (5-coordinate in solution).

2.3.4. Mossbauer Spectroscopy

The Mossbauer data for the compounds under discussion are presented in Table 18. The data for R_3SnPh (R=Me, Bu and Ph) are also given. The quadrupole splitting parameter for regular tetraorganotin compounds is usually zero or so small as to be unresolvable. The results presented here show small ΔEq values and the spectra themselves show partially resolvable lines. The one exception is (3), which appears as a broad singlet.

The small ΔEq values are the result of asymmetry in the distribution of the valence electrons about the Mossbauer nucleus. Greenwood's Rules[67] deal with tetraorganotin compounds which give a non-zero quadrupole splitting (Q.S.). There are two possible explanations for

Table 17

^{119}Sn n.m.r. studies on R_3Sn-C-bonded 1-Methylimidazole, benzothiazole and benzoxazole compounds [a,b]

Compound	δ/ppm.	R_3SnPh [c]	δ/ppm.
2-Me_3Sn-1-MI	-48.22	Me_3SnPh	-28.6
2-Bu_3Sn-1-MI	-66.74	Bu_3SnPh	-45.2
2-Ph_3Sn-1-MI	-175.66	Ph_4Sn	-120.0
Me_3Sn-BzT	-28.61		
Bu_3Sn-Bzt	-41.93		
Ph_3Sn-Bzt	-165.92		
Ph_3Sn-Box	-174.26		

[a] 1-MI: 1-Methylimidazole, Bzt: benzothiazole, Box: benzoxazole.

[b] All spectra were recorded as $CDCl_3$ solutions at 298 K using Me_4Sn as a reference.

[c] Monophenyl-tetraorganotin derivatives.

Table 18

Mossbauer Studies (78K) on organotin derivatives of 1-methylimidazole, benzothiazole and benzoxazole [a]

Compound	δ/mmsec^{-1}	ΔEq/mmsec^{-1}	Γ_1, Γ_2 mmsec^{-1} [b]
Me_3Sn-1-MI	1.19	0.75	0.88, 0.87
Bu_3Sn-1-MI	1.28	0.76	0.98, 0.76
Ph_3Sn-1-MI	1.22	0.46	0.87, 0.80
Me_3Sn-Bzt	1.27	1.12	0.98, 0.87
Bu_3Sn-Bzt	1.32	1.20	0.94, 0.96
Ph_3Sn-Bzt	1.25	0.81	1.02, 1.08
Ph_3Sn-Box	1.19	0.80	0.90, 0.90
Me_3SnPh [c]	1.26	0.00	- -
Bu_3SnPh [c]	1.35	0.00	- -
Ph_4Sn [c]	1.20	0.00	- -

[a] 1-MI: 1-methylimidazole, Bzt: benzothiazole, Box: benzoxazole

[b] Γ_1, Γ_2 refer to the full width at half height of the low and high velocity components of the doublet spectra, respectively.

[c] Ref. 68

the resolution of the Q.S. parameter in these compounds; a) that large electric field gradients (e.f.g) exist in the σ-skeletons, since the organic groups around the tin atom are all combinations of sp^3-sp^2 pairs and b) that there is a possibility of a $(p \rightarrow d)\pi$ interaction along the tin carbon σ-bond, which would enhance the e.f.g by population of the empty tin 5d orbitals. This is, in principle, reasonable since in all the compounds prepared the tin is adjacent to the sp^2-bonded heterocycle. Weak 5-coordination at the tin atom would produce an enhanced e.f.g. and a non-zero ΔEq value, however this can be ruled out by the previous n.m.r. data. From the magnitude of the measured Q.S. values the relative polarities of the Sn-R bonds can be estimated as:

R: Me, Bu < Ph, 1-MeI < Bzt, Box

This ordering can also be seen through a detailed examination of the isomer shift values (δ), although it is not immediately obvious. The isomer shift value is perturbed by changes in the 5s-electron density at tin, which is itself dependent on the electronegativity of the ligands bonded to the metal. It has already been shown that electron withdrawing groups produce lower isomer shifts than electron donating groups, (e.g. for common X groups, triaryltins- < trialkyltins). From the ΔEq values and the proposed ordering one might expect that for common R groups, 2-R_3Sn-Bzt would show a lower isomer shift value than for 2-R_3Sn-1-MI, however the reverse is true. This anomaly can be rationalized in the following way. The regular sp^3 hybridisation at tin is subtlety altered to produce an sp^3 orbital richer in p-character to bond to the sp^2 hybridised C(2) of the heterocycle, and three sp^3 orbitals richer in s-character for the R group bonding scheme. This rehybridisation produces an unsymmetrical e.f.g and therefore a resolvable quadrupole split. Since the tin-R group bonds are less polar, more 5s-character is associated with the tin nucleus and hence larger isomer shifts are generated than expected, fig 6. Therefore the greater the electronegativity of the heterocycle, the larger the isomer shift.

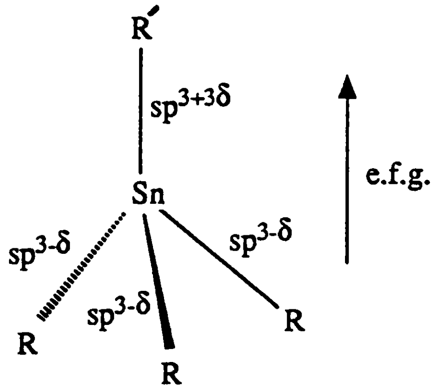


Fig 6.

A similar anomaly can be observed for Phillips and Herber's trimethyltin pyridine derivatives, in which the more electronegative pyNO and -py ligands produce greater isomer shifts than Me_3SnPh [181].

2.4 The Crystal Structure of 2-(Triphenyltin)benzothiazole (6)

Suitable crystals were obtained by recrystallisation from 60-80° petroleum ether. The structure of 2-(triphenyltin)benzothiazole, determined crystallographically is shown in Figure 7, with the expected tetrahedral geometry around the tin atom. The X-ray data are presented in Appendix II. Selected bond lengths and bond angles are presented in Tables 19 and 20 respectively. The Sn-C bond lengths cast no light on the unusual reactivity of the tin-heterocycle bond since they are all the same length within the error of the experiment.

The bond angle results show that the molecule does not have regular tetrahedral symmetry around the tin atom, but rather the heterocycle is in a unique position. All the bond angles involving Sn, the heterocyclic carbon C(19) and the phenyl ring *i* carbons are smaller than those involving purely the aromatic carbons (C(1), C(7) and C(13)) and Sn. This would suggest that the bond Sn-C(19) has slightly more *p*-character than the three Sn-Phenyl bonds, and this is in keeping with the Mossbauer results which show that these molecules have ΔEq >0, i.e. a small e.f.g. is generated. This also somewhat illuminates the regiospecificity of the halogen cleavage reactions.

The crystal structure of the *tetrakis*(2-thienyl)tin has been determined by Karipides *et al.* [13], and the Sn-C(thienyl) bond length was found to be 2.15(1)Å, very similar to the Sn-C bond lengths found for this structure.

Table 19: Selected bond lengths (Å)

Sn-C(1)	2.14(1)	C(19)-S(1)	1.76(1)
Sn-C(7)	2.14(1)	C(19)-N(1)	1.29(1)
Sn-C(13)	2.14(1)	S(1)-C(20)	1.72(1)
Sn-C(19)	2.16(1)	N(1)-C(25)	1.34(1)

Table 20: Selected bond angles (°)

C(1)-Sn(1)-C(7)	115.8(5)	Sn(1)-C(19)-S(1)	121.7(7)
C(1)-Sn(1)-C(13)	111.0(5)	Sn(1)-C(19)-N(1)	125.0(10)
C(7)-Sn(1)-C(13)	111.1(5)	S(1)-C(19)-N(1)	113.0(10)
C(19)-Sn(1)-C(1)	104.1(5)	C(19)-S(1)-C(20)	90.0(7)
C(19)-Sn(1)-C(7)	106.1(5)	C(19)-N(1)-C(25)	114.0(10)
C(19)-Sn(1)-C(13)	108.1(5)		

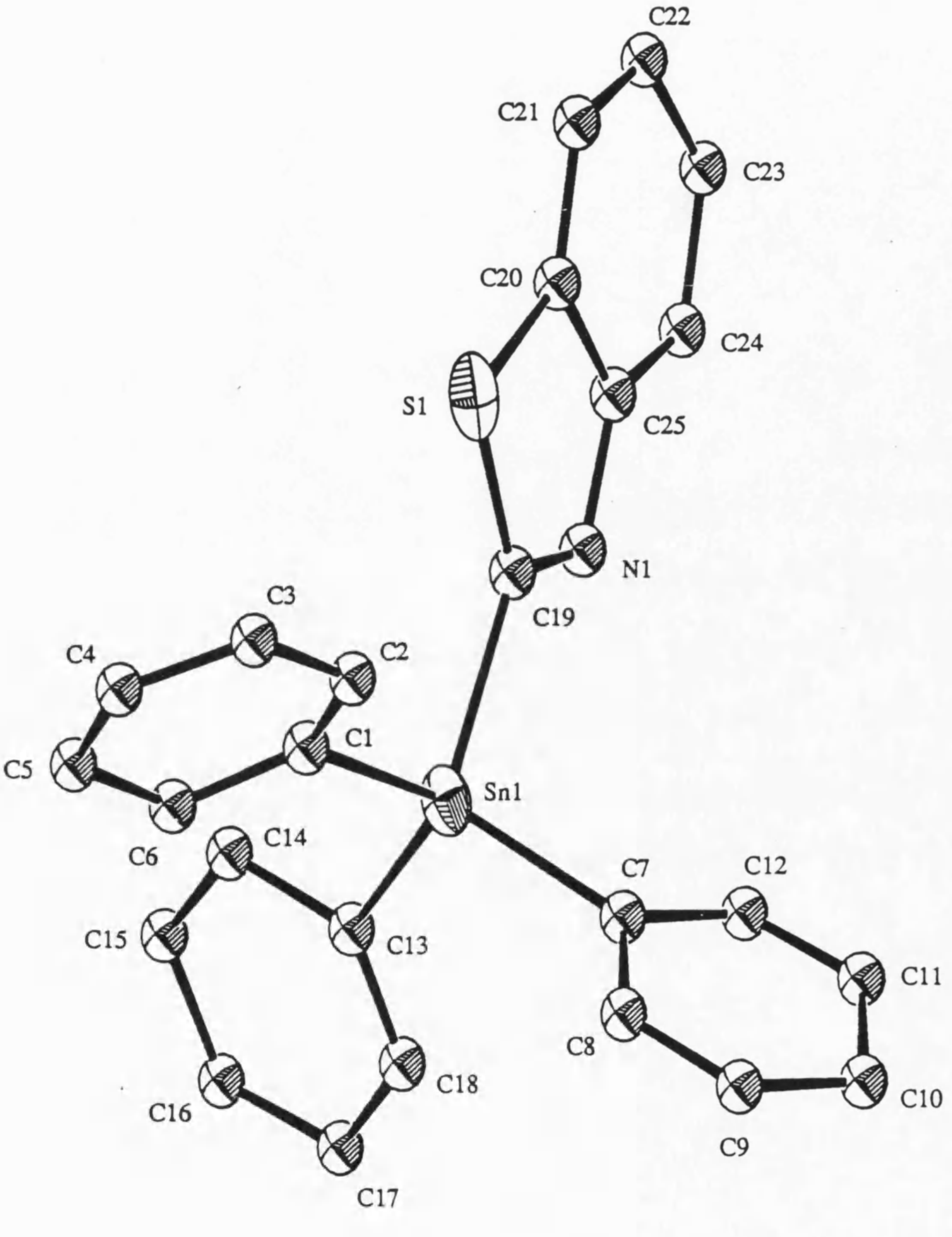
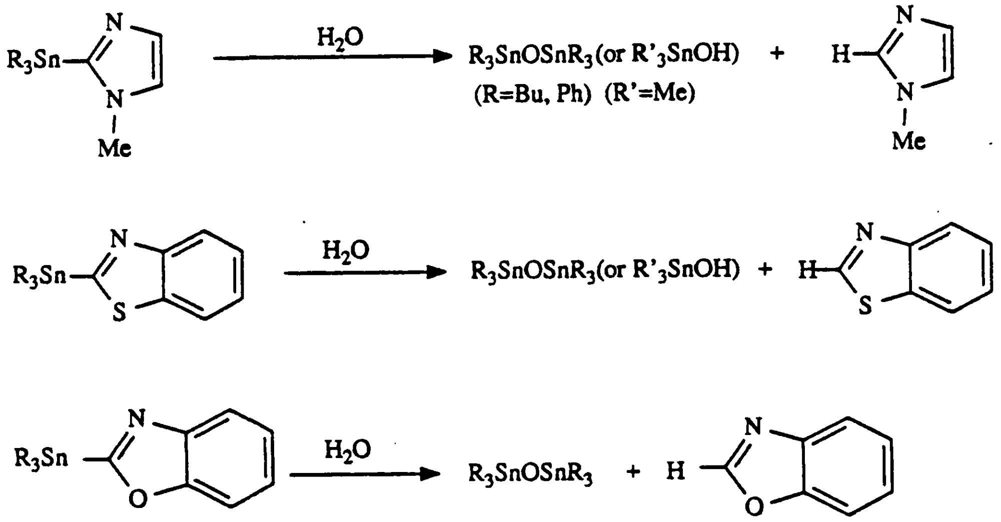

C22
C21
C23
C20
C24
S1
C25
N1
C19
C3
C4
C2
C1
C5
Sn1
C6
C14
C7
C12
C15
C13
C11
C8
C18
C10
C16
C9
C17

Figure 7: The Crystal Structure of 2-(Triphenyltin)benzothiazole

Hydrogen atoms omitted for clarity.

2.5 Reaction Chemistry

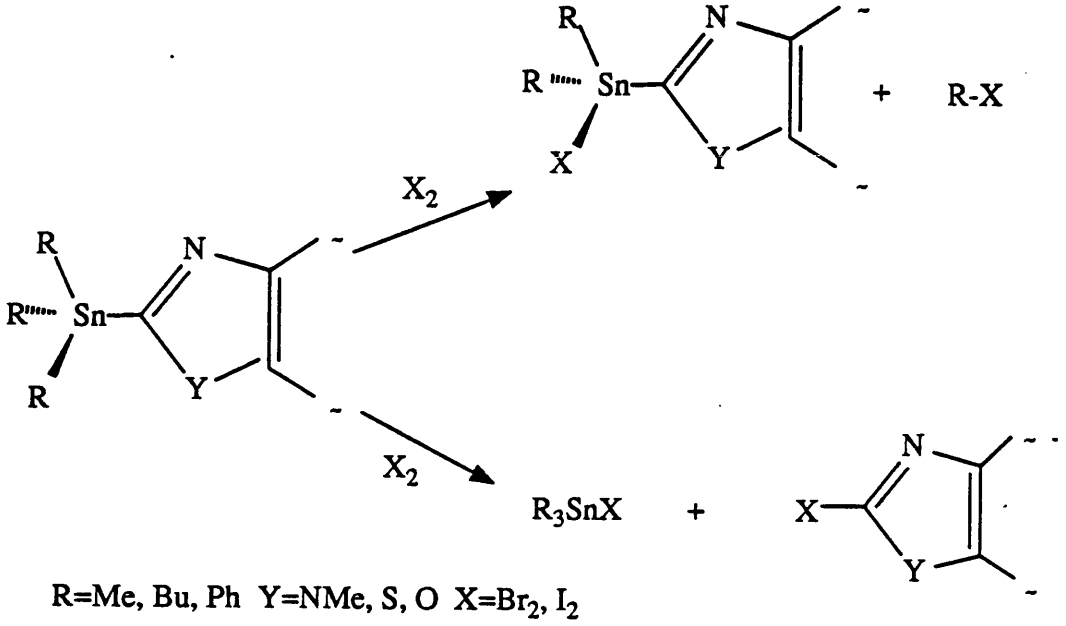
Of the seven compounds synthesised in the above section only 2-Ph_3Sn-benzothiazole, (6), and 2-Ph_3Sn-benzoxazole, (7), have shown any degree of air/moisture stability. All of the other five compounds are attacked by H_2O in the air or during aqueous work-up. This degradation leads to the free heterocycle and the corresponding organotin oxide/hydroxide, (Scheme 7).



Scheme 7

It was found that the 1-methylimidazole compounds were more sensitive than the 2-benzothiazole and 2-benzoxazole compounds and the stability to H_2O increases as R proceeds from Me<Bu<Ph. Indeed, (6) could even be purified by column chromatography on silica gel.

Electron withdrawing groups, e.g. Ph, vinyl may be preferentially cleaved from the tin atom to yield mixed triorganotin halides. In an attempt to prepare compounds of the type $R_2R'SnX$, where R' is a C-bonded heterocycle and X is an inorganic radical, halogenation reactions were studied. It was hoped that a phenyl group could be removed before the heterocyclic ligand, according to scheme 8. Two reaction pathways are possible, but the heterocyclic ligand was preferentially cleaved in every case.



Scheme 8.

The lability of the heterocycle was utilised in a redistribution reaction with a diorganotin dihalide, according to equation (18). The two materials, Ph_2SnCl_2 and Ph_3Sn-Bzt, were heated together for 2hr at 110°C as a melt and although separation of both products was not achieved, ^{119}Sn nmr analysis showed the existance of the reaction product Ph_3SnCl with $\delta(^{119}Sn)$= -46.9 ppm and a small cluster of peaks centered on -310.0 ppm which has been tentatively assigned to be $Ph_2Sn(Bzt)Cl$. The large negative δ value is indicative of 5-coordination and this is possibly the result of $Ph_2Sn(Bzt)Cl$ being dimeric, the extra coordination to tin being possibly achieved *via* N, S or Cl, one example of a possible dimer is given in fig.8

$Ph_3Sn\text{-}Bzt$ + Ph_2SnCl_2 ----------→ Ph_3SnCl + $Ph_2Sn(Bzt)Cl$ (18)

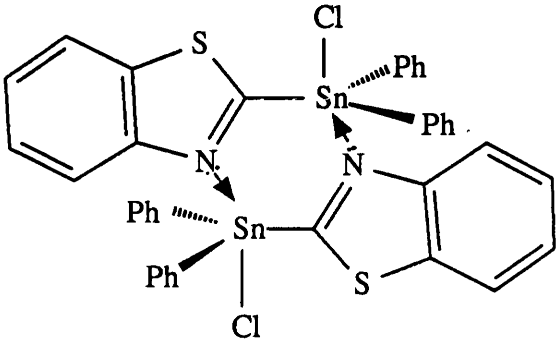


Figure 8.

In order to induce stability against hydrolysis and redirect the site of halogenation, preparation of compounds of the type $Ph_3Sn\text{-}(CH_2)_n\text{-}(Het)$ n=1,2 were attempted, with the strategy of insulating the labile heterocycle with an alkyl chain. Several routes were attempted. (Equations 19-22):

For n=1:

Ph_3SnCl + $LiCH_2\text{-}Bzt$ -------→ $Ph_3SnCH_2\text{-}Bzt$ + LiCl (19)

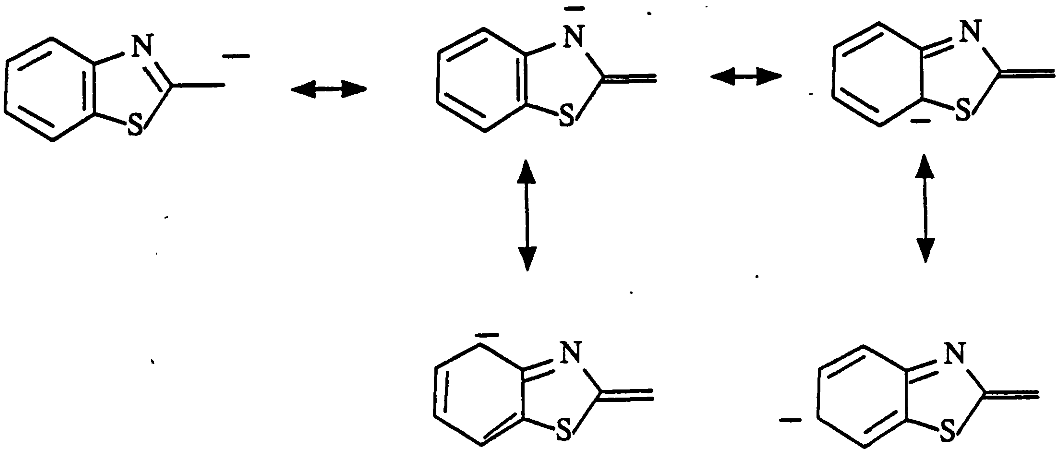
Ph_3SnCH_2I + Li-Bzt -------→ $Ph_3SnCH_2\text{-}Bzt$ + LiCl (20)

For n=2:

Ph_3SnCH_2I + $LiCH_2\text{-}Bzt$ -------→ $Ph_3SnCH_2CH_2\text{-}Bzt$ + LiCl (21)

Ph_3SnH + $CH_2{=}C(CH_3)\text{-}Bzt$ -------→ $Ph_3SnCH_2CH(CH_3)\text{-}Bzt$ + LiCl (22)

The products from Eq. (19) are similar to those of the hydrolysed R_3SnR' (R=Me, Bu, Ph; R'= 1-MeI, Bzt, Box) compounds. It may be speculated that α-lithio-2-methylbenzothiazole reacted with the tin halogen bond at some temperature above -78°C to form Ph_3SnCH_2-Bzt and LiCl, the latter being recovered on the Schlenk-Stick. It is possible to draw several resonance forms for anionic $-CH_2$-Bzt, scheme 9, and this would suggest a relatively weak $Sn-CH_2$ bond and this property enabled the facile $-CH_2$-Bzt to be very readily hydrolysed on exposure to air or moisture.



Scheme 9.

The products from equations (20) and (21) were probably formed by very similar mechanisms. In both cases $(Ph_3Sn)_2$ and 1,2-dibenzothiazolylethane were recovered. 2-lithiobenzothiazole and α-lithio-2-methylbenzothiazole are formed at -78°C and 2-lithiobenzothiazole is reported [194] to be unstable above -35°C. The reported [192] nucleophilicity of α-lithio-2-methylbenzothiazole towards halogenated carbons is very low. It can be speculated that in both cases no reaction occurs below the stability temperatures of the lithiated heterocycles, since no LiCl was precipitated, and as the solution temperature rises, scrambling reactions occur, scheme 10.

$$\begin{tikzcd}
 & Ph_3SnCH_2I + Li\text{-}Bzt \arrow[r, "/"] \arrow[d, leftrightarrow, "Temp.>-35^\circ"'] & Ph_3SnCH_2\text{-}Bzt \\
 & Ph_3SnLi + ICH_2\text{-}Bzt & \\
(Ph_3Sn)_2 & \updownarrow \arrow[l] \arrow[r] & Bzt\text{-}CH_2CH_2\text{-}Bzt \\
 & Ph_3SnI + LiCH_2\text{-}Bzt &
\end{tikzcd}$$

Scheme 10. Possible scrambling reactions in eq. (20)

T.L.C. analysis showed a great number of spots somewhat vindicating the proposed scrambling mechanisms.

The hydrostannylation reaction Eq. (22) was also attempted with N-allylbenzimidazole, N-vinylimidazole and N-allylimidazole. In these cases the heterocycle acts as a base catalyst and simply couples together two triphenyltin units forming the ditin with loss of H_2, equation (23).

$$2Ph_3SnH + CH_2{=}CH\text{-}Het \longrightarrow Ph_3SnSnPh_3 + H_2 + CH_2{=}CH\text{-}Het \quad (23)$$

This type of reaction is well documented in organotin chemistry, and has been widely used for the formation of Sn-Sn bonds, e.g. equation (24).

$$2R_2Sn(H)Cl \xrightarrow{\text{Pyridine.}} R_2Sn(Cl)\text{-}Sn(Cl)R_2 \qquad (24)$$

2.6 Experimental

All starting materials were of commercial origin, e.g. Aldrich LTD. The molarity of n-butyllithium solutions were assayed prior to use. The heterocyclic ligands were purified by distillation under reduced pressure. Trimethyltin chloride, triphenyltin hydride and triphenyl(iodomethyl)tin were prepared as described in Appendix I. The tributyl- and triphenyltin chlorides were used without further purification and the solvents were freshly distilled over sodium wire before use. The analytical data are given in Table 11.

Synthesis of 2-triorganotin-1-methylimidazole (1-3)

Freshly distilled diethyl ether (50 ml) was syringed into a clean dry flask equipped with a stirrer bar, a pressure equalising dropping funnel and a nitrogen/vacuum line tap. The flask was given a dry nitrogen atmosphere and cooled to -10°C using an ice/salt mixture. 1-Methylimidazole (3.28g, 40 mmol) was added by syringe and cooled. 1.6M n-Butyllithium solution in hexane, (25ml, 40 mmol) was added to the dropping funnel and added dropwise over a period of 1 hour. The solution was then stirred at -10°C for 1 hour.

The triorganotin chloride, (40 mmol) was dissolved in dry diethyl ether (R=Bu,Me 50ml Et_2O, R=Ph 200ml Et_2O) and the solution was added via the dropping funnel over a period of 1 hour. The milky solution was stirred at room temperature for 1 hour. The solution was then filtered using a Schlenk Stick apparatus and the clear ether filtrate was reduced in volume to dryness.

The tetraorganotin products were then purified by the following methods:

R=Bu (**2**),Me (**1**); distillation under reduced pressure, bp 145-6°C/0.5 mmHg 10.79g (73%) and 84-6°C/0.5 mmHg 6.95g (71%) respectively.

R=Ph (**3**), recrystallised from dry toluene under nitrogen, mp 89-90°C 10.77g (62%).

All the compounds are air/moisture sensitive.

Synthesis of 2-triorganotin benzothiazole (**4-6**)

Freshly distilled tetrahydrofuran (THF) (66ml) was syringed into a clean dry flask equipped with a stirrer bar, pressure equalising dropping funnel and a nitrogen/vacuum line tap. The flask was cooled to -78°C using a solid carbon dioxide/acetone bath and filled with an atmosphere of dry nitrogen. 2.6M n-Butyllithium (9.6ml, 25mmol) was dissolved in THF (20ml) and added to the flask dropwise through the dropping funnel. Benzothiazole (3.37g, 25 mmol) was dissolved in dry THF (40 ml) and added dropwise to the flask over 30 minutes. Once the addition was complete the opaque yellow solution was stirred at -78°C for 1 hour. The appropriate triorganotin chloride was dissolved in THF (50 ml) and added dropwise to the flask over 30 minutes and stirred for 30 minutes. The flask was allowed to warm to room temperature and the THF removed under reduced pressure. Dry diethyl ether (50ml) was added and LiCl was filtered off using a Schlenk Stick apparatus. The diethyl ether was reduced in volume to dryness.

The tetraorganotin products were then purified by the following methods:

R=Bu **(5)**, Me **(4)**; distillation under reduced pressure , bp 179°C /1.0mmHg 8.52g (80%) and 96-8°C/0.8mmHg 4.78g (64%) respectively.

R=Ph **(6)**, recrystallised from 60-80° petroleum ether/ethyl acetate (1:1). 9.21g, (76%), m.p. 118°C, white prisms. Of the three products only **(6)** is air/moisture stable.

Synthesis of 2-triphenyltin benzoxazole (7)

Dry THF (60 ml) was placed into apparatus as previously descibed and cooled to -115°C using a liquid nitrogen/ ether slurry bath. 2.4M n-butyllithium (10.5 ml, 25 mmol) was syringed into the flask and allowed to cool. Benzoxazole (2.97g, 24mmol) was dissolved in THF (40 ml) and added dropwise to the flask over 10 minutes and stirred for 150 minutes. With the formation of a white slurry, Ph_3SnCl (9.62g, 25 mmol) was dissolved in THF (40 ml) and added dropwise to the flask over 10 minutes. The solution was stirred for 60 minutes at -110°C then allowed to warm to room temperature. The THF was removed under reduced pressure and 60-80°C petroluem (50 ml) was added, the precipitated LiCl was removed by filtration using a Schlenk-Stick and the red filtrate was cooled in a fridge to yield 9.12g (78%) of **(7)**, a white, air stable, crystalline material m.p. 87-8°C.

Halogenation of 2-PhSn$_3$-Bzt

Bromination of 2-Ph$_3$Sn-Bzt

Compound (6), (0.967g, 2mmol) was dissolved in CCl_4 (50ml) and placed in a round bottomed flask equipped with a stirrer bar and a dropping funnel, the flask was cooled to 0°C. Br_2 (0.32g, 2mmol) was dissolved in CCl_4 and added dropwise to the flask over the period of 0.5 hours. The bromine solution was instantly decolourised. Following the addition the flask was stirred for 1 hour at room temperature.

The CCl_4 was removed at reduced pressure, the remaining oily residue was dissolved in hot 80-100° petroleum ether, filtered and allowed to cool. A white crystalline material was collected. The 80-100° petroleum ether filtrate was removed to yield a brown tacky residue.

Analysis of the white crystalline material proved it to be Ph_3SnBr (80% mp 120°C lit.[183] mp 121°C). Analysis for Ph_3SnBr:- C, 49.77 (50.28)%, H, 3.27(3.51)%. The ^1H and ^{13}C n.m.r. spectra of the brown residue proved it to be comprised of mainly 2-Br-Bzt.

Iodination of 2-Ph$_3$Sn-Bzt

Into a 250ml round bottomed flask was placed compound (6), (0.36g, 0.744mmol) and 40-60° petroleum ether (50ml). The solution was stirred at room temperature until fully dissolved. I_2 (0.19g, 0.744mmol) was dissolved in CCl_4 (50ml) and the solution added dropwise via a dropping funnel over the period of 1 hour. Once the addition was complete and the iodine fully decolourised, the solution was stirred for 1 hour.

The 40-60° petrol/CCl_4 solvent was removed under reduced pressure and the oily residue was dissolved in hot 80-100° petroleum ether, filtered and allowed to cool. White crystalline prisms (mp 120-1°C) and brown crystalline needles (mp 78-80°C) were co-crystallised. Manual separation of the different materials afforded data on both. Analysis of the white material proved it to be Ph_3SnI (75% mp 120 lit [183] mp.121°C). The C.H.N. analysis:- found (calc) C, 45.00 (45.19), H, 3.30 (3.13). Analysis of the brown needles proved it to be 2-I-Bzt , Analysis C, 31.80(32.00)%, H, 1.49(1.53)%, N, 5.32(5.36)%.

Attempted preparations of $R_3Sn-(CH_2)_n-Bzt$. (n=1,2)

Attempted preparation of triphenyltin-methylbenzothiazole

A stirred solution of 2-methylbenzothiazole (2.98g, 20mmol) in dry diethyl ether (60ml) under nitrogen was cooled to -78°C (Dry Ice/ acetone bath). 2.07M n-Butyllithium solution in hexane (9.6 ml,20 mmol) was added dropwise over 10 minutes. After 30 minutes a yellow opaque suspension had formed, this indicated that the anion formation was complete [184].

Triphenyltin chloride (7.70g, 20 mmol) was dissolved in dry THF and added dropwise to the suspension over 10 minutes. No colour change accompanied the addition. The flask was allowed to warm to room temperature. The solution slowly decolourised to a dark orange colour. The diethyl ether/THF solvents were removed and replaced with 80-100° petroleum ether (40 ml). The solution was refluxed for 30 minutes. The solution was filtered using a Schlenk stick apparatus to remove LiCl.

The petrol solution was cooled to -20°C overnight but yielded nothing crystalline. T.L.C. analysis (silica plates 1:1 ethyl acetate/80-100° petroleum ether mixture) showed that major spots corresponded to unreacted 2-Methylbenzothiazole (or decomposed α-lithio-2-methylbenzothiazole) and bis-(triphenyltin) oxide. The tin containing product, bis-(triphenyltin) oxide, was finally crystallised from 80-100° petroleum ether, mp. 118°C (Lit.[183] 118°C), 4.21g (59%).

Attempted preparation of triphenyl-benzothiazolylmethyltin

A stirred solution of 1.6M n-butyllithium solution in hexane (1.6 ml, 2.58 mmol) under nitrogen was diluted with dry diethyl ether (6 ml) and cooled to -78°C. Benzothiazole (0.35g, 2.58 mmol) was dissolved in diethyl ether (10 ml) and added dropwise over 10 minutes. After 45 minutes a yellow suspension was formed, showing anion formation was complete[184].

Triphenyl(iodomethyl)tin (1.22g, 2.48 mmol) was dissolved in dry THF (5 ml) and added dropwise to the solution over 10 minutes. The solution was stirred for 1 hour at -78°C. The flask was then allowed to warm to room temperature, upon which the solution turned a dark red colour.

The diethyl ether/THF solvents were removed by reduced pressure and cyclohexane (15 ml) added. The cyclohexane solution was dissolved in ethyl acetate (50 ml) and extracted with distilled water (3x50 ml) to remove LiI. The organic layer was dried over $MgSO_4$, filtered, and reduced in volume. T.L.C. analysis (silica plates, 1:1 ethyl acetate /60-80° petroleum) showed many spots, however two products that were isolable by crystallisation were hexaphenylditin, (0.91g 50%) from 80-

100° petrol, mp. 235°C (lit.[193] 237°C) and 1,2-dibenzothiazolyl ethane, (0.25g, 65%) from ethyl acetate, mp 134-5°C (lit [195] mp. 137.5-138°C).

Attempted preparation of 1-triphenylstannyl-2-benzothiazolyl ethane

α-Lithio-2-methylbenzothiazole (2.01g, 13mmol) was prepared as already described. Triphenyl(iodomethyl)tin (6.15g, 12.5mmol) was dissolved in THF (20 ml) and added dropwise to the solution over 20 minutes. The solution was stirred at -78°C for 2 hours, forming a dark orange solution. The flask was allowed to warm to room temperature and was stirred overnight.

The dark brown solution was filtered and reduced in volume to dryness, ethyl acetate (50 ml) was added and the solution was washed (3x50 ml) in H_2O. The organic layer was separated, dried over $MgSO_4$, filtered and reduced in volume. $Ph_3SnSnPh_3$ (3.17g 72%) was identified by spectroscopic comparison with an original sample.

Analysis for $(Ph_3Sn)_2$:- C, 61.05(61.70)%, H, 4.43(4.28)% T.L.C. analysis (silica plates, 1:1 ethyl acetate/60-80° petrol proved 1,2-dibenzothiazolyl ethane was formed but not isolated.

Attempted preparation of 1-triphenylstannyl-2-benzothiazolyl propane

Triphenyltin hydride (3.50g, 10 mmol) was prepared according to Van der Kerk [196]. 2-Benzothiazolyl-propene was prepared according to Corey and Boger [197]. The two liquid materials were stirred together under nitrogen at 80°C for five hours. Whilst heating the flask a gas was evolved. The flask and contents were allowed to cool and solidify. The crude white solid was recrystallised from 60-80° petroleum ether to yield 3.31g (91.8%) $Ph_3SnSnPh_3$. Analysis C, 61.55(61.76)%, H, 4.33 (4.31)%.

Attempted preparations of other triphenyltin-(CH_2)n-heterocyles. (n=2, 3)

Samples of N-allylbenzimidazole and N-allylimidazole were prepared by refluxing allyl bromide and the N-sodium salt of the required heterocycle in ethanol for 2 hours. N-Vinyl imidazole was purchased from The Aldrich Chemical Co. Triphenyltin hydride was stirred with equimolar quantities of the unsaturated alkyl chain derivatives of the heterocycles at 80°C for 5 hours under nitrogen. In all cases $Ph_3SnSnPh_3$ was recovered in almost quantitative yields.

Redistribution reaction of Ph_2SnCl_2 with Ph_3Sn-Bzt

Compound **(6)**, (1.41g, 2.9 mmol) and Ph_2SnCl_2 (1.00g, 2.9 mmol) were placed in a dry, nitrogen filled, flask and melted together at 110°C for 2 hours. The flask was allowed to cool and solidify. 1 ml of dry $CDCl_3$ was added. Samples of the solution were withdrawn for n.m.r. analysis. The solvent was removed and the solid residue was redissolved in Et_2O. Ph_3SnCl (0.81g 72%) was recovered.

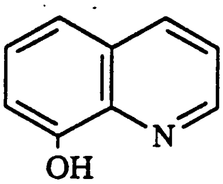
CHAPTER 3

THE SYNTHESIS AND CHARACTERISATION OF [2-(2'-PYRIDYL)ETHYL]-, [2-(4'-PYRIDYL)ETHYL]- AND [2-(N-PYRROLIDIN-2-ONE)ETHYL]TRIPHENYLTIN COMPOUNDS AND THEIR DERIVATIVES.

3.1 Introduction

In Chapter 2 several compounds containing a triorganotin moiety were successfully attached to a heterocycle, however, problems were encountered with these species due to the relative ease of nucleophilic cleavage of the heterocycle with moisture and halogens. This particular shortcoming precluded the preparation of the desired target compounds, e.g. Ph_2RSnX, where R=Heterocycle and X= a halogen. In view of the X_2 cleavage problems encountered in Chapter 2, it was speculated that an alkyl chain positioned between a suitable heterocycle and a triorganotin moiety might insulate the heterocycle somewhat from nucleophiles, and redirect the site of halogenation firmly onto a Ph-Sn bond. With this modification it was then hoped that molecules of the type $Ph_2Sn(X)CH_2CH_2$-Het might be prepared, which in addition may show structural similarities to those biologically active compounds discussed in Chapter 1, e.g. (X), which have trans-tbp structures *via* intramolecularly chelating ligands.

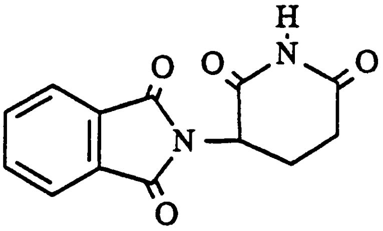
The volume of literature on the biocidal applications of the pyridyl group is vast. A major proportion of the manufactured pyridine is used in the production of the well known weedkillers "Diquat" and "Paraquat". Chloropyridines also feature strongly in the herbicide field and a variety of commercial products exist. A review of the pyridine based herbicides has been published [188]. A number of the chloropyridines or their derivatives exhibit fungicidal or bactericidal activity, e.g. 2-chloro-6-trichloromethylpyridine is selective against *Nitrosomonas* bacteria and the compound also acts to prolong the beneficial effects of fertilizers. The most significant fungicides in terms of commercial production are the benzopyridine derivatives. The mode of action is *via* metal chelation and typical of this type of compound is 8-hydroxyquinoline (XXXV)



(XXXV)

Applications of (XXXV) have been reviewed [189] and several organotin derivatives have recently been prepared and tested for biocidal activity [190]. Several pyridine derivatives have found applications in the poultry industry as antiparasitics and anthelmintics and this area has been reviewed [191]. The pyridyl group also appears in many commercial insecticides. These compounds function as cholinesterase inhibitors and exhibit a broad spectrum of insecticidal activity and low mammalian toxicity. The pyridyl group has also made advances into the field of pharmaceuticals and there are at least two review articles concerning its medicinal chemistry [192,193].

The pyrrolidine nucleus and its benzo- derivatives form the basis of many biocidal formulations but the most notorious is surely the related, but now banned, pharmaceutical thalidomide (XXXVI).



(XXXVI)

The pyrrolidine nucleus is also used in simple insecticides (e.g. nicotine), as a diuretic, as a antihistamine and several fungicidal preparations.

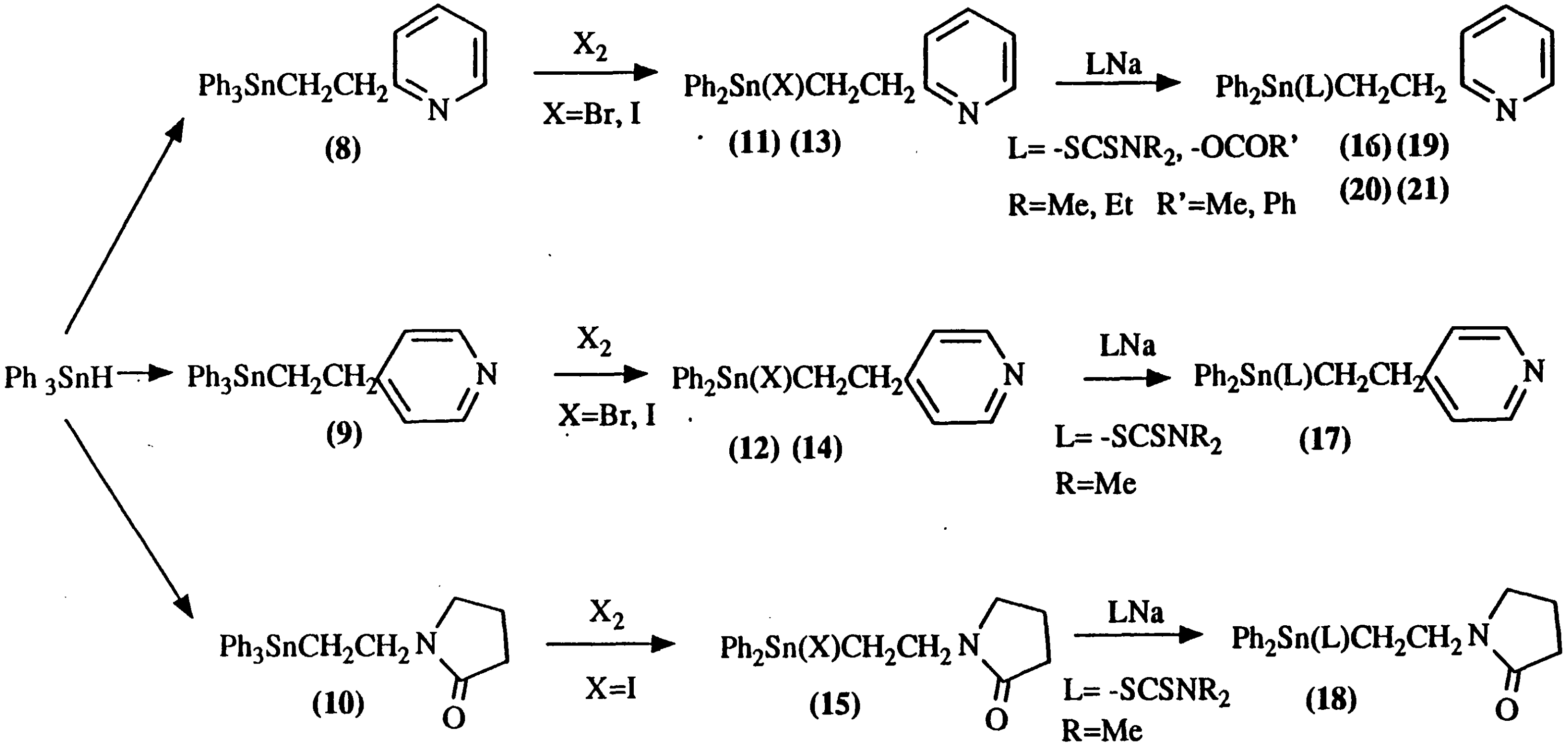
In this Chapter several compounds containing a triphenyltin group, a $-CH_2CH_2-$ chain unit and a pyridyl or a pyrrolidin-2-one heterocycle have been synthesised. The $-CH_2CH_2-$ chain unit endows the heterocycle with 'alkyl-like' stability, compared to a phenyl group, against halogen cleavage. It has therefore been possible to prepare various halide, dithiocarbamate and carboxylate derivatives of type Ph_2RSnX where $R=CH_2CH_2Py-2$, $-CH_2CH_2Py-4$ and CH_2CH_2-N-Pyrrolidin-2-one and X=Br, I, $-SCSNEt_2$, $-SCSNMe_2$, -OCOMe and OCOPh. The reaction chemistry and full spectral characterisation of these compounds have been studied and the X-ray crystal structure of N,N-dimethyldithiocarbamato [2-(2'-pyridyl)ethyl]diphenyltin(IV) has been determined.

3.2 Synthesis

Triphenyltin hydride has been added across vinyl groups attached to pyridine and pyrrolidin-2-one in a non-Markovnikov manner, i.e. the hydride becomes attached to the most substituted carbon, (8-10). The addition reactions are brought about by heating mixtures of the hydride and the olefinic substituted heterocycles at around 100°C for between 2-4 hours. No catalyst is required and the experimental yields are usually very high (>80%). The purity of the hydride seems to be important since several reactions using distilled Ph_3SnH yielded the required addition product, however, if impure Ph_3SnH was used, the reactions yielded hexaphenylditin quantitatively.

Triorganotin bromides and iodides were prepared by halogen cleavage of a phenyl ring from the metal center. Only one phenyl ring was cleaved off in each case and no example of $Sn-CH_2$ bond rupture was observed. The triorganotin halides **(11-15)** were then used as starting materials for the synthesis of other functionalised triorganotins, e.g. dithiocarbamates and carboxylates **(16-21)** by refluxing the organotin halide with either the sodium salt of the required dithiocarbamate or with a carboxylic acid and triethylamine (Scheme 11).

The purification of all the materials was accomplished *via* recrystallisation and all the compounds appear to have long term stability in air/moisture. The [2-(2'-pyridyl)ethyl]- and [2-(N-pyrrolidin-2-one)ethyl]- compounds were recrystallised easily to yield white, crystalline materials but the [2-(4'-pyridyl)ethyl]- compounds did not readily yield crystalline materials, but amorphous powders. Crystallisation for these compounds seemed to be aided by allowing the crystals to form very slowly from a moderately dilute solution. The analytical data are given in Table 21.


Ph$_3$SnH
Ph$_3$SnCH$_2$CH$_2$
N
(8)
X$_2$
X=Br, I
Ph$_2$Sn(X)CH$_2$CH$_2$
(11) (13)
LNa
Ph$_2$Sn(L)CH$_2$CH$_2$
L= -SCSNR$_2$, -OCOR'
R=Me, Et R'=Me, Ph
(16) (19)
(20) (21)
Ph$_3$SnCH$_2$CH$_2$
(9)
X$_2$
X=Br, I
Ph$_2$Sn(X)CH$_2$CH$_2$
(12) (14)
LNa
L= -SCSNR$_2$
R=Me
Ph$_2$Sn(L)CH$_2$CH$_2$
(17)
Ph$_3$SnCH$_2$CH$_2$ N
(10)
O
X$_2$
X=I
Ph$_2$Sn(X)CH$_2$CH$_2$ N
(15)
LNa
L= -SCSNR$_2$
R=Me
Ph$_2$Sn(L)CH$_2$CH$_2$ N
(18)

Scheme 11

Table 21. Analytical results of $Ph_2Sn(X)CH_2CH_2(Het)$

X	mp/°C	C:[a] %	H: %	N: %
Het=(2'-pyridyl)				
Ph	73	66.10(65.80)	5.08(5.04)	3.17(3.07)
Br	168-9	49.20(49.71)	3.93(3.92)	3.04(3.05)
I	160	45.20(45.09)	3.58(3.56)	2.76(2.76)
$SCSNMe_2$	160	52.99(52.93)	4.90(4.81)	5.58(5.61)
$SCSNEt_2$	145-6	54.50(54.60)	5.37(5.31)	5.31(5.31)
OCOPh	140-4	62.32(62.43)	4.58(4.60)	2.77(2.80)
OCOMe	80-1	57.70(57.57)	4.83(4.79)	3.16(3.19)
Het=(4'-pyridyl)				
Ph	112	64.50(65.80)	4.78(5.04)	3.04(3.07)
Br [b]	137-9	50.12(49.71)	3.99(3.92)	2.96(3.05)
I [c]	155-6	45.40(45.08)	3.59(3.55)	2.69(2.76)
$SCSNMe_2$ [c]	192-2	53.10(52.93)	5.11(4.81)	5.21(5.61)
Het=(N-pyrrolidin-2-one)				
Ph	73-5	62.30(62.37)	5.40(5.41)	2.87(3.03)
I	146	42.40(42.20)	3.97(3.90)	2.70(2.73)
$SCSNMe_2$	117	49.80(49.93)	5.21(5.15)	5.56(5.54)

[a] Found(Calc)

[b] This compound could only be recrystallised as an amorphous powder

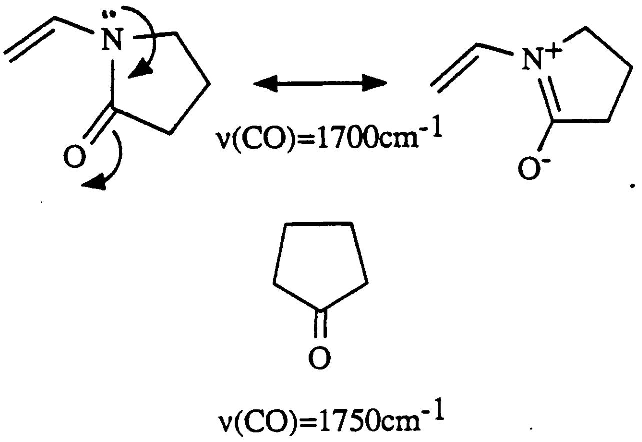
[c] Recrystallisation yielded amorphous powder and crystals.

3.3 Spectroscopy

3.3.1 Infra-red Spectroscopy

The infra-red spectral data are presented in Table 22. Many of the spectra are complex and full interpretation is not possible, however, some unambiguously assigned bands are useful from a structural viewpoint, and the course of the hydrostannylation reactions can be monitored by the ν(Sn-H) stretch for triphenyltin hydride (1825 cm^{-1}) which steadily decreases. Futhermore, although identification of the stretches due to the vinyl group on the 2- and 4-vinyl pyridines is not possible due to the many aromatic stretching modes in the 1600-1450 cm^{-1} region, the ν(C=C) stretch for N-pyrrolidin-2-one can be observed at 1630 cm^{-1} and also steadily decreases during the addition reaction.

It is possible to draw resonance forms for N-pyrrolidin-2-one and the effect of these is to reduce the bond order, and thus to decrease the stretching frequency of the carbonyl group away from a more typical carbonyl, in, for example, a saturated cyclic ketone (Scheme 12).



Scheme 12.

Table 22. The Infra-Red data for $Ph_2(X)CH_2CH_2(Het)$ [a]

Het= 2'-pyridyl:

	X	$\nu_{asym}(CO_2)$	ν(C-N)	ν(C-S)	ν(Sn-Br)
(16)	$-SCSNMe_2$	(-)	1460 s	1120, 1080	(-)
(19)	$-SCSNEt_2$	(-)	1450 s	1140, 1080	(-)
(20)	$-OCOCH_3$	1635	(-)	(-)	(-)
(21)	-OCOPh	1640	(-)	(-)	(-)
(11)	-Br	(-)	(-)	(-)	260

Het= 4'-pyridyl:

	X	$\nu_{asym}(CO_2)$	ν(C-N)	ν(C-S)	ν(Sn-Br)
(17)	$-SCSNMe_2$	(-)	1465 s	1160, 1080	(-)
(12)	-Br	(-)	(-)	(-)	264

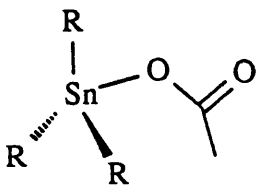
Het= N-pyrrolidin-2-one:		ν(C=O) [b]	ν(C-N)	ν(C-S)
(18)	$-SCSNMe_2$	1670	1462	1160, 1062
(15)	-I	1625		
(10)	-Ph	1680		

[a] cm^{-1}

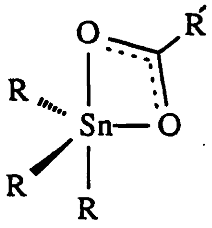
[b] For comparison cyclopentanone ν(C=O)=1750 cm^{-1}, N-vinyl-pyrrolidin-2-one, ν(C=O) = 1700 cm^{-1}.

It is highly likely that [2-(N-pyrrolidin-2-one)ethyl]triphenyltin **(10)** is tetrahedral about the metal and the carbonyl group attached to the pyrrolidine, [ν(C=O) at 1680 cm^{-1}] does not interact in any significant way with the tin atom. The dithiocarbamate derivative **(18)** has a similar ν(C=O) stretching frequency (1670 cm^{-1}) and again it may be rationalised that there is no carbonyl-tin interaction here either. However, the iodide derivative **(15)** has a significantly lower ν(C=O) (1625 cm^{-1}) than **(10)** or **(18)** and therefore it might be anticipated that here there is an appreciable CO→Sn interaction.

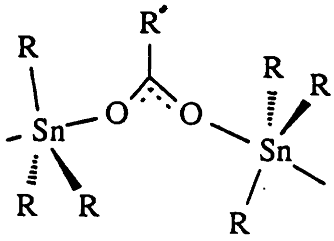
Triorganotin carboxylate compounds can exhibit three identified structures (XXXVII-XXXIX) and generally do not exhibit ν(C=O) stretches similar to those found for esters at 1750 cm^{-1}.



(XXXVII)



(XXXVIII)



(XXXIX)

Instead ν_{asym}(C-O) and ν_{sym}(C-O) stretches are observed and their position may vary with the R groups on the tin or the R' groups on the carboxylate. For example, Molloy *et al.*[134] have reported several triphenyltin benzoate compounds with tetrahedral structures, (XXXVII), and these compounds have ν_{asym}(C-O) in the range 1605-1648 cm^{-1}. Compounds are also known that adopt trans-tbp geometry, (XXXIX) and these compounds have ν_{asym}(C-O) in the range 1540-1550 cm^{-1} .

Compounds (20) and (21), the acetate and benzoate derivatives, respectively, show ν_{asym}(C-O) stretches at 1635 and 1640 cm^{-1} respectively. These figures suggest that the carboxylate groups in these two compounds are monodentate, and interact with the tin in a similar fashion to that in (XXXVII).

The infra-red data for the dithiocarbamate derivatives show the ν(C-N) stretching bands in the range 1450-1465 cm^{-1} and the ν(C-S) bands in the range 1050-1160 cm^{-1}. The figures are in general agreement with those found by Holt *et al.* [195] and Molloy *et al.* [194]. Both groups have reported the infra-red data for a series of organotin dithiocarbamate derivatives, however, neither group could unambigously deduce any structural implications for the bonding of the dithiocarbamate ligands purely on these data.

3.3.2 N.M.R. Spectroscopy

The ^{1}H nmr data are presented in Table 23. It has been shown that the $^{2}J(^{119}Sn, ^{1}H)$ coupling constant is a probe of the local geometry around the tin atom. The $^{2}J(^{119}Sn, ^{1}H)$ values for the series of compounds are in the range 51-141 Hz. and encompasses tetrahedral to arguably six coordination around the tin.

Verdonck *et al.* [196] have measured the $^{2,3}J(^{119}Sn, ^{1}H)$ values for a series of compounds $R_3SnCH_2CH_2Z$ (R=Ph, ^{n}Pr, ^{n}Bu, Z=CN, Ph, OPh, $OCOCH_3$). The values they found are in close agreement with the tetraorganotin compounds studied in this work. The tetraorganotin coupling constants $^{2}J(^{119}Sn, ^{1}H)$, prepared in this work, are found in the range 51-71 Hz. The triorganotin halide compounds can be convieniently divided into two groups. The first group, containing

Table 23. ^{1}H nmr studies on $Ph_2Sn(X)CH_2CH_2(Het)$ [a,b,c]

Het=(2'-pyridyl)

X	Phenyl	$CH_2(\alpha)$	J^2(Sn-H)	$CH_2(\beta)$	J^3(Sn-H)	Het	Others
Ph	8.24-	3.21	68.6	1.85	52.9	8.24	-
(8)	6.94		72.0		56.3	6.94	
	(15H,m)	(2H,t)		(2H,t)		(4H,m)	
Br	7.91-	3.44	110.8	2.08	77.5	7.91-	-
(11)	7.12		114.8		82.1	7.13	
	(10H,m)	(2H,t)		(2H,t)		(4H,m)	
I	7.83-	3.42	112.9	2.16	74.3	7.84-	-
(13)	7.06		118.8		78.6	7.06	
	(10H,m)	(2H,t)		(2H,t)		(4H,m)	
[SCS-	7.70-	3.43	135.0	2.27	80.2	7.71-	Me=3.39
NMe_2]	6.93		141.3		84.1	6.94	(6H,s)
(16)	(10H,m)	(2H,t)		(2H,t)		(4H,m)	
[SCS-	7.70-	3.42	129.8	2.28	80.3	7.70-	CH_3=1.19
NEt_2]	6.92		138.0		83.3	6.92	CH_2=3.87
(19)	(10H,m)	(2H,t)		(2H,t)		(4H,m)	(6H,t) &
							(4H,q)

Table 23 continued,

OCOPh	7.82-	3.38	117.0	1.94	64.8	7.83-	Ph=7.82-
(21)	7.03		124.2		72.0	7.03	7.03
	(10H),m)	(2H,t)		(2H,t)		(4H,m)	(5H, m)
OCOMe	7.82-	3.38	117.0	1.94	65.3	7.82-	CH_3=1.98
(20)	7.03		125.0		67.9	7.03	
	(10H,m)	(2H,t)		(2H,t)		(4H,m)	(3H,s)
Het=(4'-pyridyl)							
Ph	7.58-	2.95	44.4	1.76	50.6	8.42-	-
(9)	7.19		51.8		54.0	7.01	
	(15H,m)	(2H,t)		(2H,t)		(4H,m)	
Br	7.62-	3.07	63.7	2.08	44.7	8.45-	-
(12)	7.12		66.8		47.1	7.02	
	(10H,m)	(2H,t)		(2H,t)		(4H,m)	
I	7.64-	3.04	65.6	2.00	48.6	8.40-	-
(14)	7.25		68.9		51.3	7.10	
	(10H,m)	(2H,t)		(2H,t)		(4H,m)	
[SCS-	7.75-	3.13	64.7	2.09	56.2	8.48-	CH_3=3.38
NMe_2]	7.35		68.6		59.4	7.02	(6H,s)
(17)	(10H,m)	(2H,t)		(2H,t)		(4H,m)	

Table 23 continued,

Het=(N-pyrrolidin-2-one)

						Pyrrolidin-2-one			
X	Ph	$CH_2(\alpha)$	$J^2(Sn,H)$	$CH_2(\beta)$	$^3J(Sn,H)$	C_3	C_4	C_5	Me
Ph	7.64-	3.65	52.9	1.71	40.5	2.12	1.72	3.33	-
(10)	7.22		56.8		46.1				
	(15H,m)	(2H,t)		(2H,t)		(2H,t)	(2H,m)	(2H,t)	
I	8.04-	3.59	126.0	2.02	66.4	2.24	1.92	3.42	-
(15)	7.23		132.8		69.8				
	(10H,m)	(2H,t)		(2H,t)		(2H,t)	(2H,m)	(2H,t)	
[SCS-	7.80-	3.77	68.0	2.07	62.4	2.21	1.84	3.37	3.42
NMe_2]	7.25		72.0		65.8				
(18)	(10H,m)	(2H,t)		(2H,m)		(2H,t)	(2H,m)	(2H,t)	(6H,s)

[a] All chemical shift data given in ppm.

[b] All samples recorded as $CDCl_3$ solutions and TMS used as a reference.

[c] Coupling constants are $^{117,119}Sn$ respectively and are given in Hz.

compounds (11), (13) and (15), are sterically capable of forming trans-tbp intramolecularly chelated structures, e.g. similar to (X). The coordination around the tin expands from 4 to 5 and a concommitant rise in the $^{2}J(^{119}Sn, ^{1}H)$ is observed. The $^{2}J(^{119}Sn, ^{1}H)$ values for compounds (11), (13) and (15) are in the range 114-132 Hz. and are significantly larger than the 4-coordinate tetrahedral compounds discussed earlier. The structures of compounds (11) and (13) are probably very similar.

The second group of compounds, (12) and (14), are not sterically capable of forming trans-tbp intramolecular chelated structures. The $^{2}J(^{119}Sn, ^{1}H)$ values are in the range 66-69 Hz. and are similar in magnitude to the tetraorganotin 4-coordinate compounds. Thus, in solution, these compounds are, in all likelihood, also 4-coordinate.

Both carboxylate derivatives, (20) and (21) have $^{2}J(^{119}Sn, ^{1}H)$ in the range 124-125 Hz and as such, one can speculate that these compounds are 5-coordinate species. It was evident from the infra-red data $[v_{asym}(C-O)]$ that the carboxylate groups in these compounds are monodentate, therefore the 5-coordinate geometry must arise from the coordination of the pyridyl groups, in a similar way to that proposed above for the halides.

The dithiocarbamate derivatives, (16) and (19) of the 2-pyridyl organotin compounds have $^{2}J(^{119}Sn, ^{1}H)$ values in the range 138-141 Hz. and using a similar rationale to that used in the discussion of the halides it is evident that these compounds are at least 5-coordinate about tin. The dithiocarbamate derivative, (17), of the 4-pyridyl analogue has a relatively low $^{2}J(^{119}Sn, ^{1}H)$ of 68.3 Hz. This would suggest that this compound has a monodentate dithiocarbamate ligand

and a 4-coordinate geometry at the tin.

The dithiocarbamate derivative of the pyrrolidin-2-one analogue, (18) has a slightly larger $^{2}J(^{119}Sn, ^{1}H)$ value (72 Hz.) but it is not as clearly 5-coordinate as the corresponding halide (15). In addition, the infra-red data of (18) shows that there is very little CO→Sn interaction, as was observed for the halide (15). Therefore the slightly larger $^{2}J(^{119}Sn, ^{1}H)$ value must be attributed to a weak long-range S→Sn interaction, but it must be stressed that any additional interaction over 4-coordination is very weak.

The ^{13}C nmr data are presented in Table 24. Holecek *et al.* have reported the $\delta(^{13}C)$ values for 4- and 5-coordinate triphenyltin compounds [100]. The chemical shift of the *i* carbon on the phenyl rings is a probe of geometry around the tin. $\delta(^{13}C)$ values below 140 ppm are generally indicative of 4-coordinate geometry and values above correspond generally to 5- or higher coordination numbers at tin. As expected, the tetraorganotin compounds (9) and (10) and all the [2-(4'-pyridyl)ethyl]diphenyltin derivatives, (12), (14) and (17) show $\delta(^{13}C)$ resonances at 138 ppm. or lower and reinforce the evidence given by ^{1}H nmr and IR that these compounds are tetrahedral.

The dithiocarbamate and the carboxylate derivatives of the [2-(2'-pyridyl)ethyl]diphenyltin compounds, (16) and (19 - 21) show $\delta(^{13}C)$ values for the *i* carbons to be >140 ppm., and these are confirmed to have at least 5-coordinate geometry. The dithiocarbamate derivative of the N-pyrrolidin-2-one (18) has a $\delta(^{13}C)$ *i* value of 142.2 ppm and as such, the speculation that there is a long range cis Sn---S interaction receives greater credibility. The triorganotin halide derivatives (11), (13) and (15) have $\delta(^{13}C)$ *i* values in the range

Table 24: ^{13}C nmr studies on $Ph_2Sn(X)CH_2CH_2(Het)$ [a]

Het=(2'-pyridyl)

Aromatic organotin carbons

X	*i*	*o*	^2J(C-Sn)	*m*	^3J(C-Sn)	*p*	^4J(C-Sn)
Ph	140.3	136.9	35.9	128.1	51.4	128.4	12.9
Br	139.2	135.9	47.1	128.4	65.9	128.9	13.4
I	141.7	135.8	47.6	128.2	65.4	128.8	14.3
$SCSNMe_2$	142.1	136.1	39.6	128.2	63.4	128.6	13.2
$SCSNEt_2$	144.6	136.2	38.3	127.9	60.1	128.4	13.3
OCOPh	144.8	136.2	38.2	127.4	63.2	127.2	14.1
OCOMe	144.9	136.2	38.0	127.8	62.5	127.8	14.3

Alkyl chain, pyridine carbons and others

X	C(α)	C(β)	2'	3'	4'	5'	6'	Others
Ph	10.48	33.93	162.7	122.4	136.2	121.0	148.7	-
Br	16.12	31.79	161.2	124.6	136.3	122.9	146.3	-
I	18.86	31.80	160.8	124.6	139.3	122.9	145.9	-
$SCSNMe_2$	20.02	31.98	160.5	123.6	137.7	121.9	146.4	NMe_2 =44.6 SCS= 201.8
$SCSNEt_2$	20.34	32.01	160.9	123.6	137.3	121.9	146.4	CH_2= 48.5 CH_3= 12.1 SCS= 201.8

Table 24 continued,

OCOPh

OCOMe	12.85	31.53	160.9	124.1	138.5	122.4	146.2	CO_2= 177.4 Me = 22.9
OCOPh	13.21	29.98	160.2	123.7	138.2	121.9	146.1	CO_2= 169.8 *i* = 130.6 *o* = 129.7 *m* = 128.5 *p* = 132.9

Het=(4'-pyridyl)

Aromatic organotin carbons

X	*i*	*o*	^2J(C-Sn)	*m*	^3J(C-Sn)	*p*	^4J(C-Sn)
Ph	137.9	136.8	35.1	128.5	48.4	128.9	12.1
Br	136.9	136.3	45.3	129.3	59.3	130.1	13.3
I	136.8	135.9	48.4	128.9	58.1	130.0	13.3
$SCSNMe_2$	135.6	136.3	41.4	128.4	52.7	129.0	7.5

Alkyl chain, pyridine and others

X	C(α)	C(β)	2'	3'	4'	5'	6'	Others
Ph	11.19	31.69	149.6	123.1	153.2	=3'	=2'	-
Br	17.89	31.55	149.7	123.3	153.4	=3'	=2'	-
I	17.23	31.92	149.7	123.4	153.2	=3'	=2'	-
$SCSNMe_2$	20.63	31.46	149.5	123.4	153.2	=3'	=2'	Me=45.8 SCS=201.2

Table 24 continued,

Het=(N-pyrrolidin-2-one)

Aromatic organotin carbons

X	*i*	*o*	^2J(C-Sn)	*m*	^3J(C-Sn)	*p*	^4J(C-Sn)
Ph	137.8	136.9	38.9	128.5	61.7	129.0	14.9
I	141.4	136.7	39.8	128.1	64.7	128.9	15.7
SCSNMe$_2$	142.2	136.2	40.5	128.2	65.9	128.8	15.6

Alkyl chain, pyrrolidin-2-one and others

X	C(α)	C(β)	C(2')	C(3')	C(4')	C(5')	Others
Ph	9.41	30.88	174.35	46.15	17.39	40.32	-
I .	17.94	31.63	178.70	50.95	22.84	44.95	-
SCSNMe$_2$	17.58	31.11	174.90	47.13	18.62	41.06	SCS=197.6 NMe$_2$=45.5

[a] All spectra were recorded as CDCl$_3$ solutions at 298K. TMS was used as a reference.

All chemical shift values given in ppm.

Coupling constants refer to $^1J(^{13}C, ^{119}Sn)$ and are given in Hz.

139.2-141.7 ppm. Other evidence points to the fact that all of these compounds have 5-coordinate geometry around tin and it suggests that the chemical shift ranges for the *i* carbons set by Holecek *et al.* may only be used as a tentative guide to the coordination at tin since the 4-coordinate tetraorganotin compound **(8)** has *i* carbons resonating at 140.3 ppm. and the proposed 5-coordinate compound **(11)** has $\delta(^{13}C\ i)$ at 139.2 ppm.

If the heterocycle in this series of compounds does engage in an intramolecular chelation with the tin atom, the ^{13}C nmr δ values of the ring atoms, especially C(2') and C(6'), would be expected to shift from the δ values of the same heterocyclic ring in the corresponding tetraorganotin compound. These effects were indeed observed for all the compounds suspected of having 5-coordination in solution, i.e. **(11)**, **(13)**, **(15)**, **(16)** and **(18 - 21)**.

The ^{119}Sn nmr data for the compounds are presented in Table 25. The $\delta(^{119}Sn)$ values can be compared to similar triphenyltin derivatives of known geometry. Since $\delta(^{119}Sn)$ is known to become more negative with enhanced coordination for similar systems, a comparison of the data will provide an insight into the local geometry around the tin atom. For example, compare the systems $Ph_3SnCH_2CH_2X$, :X=H, the 4-coordinate compound gives $\delta(^{119}Sn)$= -98.6 ppm.(C_6H_6) [197], vs. X=2'-pyridyl, $\delta(^{119}Sn)$= -110.8 ppm. ($CDCl_3$). Both values are similar and this result together with other evidence demonstrates unequivocably that the 2-pyridyl compound **(8)** is tetrahedral. A similar approach shows that the remainder of the tetraorganotin compounds and all of the [2-(4'-pyridyl)ethyl]diphenyltin derivatives are 4-coordinate.

Table 25: Mossbauer [a] and ^{119}Sn nmr [b] data for $Ph_2Sn(X)CH_2CH_2(Het)$

	X	$\delta(^{119}Sn)$ [c]	I.S. (δ)	ΔEq	Γ_1, Γ_2 [d]
Het=(2'-Pyridyl)					
(8)	Ph	-110.81	1.22	0.63	0.99, 0.96
(11)	Br	-143.47	1.32	2.98	0.95, 0.96
(13)	I	-109.33	1.35	2.95	0.96, 0.98
(16)	$SCSNMe_2$	-201.98	1.27	2.55	0.91, 0.91
(19)	$SCSNEt_2$	-198.22	1.27	2.35	0.92, 0.94
(21)	OCOPh	-175.21	1.26	2.41	0.93, 0.95
(20)	OCOMe	-177.34	1.26	2.71	0.96, 0.98
Het=(4'-Pyridyl)					
(9)	Ph	-101.84	1.25	0.32	0.87, 0.96
(12)	Br	-85.75	1.33	2.95	1.38, 1.55
(14)	I	-61.68	1.34	2.92	0.96, 0.96
(17)	$SCSNMe_2$	-128.06	1.27	2.55	0.93, 0.94
Het=(N-pyrrolidin-2-one)					
(10)	Ph	-109.29	1.23	0.39	0.88, 0.91
(15)	I	-147.24	1.33	3.14	0.99, 0.99
(18)	$SCSNMe_2$	-182.78	1.30	2.18	0.88, 0.87

Table 25 continued,

[a] Mossbauer experiments performed at 78K, values in $mmsec^{-1}$

[b] ^{119}Sn nmr experiments performed in $CDCl_3$ at 298K
Me_4Sn used as a reference.

[c] Values in ppm.

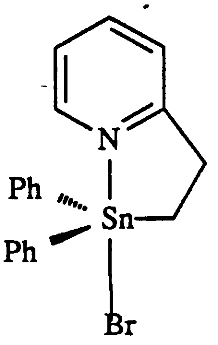
[d] Refers to maximum width at half height of the high and low velocity spectral components in $mmsec^{-1}$.

All the triorganotin halide, carboxylate and dithiocarbamate derivatives of compound (8) show more negative $\delta(^{119}Sn)$ values than the tetraorganotin and other similar species, which suggests that the coordination number for these compounds is > 4. Only compound (13), [$\delta(^{119}Sn)$= -109.3 ppm.], has a shift which does not suggest a coordination number > 4 and is at odds with the other nmr evidence. However, it must be noted that the 4-coordinate compound (14) shows a much less negative $\delta(^{119}Sn)$ value (= -61.7 ppm.) than similar compounds of the same coordination number, so the above shift for (13) may be an artefact of the system.

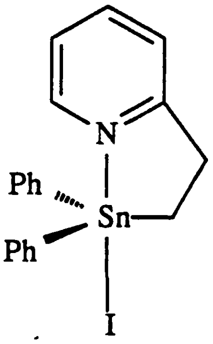
3.3.3 Mossbauer Spectroscopy

The Mossbauer spectral data are presented on Table 25. As expected the tetraorganotin compounds yield ΔEq values very close to, but not zero. The compounds are discrete tetrahedral molecules. All three compounds contain a $Ph_3SnCH_2CH_2X$ system which should generate a small e.f.g. in the σ skeletons. It is therefore surprising that the reported Mossbauer parameters of similar systems e.g. $Ph_3SnCH_2CH_2CH_2COMe$ [198], $Ph_3SnCH_2CH=CH_2$ [199] and $Ph_3Sn(CH_2)_4SnPh_3$ [200] all quote ΔEq as zero.

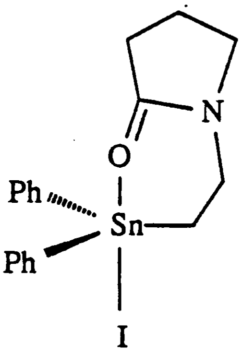
All of the halide derivatives show ΔEq values in the range 2.92-3.14 $mmsec^{-1}$ and the isomer shift values in the range 1.32-1.35 $mmsec^{-1}$. These figures would suggest that all the molecules have trans-tbp R_3SnX_2 geometry, distorted to varying degrees, and it is apparent that in the solid state the heterocyclic ligands engage in intra- or intermolecular chelation. Briefly summarizing the evidence for a 5-coordination geometry in solution for the triorganotin halides, **(11)**, **(13)** and **(15)**, it has been shown that: (i) these compounds have $^2J(^{119}Sn, ^1H)$ values in the range 114.8-132.7 Hz., well above that of the 4-coordinate tetraorganotins, (ii) these compounds have ^{13}C nmr *i* carbon δ values in the range 139.2-141.7 ppm., which, according to Holecek *et al*, is evidence of 5-coordination, (iii) the ^{119}Sn nmr chemical shifts suggest that these compounds have coordination >4, and (iv) the carbonyl ν(C=O) band in **(15)** is significantly lower than in the parent tetraorganotin compound, suggesting a CO→Sn interaction, (XXXX-XXXXII). The evidence for 4-coordination in the triorganotin halide compounds **(12)** and **(14)** in solution is as follows: (i) these compounds have $^{2}J(^{119}Sn, ^{1}H)$ values similar to the parent 4-coordinate tetraorganotin **(9)**, (ii) the ^{13}C nmr *i* δvalues are well below 140 ppm. suggesting 4-coordination, (iii) the ^{119}Sn nmr values are not sufficiently negative enough to warrant 5-coordinate assignments. Combining these arguments it can be stated that compounds **(11)**, **(13)** and **(15)** are 5-coordinate intramolecular chelates in the solid and the solution state and that compounds **(12)** and **(14)** are 4-coordinate in solution (XXXXIII) but 5-coordinate intermolecularly linked polymers in the solid state, (XXXXIV).



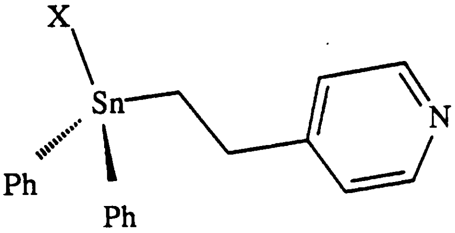
(XXXX)



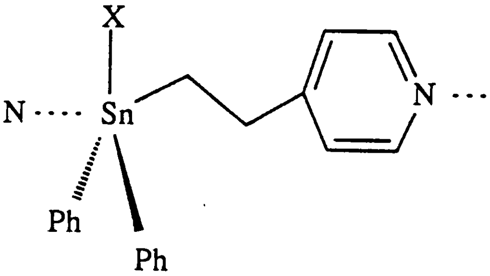
(XXXXI)



(XXXXII)

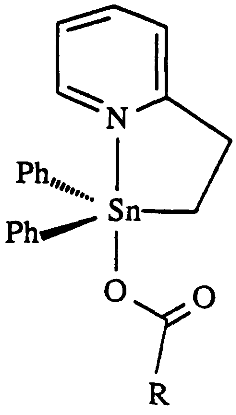


(XXXXIII)



(XXXXIV)

The Mossbauer data for the [2-(2'-pyridyl)ethyl]diphenyltin carboxylate derivatives, **(20)** and **(21)**, suggest that their structures also have trans-tbp geometry, very similar to the halide derivatives. A resume of the spectral information discussed above reveals that: (i) these compounds have large $^{2}J(^{119}Sn, ^{1}H)$ values (124.2-125.0 Hz.), indicating 5-coordination, (ii) the ^{13}C nmr *i* δ values are well above 140 ppm. (144.8-144.9), (iii) the large negative $\delta(^{119}Sn)$ nmr results are indicative of 5-coordination and (iv) it is implied from IR data that the carboxylate ligands are monodentate. It can be concluded that **(20)** and **(21)** are 5-coordinate intramolecular chelates with trans-tbp type geometry in the solid and the solution state, and with the 2-pyridyl ligands providing the extra coordination to the tin atom, (XXXXV).



(XXXXV)

The Mossbauer parameters of the dithiocarbamate derivatives **(16)**, **(17)** and **(19)** are very similar. The ΔEq values are in the range 2.35-2.55 mmsec^{-1} and all of the isomer shift values are 1.27 mmsec^{-1}. The X-ray study of [2-(2'-pyridyl)ethyl]diphenyltin N,N-dimethyldithiocarbamate,

(16) has shown it to be a distorted trans-R_3SnNS structure, and so, presumably, are the other two derivatives.

The Mossbauer parameters indicate that the [2-(4'-pyridyl)ethyl] diphenyltin derivatives have trans-tbp 5-coordinate geometry and it was reasoned that these molecules achieve this structure *via* intermolecular coordination through the pyridyl nitrogen, since they are monomeric and 4-coordinate in solution. The [2-(2'-pyridyl)ethyl] diphenyltin derivatives achieve 5-coordination *via* intramolecular chelation through the pyridyl nitrogen and consequently have pentacoordinate tin in the solid and the solution state. It is interesting to note that Barbieri *et al.*[201] have predicted the ΔEq values for trans-tbp R_3SnNS type structures (R=Alk, Ph) thought to be created when R_3Sn units bind to proteins. The ΔEq_{calc} values of (R=Ph), 1.68 $mmsec^{-1}$ and (R=alk), 2.13 $mmsec^{-1}$ are significantly lower than the values found experimentally for compounds **(16)**, **(17)** and **(19)**, (even allowing for the 0.4 $mmsec^{-1}$ error present in the model. It is possible that Barbieri *et al* may have underestimated the ΔEq_{calc} values. The [2-(N-pyrrolidin-2-one)ethyl]diphenyltin derivative **(18)** has a smaller ΔEq value (2.18 $mmsec^{-1}$) than the other dithiocarbamate derivatives and this value might suggest a cis-tbp R_3SnX_2 structure. The point-charge model [78] predicts a ΔEq value of 1.70-2.40 $mmsec^{-1}$. for this geometry.

Combining all the spectral data relating to the structures of the dithiocarbamate compounds, it can be seen that in the solution ($CDCl_3$) and the solid states both compounds **(16)** and **(19)** are 5-coordinate R_3SnNS intramolecular chelates. Compound **(17)** is 4-coordinate in solution ($CDCl_3$) and a 5-coordinate R_3SnNS intermolecular polymer in the solid state. Compound (18) appears to be have a *cis*-tbp type structure in the solution and the solid state, however in solution the Ph groups appear to be equivalent, which would not be expected if the structure was rigidly 5-coordinate, therefore any additional interaction over 4-coordination must be very weak.

The variable temperature Mossbauer technique, described in Chapter 1, was used to study the four compounds: **(8)**, **(9)**, **(11)** and **(14)**. The experiments were performed to examine the extent of intermolecular coordination in the latter compound. The data are presented in Table 26, and plotted in Fig 9. The three sets of data with the most negative slopes show discrete molecules (coordination numbers 4 or 5) with no intermolecular interactions. The set of data with the least negative slope ($-1.37\mathrm{x}10^{-2}$) somewhat vindicates the proposed intermolecular tbp structure for the [2-(4'-pyridyl)ethyl]diphenyltin halides since it suggests a loosely coiled intermolecular polymer [92].

3.4 The Crystal and Molecular Structure of [2-(2'-pyridyl)ethyl]diphenyltin tin(IV) N,N-dimethyldithiocarbamate. (16)

Suitable crystals were obtained by recrystallisation from a 60-80° petroleum ether/ethyl acetate solvent mixture (1:1). The structure of **(16)**, determined crystallographically is shown in Fig. 10. The molecular packing in the unit cell is shown in Fig 11. Atomic positional coordinates are given in Table 27. The intramolecular bond lengths and bond angles are given in Table 28 and Table 29 respectively. Table 30 lists various structural parameters for analogous dithiocarbamate compounds and Table 31 compares structural

Table 26. Variable temperature Mossbauer data for $Ph_2Sn(X)CH_2CH_2(Het)$[a]

Het=(2'-pyridyl), X=Ph (8)

Temperature (K)	Area	$\ln[A_{(T)}/A_{(78)}]$	a (K^{-1})
78.5	2.196	0	-1.96×10^{-2}
85.0	1.940	-0.123	
95.0	1.633	-0.296	
105.0	1.331	-0.500	
115.0	1.064	-0.724	
125.0	0.842	-0.957	
135.0	0.723	-0.110	

Het=(2'-pyridyl), X=Br (11)

78.9	2.785	0	-1.75×10^{-2}
85.0	2.402	-0.147	
95.0	2.107	-0.279	
105.0	1.735	-0.473	
115.0	1.465	-0.642	
125.0	1.232	-0.815	
135.0	1.028	-0.996	

Table 26 continued,

Het=(4'-pyridyl), X=Ph **(9)**

78.0	2.388	0	-1.60×10^{-2}
85.0	2.183	-0.090	
95.0	1.856	-0.252	
105.0	1.590	-0.407	
115.0	1.331	-0.585	
125.0	1.129	-0.752	
135.0	0.920	-0.954	

Het=(4'-pyridyl), X=I **(14)**

79.0	4.281	0	-1.38×10^{-2}
85.0	4.010	-0.064	
95.0	3.430	-0.220	
105.0	3.016	-0.350	
115.0	2.580	-0.506	
125.0	2.312	-0.616	
135.0	1.880	-0.817	

* Temperatures accurate to +/- 0.1K

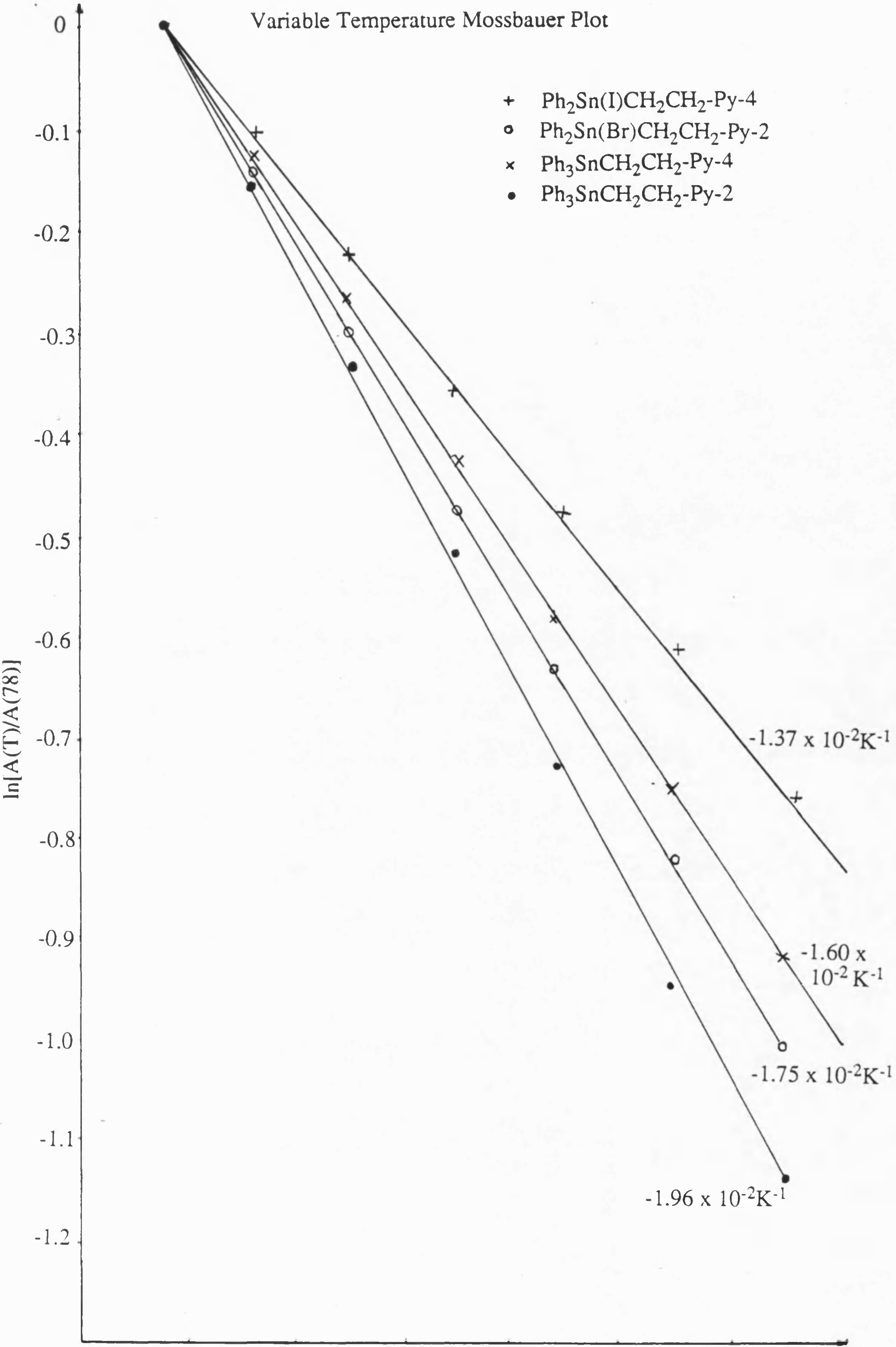

Variable Temperature Mossbauer Plot
+ $Ph_2Sn(I)CH_2CH_2$-Py-4
o $Ph_2Sn(Br)CH_2CH_2$-Py-2
× $Ph_3SnCH_2CH_2$-Py-4
● $Ph_3SnCH_2CH_2$-Py-2
0
-0.1
-0.2
-0.3
-0.4
-0.5
-0.6
-0.7
-0.8
-0.9
-1.0
-1.1
-1.2
ln[A(T)/A(78)]
-1.37 x $10^{-2}K^{-1}$
-1.60 x 10^{-2} K^{-1}
-1.75 x $10^{-2}K^{-1}$
-1.96 x $10^{-2}K^{-1}$
70
80
90
100
110
120
130
140
Temperature/K

Figure 9

data for analogous organotin compounds containing intramolecular chelating groups containing a nitrogen donor atom. Further details concerning the crystallographic analysis are given in Appendix II.

The geometry around the tin is best described as a distorted *trans*-tbp structure. The axial dithiocarbamate ligand is considered monodentate and the other axial position is occupied by a pyridyl nitrogen which is chelated in an intramolecular fashion. The two phenyl groups and the alkyl chain unit are in the equatorial positions. The C=S sulphur does have a long Sn----S(2) contact distance of 3.466 Å and it is well within the sum of the respective van der Waals radii of 4.05 Å. It must be also noted that the equatorial <C(2)-Sn-C(11) opens out to 128°(3), away from the ideal 120° tbp angle and the Sn----S(2) vector bisects this angle. If there was no Sn----S(2) interaction at all, the Sn-C bonds in the equatorial plane might be expected to rehybridise, with the result that <C(17)-Sn-C(11) would be <120°, whilst <C(17)-Sn-C(2) and <C(2)-Sn-C(11) would be >120°. However, although it is true that <C(17)-Sn-C(11) does become <120° and <C(2)-Sn-C(11) does become >120°, <C(17)-Sn-C(2) is <120°, (Figure 12.) This might suggest that the <C(2)-Sn-C(11) is wider than necessary for purely rehybridisation requirements.

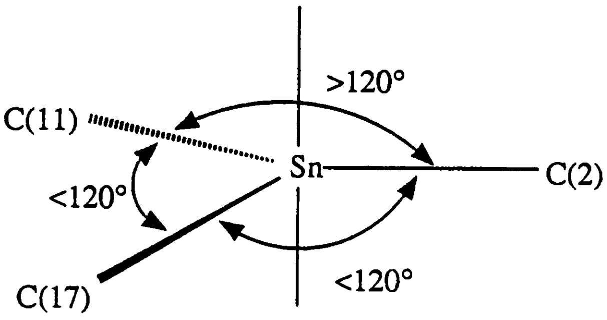


Figure 12.

However compounds that have been shown to exhibit unambiguous anisobidentate dithiocarbamate bonding have much shorter Sn----S(2) distances, e.g. $Me_2Sn(S_2CNMe_2)_2$, Sn----S(2) =2.954Å. With shorter Sn--S distances there is a concommitant rise in the <S(1)-Sn-S(2), e.g. 64.3° (average) for the latter compound vs. 57.1° for the title compound. A recent structure of bis (*tert*-butyl) bis (N,N-dimethyldithiocarbamato)tin(IV) [202] has been determined and shows mono- and bidentate dithiocarbamate bonding in the same compound, which is unusual for a diorganotin. The data for the dithiocarbamate ligand in the title compound is most similar to the monodentate ligand, (Table 30), in the above example. The Sn-S(1) bond length of 2.559 Å is not typical of R_3Sn dithiocarbamate derivatives, which generally have Sn-S(1) bond lengths in the range 2.466-2.499 Å (R= Me, ^{n}Bu and Ph). This larger bond length is more typical of the shorter Sn-S bond length associated with an anisodentate bonded dithiocarbamate ligand. However, the longer Sn-S(1) distance found here can also be rationalised as being due to the increase in coordination caused by the pyridyl nitrogen donor atom in the trans-axial position. This point is exemplified by examining the length of a typical Sn-Br bond found in a tetrahedral structure, e.g. Ph_3SnBr, d(Sn-Br)=2.490 Å and 2.500 Å vs. the lengths of the Sn-Br bonds(2.63-2.74 Å) found in the trans-tbp chelated compounds in Table 31. The effect, in all the examples, is caused by an increase in coordination due to the trans-axial chelated nitrogen donor atoms.

The Sn-N(2) distance of 2.486 Å is very typical of compounds with intramoleculaly chelated R groups containing a nitogen donor atom, (Table 31), and is significantly less than the Sn---N intermolecular

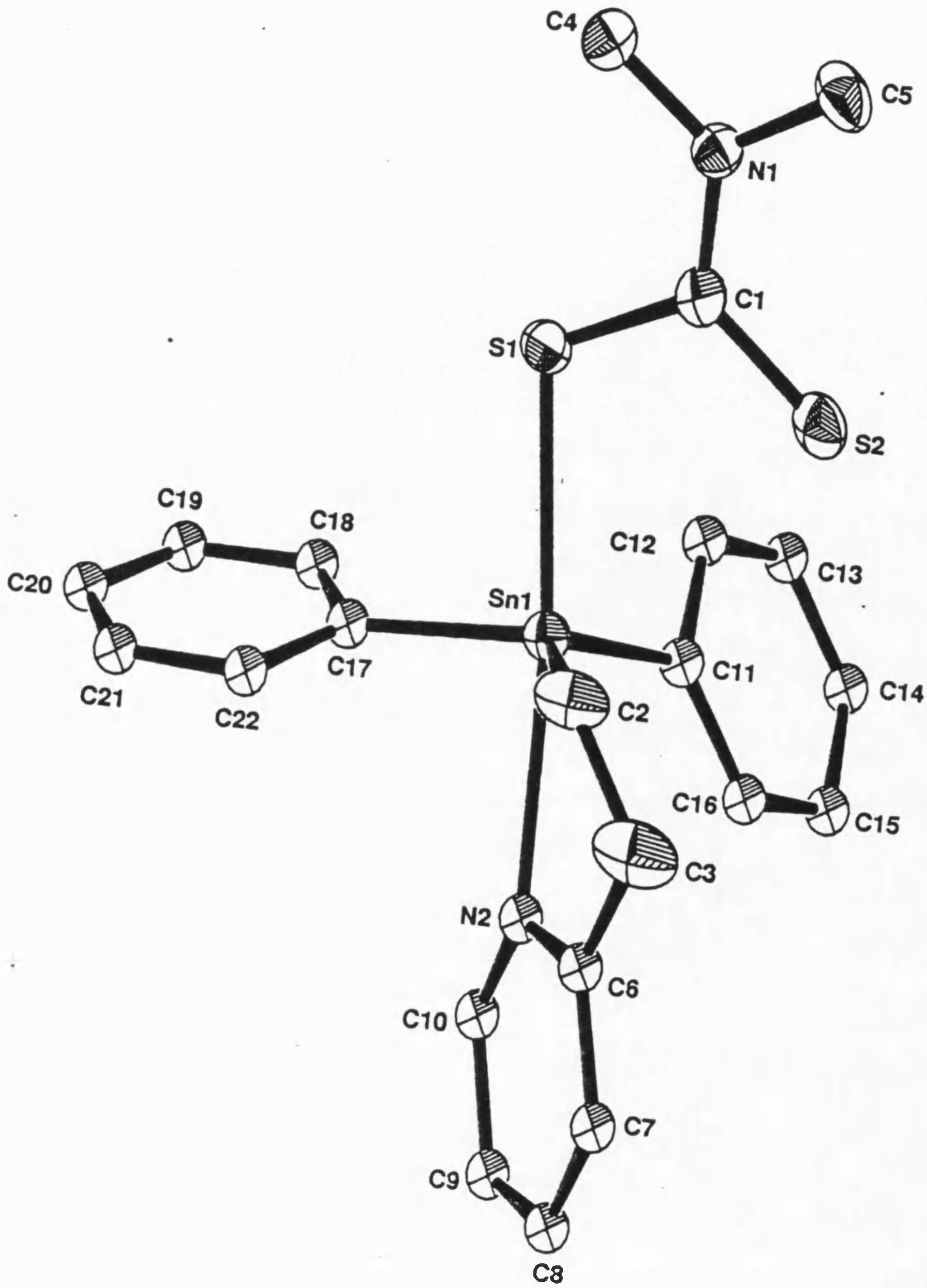

C4
C5
N1
C1
S1
S2
C19
C18
C12
C13
C20
Sn1
C17
C11
C14
C21
C22
C2
C16
C15
C3
N2
C6
C10
C7
C9
C8

Figure 10: The Crystal Structure of [2-(2'-pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate

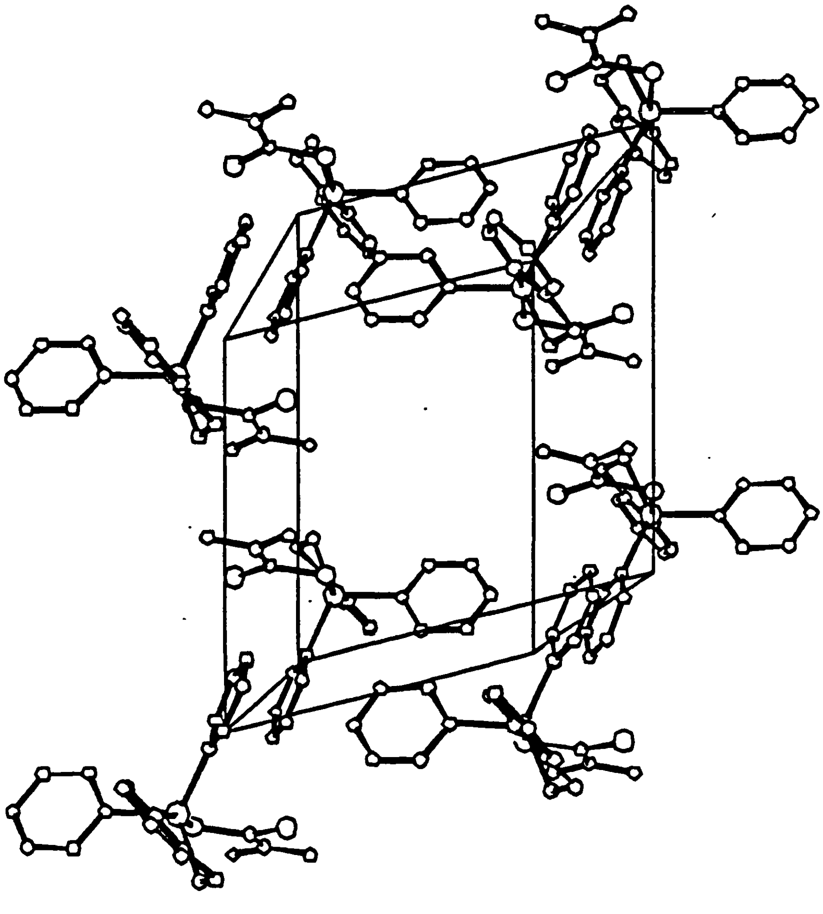


Figure 11: The Molecular Packing Structure of

[2-(2'-pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate

Table 27. Fractional Atomic Coordinates and thermal parameters (Å) for [2-(2'-pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate.

Atom	x	y	z	U_{iso} or U_{eq}
Sn	0.1599(1)	0.3146(1)	0.2537(0)	0.0438(4)
S(1)	0.4416(2)	0.2157(2)	0.2668(2)	0.0501(12)
S(2)	0.3405(3)	-0.0426(3)	0.3343(2)	0.0726(16)
N(1)	0.6064(8)	-0.0345(8)	0.3467(7)	0.0508(43)
N(2)	-0.1230(8)	0.4302(7)	0.2709(6)	0.0508(17)
C(1)	0.4735(9)	0.0349(9)	0.3195(7)	0.0530(51)
C(2)	0.0458(11)	0.2742(12)	0.4261(8)	0.0555(54)
C(3)	-0.1131(13)	0.2612(15)	0.4392(10)	0.0687(67)
C(4)	0.7192(12)	0.0364(11)	0.3391(10)	0.0665(61)
C(5)	0.6448(13)	-0.1876(10)	0.3926(10)	0.0930(76)
C(6)	-0.2013(10)	0.3692(9)	0.3647(8)	0.0561(22)
C(7)	-0.3642(12)	0.4052(11)	0.3885(10)	0.0700(27)
C(8)	-0.4395(12)	0.4995(11)	0.3127(10)	0.0717(27)
C(9)	-0.3544(12)	0.5600(12)	0.2131(10)	0.0765(29)
C(10)	-0.1957(11)	0.5216(10)	0.1973(9)	0.0663(26)
C(11)	0.1729(9)	0.2206(8)	0.1190(7)	0.0438(18)
C(12)	0.3157(10)	0.1741(9)	0.0449(8)	0.0541(21)
C(13)	0.3255(12)	0.1189(11)	-0.0491(9)	0.0703(27)
C(14)	0.1990(13)	0.1055(12)	-0.0641(11)	0.0800(30)
C(15)	0.0549(12)	0.1509(12)	0.0097(10)	0.0778(30)
C(16)	0.0423(10)	0.2084(10)	0.1019(8)	0.0586(23)
C(17)	0.1911(9)	0.5190(8)	0.2005(7)	0.0468(19)

Table 27 continued

C(18)	0.2831(11)	0.5547(10)	0.0962(9)	0.0639(24)
C(19)	0.3126(12)	0.6838(11)	0.0664(10)	0.0735(27)
C(20)	0.2506(12)	0.7799(11)	0.1415(11)	0.0716(27)
C(21)	0.1583(12)	0.7504(11)	0.2410(10)	0.0731(28)
C(22)	0.1245(11)	0.6226(10)	0.2730(9)	0.0621(24)

Table 28. Intramolecular Bond Lengths (Å) for [2-(2'-pyridyl)ethyl] diphenyltin(IV) N,N-dimethyldithiocarbamate

Sn-S(1)	2.559(2)	C(11)-C(12)	1.383(11)
Sn-S(2)	3.466(-)	C(12)-C(13)	1.424(14)
Sn-N(2)	2.486(7)	C(13)-C(14)	1.352(15)
Sn-C(11)	2.138(8)	C(14)-C(15)	1.387(15)
Sn-C(17)	2.136(8)	C(15)-C(16)	1.408(15)
Sn-C(2)	2.145(9)	C(11)-C(16)	1.397(12)
S(1)-C(1)	1.752(9)	C(17)-C(18)	1.394(13)
S(2)-C(1)	1.680(8)	C(18)-C(19)	1.390(14)
C(1)-N(1)	1.322(11)	C(19)-C(20)	1.391(15)
N(1)-C(4)	1.483(12)	C(20)-C(21)	1.336(15)
N(1)-C(5)	1.480(12)	C(21)-C(22)	1.397(13)
		C(22)-C(17)	1.421(12)
C(2)-C(3)	1.534(14)		
C(3)-C(6)	1.470(16)		
C(6)-C(7)	1.412(13)		
C(7)-C(8)	1.369(16)		
C(8)-C(9)	1.412(16)		
C(9)-C(10)	1.383(15)		
C(10)-N(2)	1.327(13)		
N(2)-C(6)	1.340(12)		

Table 29. Intramolecular Bond Angles(°) for [2-(2'-pyridyl)ethyl] diphenyltin(IV) N,N-dimethyldithiocarbamate.

N(2)-Sn-S(1)	169.6(2)	C(3)-C(2)-Sn	110.2(7)
C(2)-Sn-S(1)	99.0(3)	C(6)-C(3)-C(2)	113.7(9)
C(2)-Sn-N(2)	73.5(3)	C(3)-C(6)-N(2)	118.4(8)
C(11)-Sn-S(1)	101.8(2)	C(7)-C(6)-N(2)	120.2(9)
C(11)-Sn-N(2)	88.5(3)	C(7)-C(6)-C(3)	121.3(9)
C(11)-Sn-C(2)	128.8(3)	C(8)-C(7)-C(6)	118.9(9)
C(17)-Sn-S(1)	87.4(2)	C(9)-C(8)-C(7)	120.0(10)
C(17)-Sn-N(2)	89.3(3)	C(10)-C(9)-C(8)	117.4(11)
C(17)-Sn-C(2)	114.7(4)	C(9)-C(10)-N(2)	122.5(9)
C(17)-Sn-C(11)	112.6(3)	C(12)-C(11)-Sn	118.3(6)
S(2)-S(1)-Sn	76.9(1)	C(16)-C(11)-Sn	122.5(6)
C(1)-S(1)-Sn	105.5(3)	C(16)-C(11)-C(12)	119.2(8)
C(1)-S(1)-S(2)	28.9(3)	C(13)-C(12)-C(11)	119.3(8)
C(1)-S(2)-S(1)	30.2(3)	C(14)-C(13)-C(12)	121.1(10)
C(4)-N(1)-C(1)	122.6(7)	C(15)-C(14)-C(13)	120.4(11)
C(5)-N(1)-C(1)	120.5(8)	C(16)-C(15)-C(14)	119.3(10)
C(5)-N(1)-C(4)	116.8(8)	C(15)-C(16)-C(11)	120.7(9)
C(6)-N(2)-Sn	108.9(6)	C(18)-C(17)-Sn	122.1(6)
C(10)-N(2)-Sn	129.5(6)	C(22)-C(17)-Sn	120.9(6)
C(10)-N(2)-C(6)	120.9(8)	C(22)-C(17)-C(18)	116.9(8)
S(2)-C(1)-S(1)	120.9(5)	C(19)-C(18)-C(17)	121.3(9)
N(1)-C(1)-S(1)	116.0(6)	C(20)-C(19)-C(18)	120.0(10)
N(1)-C(1)-S(2)	123.1(7)	C(21)-C(20)-C(19)	120.1(10)

Table 29 continued

C(22)-C(21)-C(20)	121.4(10)	C(21)-C(22)-C(17)	120.2(9)

Table 30. Selected bond lengths for compounds containing anisobidentate dithiocarbamate ligands (Å).

	d(Sn-S-C=S→Sn)					
Compound	Sn-S(1)	S-C	C=S	S(2)→Sn	<S(1)-Sn-S(2)°	Ref.
(16)	2.559	1.752	1.680	3.466	57.1	[c]
$Sn[S_2CN(CH_3)_2]_4$	2.500	1.740	1.690	3.439	-	203
	2.536	1.710	1.670	3.643	-	
	2.516	1.720	1.690	2.707	-	
	2.510	1.730	1.710	2.595	-	
$[{}^nBu(Ph)_2Sn{-}S_2CNMe_2]$	2.466	1.762	1.680	3.079	63.8	204
$[{}^nBu(Ph)ClSn{-}S_2CNMe_2]$	2.454	1.742	1.703	2.764	68.8	205
$[Me_2(Cl)Sn{-}S_2CNMe_2]$	2.48(eq.)	1.740	1.680	2.79(ax.)	68.2	206
$[Ph_3Sn{-}S_2CN(CH_2)_4]$	2.468	1.776	1.702	3.106	63.6	195
$[Bu^t_2Sn{-}(S_2CNMe_2)_2]$	2.573 [a]	1.752	1.686	3.532	(-)	202
	2.489 [b]	1.738	1.709	2.795	67.5	
$[Ph_2Sn{-}(S_2CNEt_2)_2]$	2.613	1.72	1.72	2.637	67.6	207
	2.548	1.76	1.72	2.790	67.6	

[a] Data presented is for the monodentate dithiocarbamate ligand

[b] Data presented is for the anisobidentate dithiocarbamate ligand.

[c] This work.

Table 31. Selected bond lengths for pentacoordinated organotins with a intramolecularly chelating R group with a nitrogen donor atom.

Compound	Sn-N(ax.)	Sn-E(ax.)	<N-Sn-E	<Equatorial	Ref
(16)	2.486	2.559 [a]	169.6	112.6 [c] 114.7 [d] 128.8 [e]	[o]
[Ph$_2$(Br)Sn-C$_6$H$_4$CH$_2$NMe$_2$-2]	2.51	2.63 [b]	171.0	122.0 [f] 114.5 [g] 121.2 [h]	30
[Ph$_2$(Br)Sn-C$_6$H$_4$CH(Me)NMe$_2$-2]	2.476	2.683 [b]	168.9	114.8 [i] 116.1 [j] 127.8 [k]	208
[1-(Ph(Me)(Br)Sn)-6-MeO-9-CH$_2$NMe$_2$-Napth].	2.401	2.739 [b]	174.3	122.4 [l] 112.0 [m] 125.3 [n]	209

[a] E=S

[b] E=Br

[c] <Ph-Sn-Ph, [d] <Ph-Sn-CH$_2$-, [e] <Ph-Sn-CH$_2$

[f] <Ph-Sn-Ph, [g] <Arom-Sn-Ph, [h] <Arom-Sn-Ph

[i] <Ph-Sn-Me, [j] <Arom-Sn-Ph, [k] <Arom-Sn-Me

[l] <Ph-Sn-Me, [m] <Napth-Sn-Ph, [n] <Napth-Sn-Me

[o] This work.

distance of 2.62 Å found in the crystal structure of $Ph_3SnS(C_5H_4N-4)$ [210]. The <N(2)-Sn-S(1) is 169.6° and shows that the structure does not have ideal tbp symmetry. The <N(2)-Sn-C(2), in the five membered ring caused by the chelation, 73.5°, is almost that of an ideal pentagon, i.e. 72°, the CH_2CH_2 chain puckers to reduce the ring strain.

3.5 Experimental

Triphenyltin hydride was prepared according to Van der Kerk *et al.*[196]. 2-Vinyl and 4-vinyl pyridine were of commercial origin (Aldrich) and were distilled under reduced pressure prior to use. N-vinyl pyrrolidin-2-one, N,N-dimethyl- and N,N-diethyldithiocarbamate were of commercial origin (Aldrich) and were used without further purification. Analytical data are presented in Table 21.

Synthesis of [2-(2'-pyridyl)ethyl]triphenyltin(IV) (8)

Triphenyltin hydride (2.84g, 7.37 mmol) and 2-vinylpyridine (1.15g, 11 mmol) were stirred together as a melt at 100°C for 2 hours under dry nitrogen. The solid residue was recrystallised from 60-80° petroleum ether to yield hexaphenylditin (0.56g, 0.8 mmol). The mother liquor was reduced in volume to dryness and the remaining solid recrystallised from methanol/diethyl ether (1:1) to yield the product (8) (2.71g, 80%, m.p.= 73°C, lit. [211] m.p.=72-4°C.)

Synthesis of [2-(4'-pyridyl)ethyl]triphenyltin(IV) (9)

Triphenyltin hydride (3.50g, 10 mmol) and 4-vinyl pyridine (1.05g, 10 mmol) were placed together in a dry, nitrogen filled flask and stirred together at 100°C as a melt for 30 minutes. Following this the flask was allowed to cool and the solid residue recrystallised from 60-80°C petroleum ether, to yield the product (9) as a white crystalline solid, (4.12g, 90%, m.p.= 112°C, lit.[212] m.p.= 112-3°C).

Synthesis of [2-(N-pyrrolidin-2-one)ethyl]triphenyltin **(10)**
Triphenyltin hydride (3.50g, 10mmol) and N-vinyl pyrrolidin-2-one (1.11g, 10 mmol) were stirred together as a melt at 90°C for 4 hours under dry nitrogen. The flask was allowed to cool and the solid residue was recrystallised from 60-80° petroleum ether to yield the product **(10)** as white rosettes (3.93g, 85%, m.p.= 73-5°C, lit.[211] m.p.=74-6°C)

Halogenation of compounds **(8)**, **(9)** and **(10)**

Synthesis of [2-(2'-pyridyl)ethyl]diphenyltin(IV) bromide **(11)**
Compound **(8)** (5.07g, 11.1 mmol) was dissolved in CCl_4 (75 ml) and cooled to 0°C. Br_2 (1.77g, 11.1 mmol) was dissolved in CCl_4 (50 ml) and added to the stirred solution of **(8)** dropwise over the period of 1 hour. The bromine solution was completely decolourised. Following addition, the solvent was removed and the oily residue was dissolved, with heating, in 60-80° petroleum ether/ethyl acetate (9:1). The solution was allowed to cool to yield the product **(11)** as white crystalline needles (4.67g, 91%, m.p.=168-9°C)

Synthesis of [2-(4'-pyridyl)ethyl]diphenyltin(IV) bromide **(12)**
Compound **(9)** (1.76g, 3.86 mmol) was dissolved in CCl_4 (40 ml) and cooled to 0°C. Bromine (0.61g, 3.86 mmol) was also dissolved in CCl_4 (40 ml) and added dropwise to the solution of **(9)** over 1 hour. The flask was stirred overnight to yield a white suspension. The solvent was removed and the solid residue dissolved, with heating, in dry ethanol. A white powder **(12)** was collected (1.42g, 80%, m.p.=137-9°C).

Recrystallisation from various solvents yielded only an amorphous powder.

Synthesis of [2-(2'-pyridyl)ethyl]diphenyltin(IV) iodide **(13)**

Compound **(8)** (1.0g, 2.2 mmol) was dissolved in 60-80° petroleum ether (50 ml) and stirred at room temperature. Iodine (0.55g, 2.2mmol) was dissolved, with heating, in 60-80° petroleum ether (100 ml), and added to the solution of **(8)** over a period of 1 hour. Following addition the iodine solution had totally decolourised to yield a pale yellow suspension. A solid was filtered off and recrystallised from ethyl acetate/40-60° petroleum ether (9:1) to yield the product **(13)**, as yellow needles, (0.85g, 76%, m.p.=160°C).

Synthesis of [2-(4'-pyridyl)ethyl]diphenyltin(IV) iodide **(14)**

Essentially as for preparation of **(13)**, with $CHCl_3$ used as the solvent. Recrystallisation from 60-80° petroleum ether yielded small yellow rosets, (54%, m.p.=155-6°C)

Synthesis of [2-(N-pyrrolidin-2-one)ethyl]diphenyltin(IV) iodide **(15)**

Compound **(10)**, (1.88g, 4.06 mmol) was dissolved in $CHCl_3$ (100 ml) and stirred at room temperature. Iodine (1.03g, 4.06 mmol) was dissolved in $CHCl_3$ (100 ml) and added dropwise to the solution of **(10)** over a period of 30 minutes. Following addition the solution was reduced in volume and the oily residue redissolved, with heating, in ethyl acetate/60-80° petroleum ether (1:1). The flask was allowed to cool to yield the product **(15)**, as white crystals (1.77g, 85%, m.p.=146°C).

Synthesis of dithiocarbamate and carboxylate derivatives of compounds **(8)**, **(9)** and **(10)**

Synthesis of [2-(2'-pyridyl)ethyl]-N,N-dimethyldithiocarbamato diphenyltin(IV) **(16)**

Compound **(11)**, (1.60g, 3.48 mmol) and $Me_2NCS_2Na.2H_2O$ (0.65g, 3.48 mmol) were dissolved in ethanol/ethyl acetate (1:1), (100 ml) and stirred at 50°C for 30 minutes, then heated at reflux for 30 minutes. The solution was allowed to cool and the solvent removed. The solid residue was dissolved in distilled water (50 ml) and ethyl acetate (50 ml). The organic layer was separated, dried over $MgSO_4$, filtered, reduced in volume and cooled to yield **(16)** as white needles, (1.42g, 81%, m.p.=160°C).

Synthesis of [2-(4'-pyridyl)ethyl]-N,N-dimethyldithiocarbamato diphenyltin(IV) **(17)**

Essentially as for preparation of **(16)**, but using **(12)** as the starting material. Product obtained as a semi-crystalline solid, (66%, m.p.=191-2°C).

Synthesis of [2-(N-pyrrolidin-2-one)ethyl]-N,N-dimethyldithiocarbamato diphenyltin(IV) **(18)**

Essentially as for preparation of **(16)**, but using **(15)** as the starting material. Product obtained as white crystals, (81%, m.p.=117°C).

Synthesis of [2-(2'-pyridyl)ethyl]-N,N-diethyldithiocarbamato diphenyltin(IV) **(19)**

Essentially as for preparation of **(16)**, except using $Et_2NCS_2Na.3H_2O$. Product obtained as white crystals, (72%, m.p.=145-6°C).

Synthesis of [2-(2'-pyridyl)ethyl]diphenyltin acetate **(20)**

Compound **(11)**, (3.03g, 6.6 mmol) and glacial acetic acid (0.40g, 6.6 mmol) were dissolved in acetone (40 ml). Et_3N (0.67g, 6.6 mmol) was dissolved in acetone (10 ml) and added to the stirred solution of **(11)** dropwise over 30 minutes. Stirring was continued for 30 minutes, to yield a white suspension of Et_3NHBr. The by-product was filtered off, (1.0g, 83%) and the filtrate reduced in volume to dryness. The oily residue was redissolved, with heating, in ethyl acetate/60-80° petroleum ether (1:9). Following cooling **(20)** was obtained, by filtration, as a white crystalline solid (2.31g, 79%, m.p.=80-1°C).

Synthesis of [2-(2'-pyridyl)ethyl]diphenyltin benzoate **(21)**

Preparation as for **(20)**, except for using benzoic acid as the reacting ligand. Product was obtained as a semi-crystalline solid **(21)**, (61%, m.p.=140-4°C).

CHAPTER 4.

SYNTHESIS OF (HETEROCYCLIC THIOMETHYL) TRIPHENYLTIN COMPOUNDS AND THEIR DERIVATIVES

4.1 Introduction

Chapter 4 continues the theme, introduced in Chapter 3, of separating the organotin moiety from the heterocycle with a passive chain unit, in this case $-CH_2S-$. This approach has enabled several triorganotin halides to be produced and fully characterised. The primary synthetic reaction employed here has great utility since virtually any heterocycle containing a mercapto group can theoretically be attached, to make the tetraorganotin.

The biological uses of benzothiazole, benzoxazole and imidazole have already been discussed in Chapter 2. The mercapto heterocycles, especially 2-mercaptobenzothiazole, are well known for their fungicidal activity and their potential for multidentate bonding. The mode of action of 2-mercaptobenzothiazole is not clearly understood, but it is thought to involve the opening of the thiazole ring to yield toxic dithiocarbamates, though it may also involve metal chelation.

Czerwinska *et al.* [213] have reported the fungicidal activity of $Ph_3SnS(Bzt)$, $Ph_3SnS(Box)$ and $Bu_3SnS(Box)$, but detailed no structural work. Molloy *et al.* [214] have reported the structural details of various triorganotin dithocarbamates and listed their biocidal activities. Brasington and Poller [215] have reported the preparation of $(RSCH_2)_4Sn$ from $(BrCH_2)_4Sn$ (R=Ph, Bu), and measured their Mossbauer parameters.

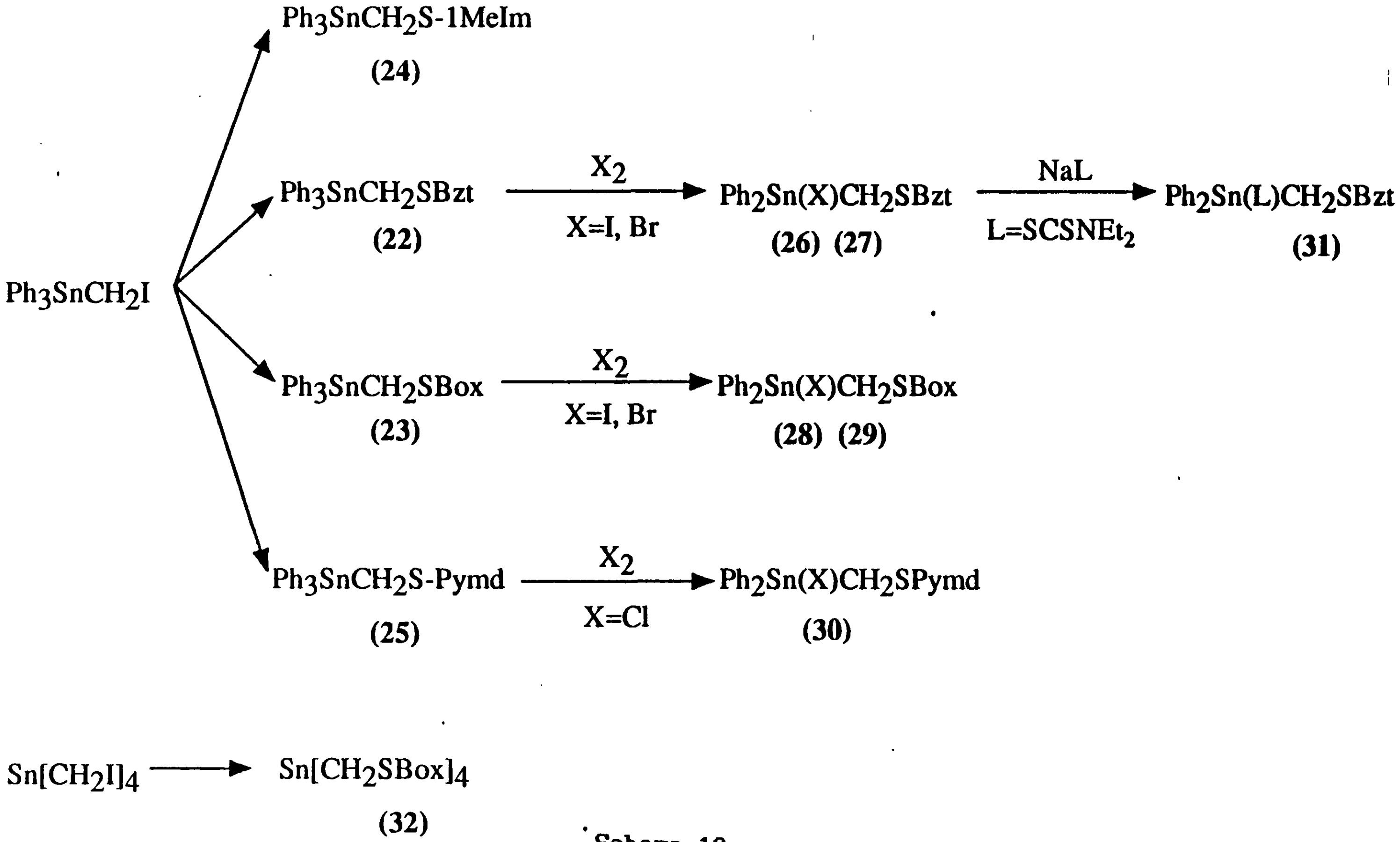
Taylor and Wardell [216] have prepared compounds of the type $Ph_3M(CH_2)_nSC_6H_4Me$-*p* (M=Sn, Ge and n=1, 2), but again, no structural studies were carried out. Following on from their work on biologically active pyrimidines, purines and their analogues, Parkanyi *et al.*[163] have recently studied the organostannyl and organosilyl derivatives of these heterocycles. However, again, no structural details were reported and no $\delta(^{119}Sn)$ nmr or ^{119m}Sn Mossbauer parameters were reported.

4.2 Synthesis

Several mercapto heterocycles have been reacted with triphenyl (iodomethyl)tin to form compounds containing a $-CH_2S-$ unit linking the organotin with the heterocyclic moieties. The substitution reactions are brought about by refluxing the sodium salt of the mercapto heterocycle with triphenyl(iodomethyl)tin in absolute ethanol for at least 12 hours. The product is formed along with the inorganic by-product NaI. The *tetrakis* product, $Sn(CH_2SR)_4$ can also be formed by heating at reflux four equivalents of the sodium salt of the mercapto heterocycle with one equivalent of *tetrakis*(iodomethyl)tin, as exemplified by the reaction between sodium mercaptobenzoxazole and *tetrakis*(iodomethyl)tin (Scheme 13).

Halogen cleavage reactions to produce triorganotin compounds have yielded single organotin products, usually in good yield (>64%), and in every case a phenyl group was cleaved rather than the $-CH_2SHet$ unit. A representative selection of mixed triorganotin halides have been prepared in this manner, and used as starting points for the synthesis of other derivatives by conventional nucleophilic displacement reactions (Scheme 13).

All of the products are crystalline and appear to be air and moisture stable. The products were purified by repeated crystallisation and have been characterised spectroscopically. Analytical data are given in Table 32.


Ph3SnCH2S-1MeIm
(24)
Ph3SnCH2SBzt
(22)
X2
X=I, Br
Ph2Sn(X)CH2SBzt
(26) (27)
NaL
L=SCSNEt2
Ph2Sn(L)CH2SBzt
(31)
Ph3SnCH2I
Ph3SnCH2SBox
(23)
X2
X=I, Br
Ph2Sn(X)CH2SBox
(28) (29)
Ph3SnCH2S-Pymd
(25)
X2
X=Cl
Ph2Sn(X)CH2SPymd
(30)
Sn[CH2I]4
Sn[CH2SBox]4
(32)

Scheme 13

Table 32: Analytical Results for $Ph_2Sn(X)CH_2S(Het)$

	X	mp/°C	C: % *	H: % *	N: % *
Het=Benzothiazole					
(22)	Ph	103	58.90(58.90)	3.95(3.96)	2.47(2.64)
(26)	I	166	41.20(41.40)	2.80(2.76)	2.41(2.41)
(27)	Br	169-70	45.36(45.06)	3.04(3.00)	2.58(2.62)
(31)	$SCSNEt_2$	154	49.87(49.99)	4.26(4.32)	4.64(4.66)
Het=Benzoxazole					
(23)	Ph	60	60.60(60.70)	4.12(4.08)	2.71(2.72)
(28)	I	159	42.80(42.58)	2.78(2.83)	2.48(2.48)
(29)	Br	153	46.60(46.45)	3.10(3.09)	2.70(2.70)
(32)	(-)	89	50.10(49.56)	3.31(3.09)	7.06(7.22)
Het=1-Methylimidazole					
(24)	Ph	72	57.10(57.89)	4.52(4.61)	5.77(5.87)
Het=Pyrimidine					
(25)	Ph	81-2	58.60(58.14)	4.19(4.21)	5.80(5.89)
(30)	Cl	150-1	47.00(47.10)	3.46(3.46)	6.44(6.46)

* Calculated values in parentheses

4.3 Spectroscopy

4.3.1. Infra-red spectroscopy

The infra-red spectra were complex and only a few bands could be assigned. The aromatic absorption bands, ν(C-H) stretch and def(C-H), were typically at 3070 and 730 cm^{-1} respectively, the latter being a complex set of peaks due to the aromatic protons associated with the heterocycle.

The tin-alkyl carbon stretching frequencies were within the expected range 590-500 cm^{-1}, typically 550 cm^{-1}. The tetraorganotin compounds appear to have slightly lower stretching frequencies than the tin halide and tin dithiocarbamate derivatives. This is presumably due to a slightly higher electron density associated with the tin carbon bond in the tetraorganotin examples, and thus a higher frequency is needed to stretch the bond.

The symmetric tin-alkyl carbon stretch was not observed for $(BoxSCH_2)_4Sn$ since the molecule has a center of symmetry and this stretching mode would be Raman active only. A small cluster of weak stretches were observed between 540-500cm $^{-1}$ and one of these may be the antisymmetric mode.

4.3.2 N.M.R. Spectroscopy

The ^1H nmr data are presented in Table 33. The $^2J(^{119}Sn, ^1H)$ coupling constant data for the tetraorganotin compounds (22-25) and (32) are in the range 37.1-66.5 Hz, However, it must be noted that the figure of 66.5 Hz for (24) is not typical, since the other tetraorganotin compounds have $^2J(^{119}Sn, ^1H)$ values below 41 Hz. Presumably, these values typifify 4-coordinate organotin species of this type. The $^2J(^{119}Sn, ^1H)$ values are particularly low and are considerably lower than the analogous compound $Ph_3SnCH_2SC_6H_4Me$-*p*, $^2J(^{119}Sn, ^1H)$=50.0 Hz. observed by Taylor *et al.*[216]. One possible explanation may be that the low figure is due to the electron withdrawing effects due to the heterocycles. Indeed, it appears that the more electronegative heterocycles e.g. benzothiazole and benzoxazole produce slightly lower $^2J(^{119}Sn, ^1H)$ values than the less electronegative heterocycles e.g. 1-methylimidazole and pyrimidine.

The $^2J(^{119}Sn, ^1H)$ values for the triorganotin derivatives (26-31) are in the range 63.0-72.5 Hz. These figures are too large for the compounds to be purely 4-coordinate, and one must speculate that the compounds have a certain degree of 5-coordinate character. It is interesting to note that for each triorganotin derivative, the spread of the aromatic proton signals due to the heterocycle is greater in that of the heterocycle in the parent tetraorganotin compound. This would suggest that the heterocyclic ligand is in a different environment than when it is in the parent tetraorganotin, and indicates that it is possibly one of the hetero atoms in the heterocyclic ligand that is responsible for causing an increase in

Table 33: ^{1}H nmr studies of Ph$_2$ Sn(X)CH$_2$S(Het) [a,b,c]

Compound	X	Ph Arom	Het Arom	CH$_2$	^{2}J(Sn-C-H) [d]
Het=Benzothiazole [e]					
(22)	Ph	7.24-7.68	7.08-7.52	3.09	37.1, 39.4
		(m,15H)	(m,4H)	(s,2H)	
(26)	I	7.24-7.82	6.70 (d,2H)	3.27	60.8, 64.1
		(m,10H)	7.01 (td,1H)	(s,2H)	
			7.17 (td,1H)		
(27)	Br	7.26-7.82	6.78 (d,2H)	3.17	64.1, 68.6
		(m,10H)	7.05 (td,1H)	(s,2H)	
			7.20 (td,1H)		
(31)	SCSNEt$_2$	7.23-7.65	7.08-7.53	3.31	63.2, 65.2
		(m,10H)	(m,4H)	(s,2H)	
		* CH$_2$=1.19 ppm (q,4H), CH$_3$=3.87 ppm. (t,6H)*			
Het=Benzoxazole [f]					
(23)	Ph	7.28-7.70	7.15 (m,2H)	3.09	36.6, 38.2
		(m,15H)	7.25 (d,1H)	(s,2H)	
			7.43 (d,1H)		
(28)	I	7.26-7.88	6.79 (d,1H)	3.36	60.2, 63.0
		(m,10H)	7.11 (td,1H)	(s,2H)	
			7.21 (td,1H)		
			7.42 (d,1H)		

Table 33 continued

(29)	Br	7.29-7.88 (m,10H)	6.89 (d,1H) 7.14 (td,1H) 7.24 (td,1H) 7.45 (d,1H)	3.27 (s,2H)	64.13, 67.51
(32)	---		7.21 (td,4H) 7.26 (d,4H) 7.37 (d,4H) 7.62 (d,4H)	2.74 (s,8H)	34.88, 37.13

Het=1-methylimidazole [g]

(24)	Ph	7.20-7.80 (m,15H)	6.63 (d,1H) 6.75 (d,1H) * Me:3.42 (s,3H)	3.20 (s,2H)	63.17, 66.48

Het=Pyrimidine [h]

(25)	Ph	7.24-7.66 (m,15H)	6.70 (t,1H) 8.16 (d,2H)	2.83 (s,2H)	39.00, 40.50
(30)	Cl	7.30-7.72 (m,10H)	6.91 (t,1H) 8.25 (m,2H)	2.94 (s,2H)	70.51, 72.51

Table 33 continued,

[a] All chemical shift data is given in ppm.

[b] All coupling constant data given in Hz.

[c] All samples recorded as $CDCl_3$ solutions at 298K using TMS as a standard.

d ^2J(Sn-C-H) coupling constants refer to $^{117/119}$Sn values respectively

[e] ^{1}H nmr: 7.61 (d,1H), 7.37, (d,1H), 7.17 (t,1H), 6.99 (t,1H)

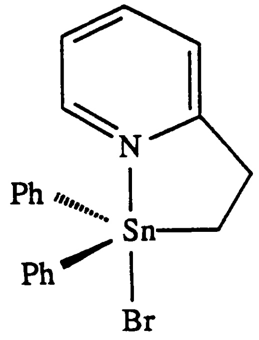
[f] ^{1}H nmr: 7.46 (d,1H), 6.90, (d,1H), 7.25 (t,1H), 7.15 (t,1H)

[g] ^{1}H nmr: 8.85 (d,1H), 6.65, (d,1H), Me 3.2, (s,3H)

[h] ^{1}H nmr: 8.15 (d,2H), 6.60, (t,1H)

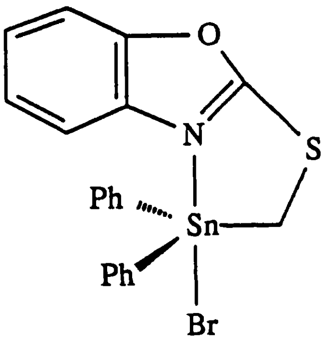
coordination number at the metal center.

In Chapter 3 it was shown that various organotin halide derivatives demonstrated large $^{2}J(^{119}Sn, ^{1}H)$ values due to intramolecular chelation effects, (XXXXVI). The triorganotin derivatives, (25-31), discussed here are sterically capable of producing similar effects, and it is interesting to note that there are two possibilities of intramolecular chelation, for example compound (29), (XXXXVII) and (XXXXVIII). The $^{2}J(^{119}Sn, ^{1}H)$ values suggest that this interaction is not as strong as found in the compounds discussed in Chapter 3.

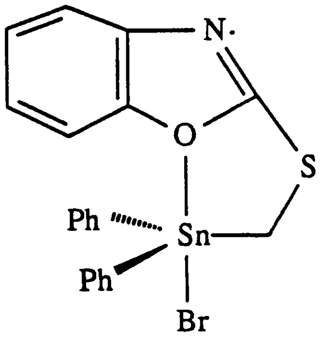


(XXXXVI)

$^{2}J(^{119}Sn, ^{1}H)$=114.8 Hz.



(XXXXVII)

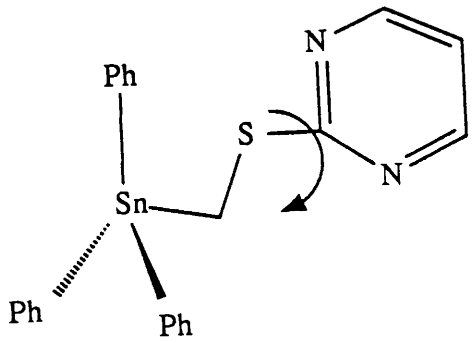


(XXXXVIII)

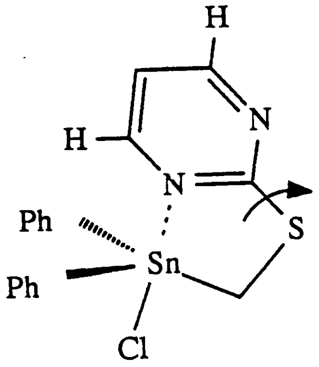
=67.5 Hz.

It is apparent from the small $^{2}J(^{119}Sn, ^{1}H)$ values that the hetero donor atoms , i.e. N, O and S, in these compounds are only just sufficiently Lewis basic enough at 298K to yield 5-coordinate structures, however, it is quite possible that if the temperature was reduced in the nmr experiment the thermodynamics might permit structures with more stable E:→Sn bonds (E=N,S, and O) and larger $^{2}J(^{119}Sn, ^{1}H)$ coupling constants may be obtained.

The strength of the intramolecular chelation effects in these compounds can be appreciated if the ^{1}H nmr signals for the pyrimidine group are considered for (25) and (30) . The spectrum of the tetraorganotin species, (25), displays a triplet (1H) and a doublet (2H) for the pyrimidine group, which would indicate that the group is free to rotate, i.e. not bonded to the tin, and the two meta-protons are equivalent (XXXXIX). However, the signals for (30) are somewhat different, since although the triplet due to the para-proton is still present, the meta protons now do not form a doublet but appear as a very broad smear. The two meta-protons are no longer equivalent, but the pyrimidine group cannot be stationary, for if it were, the meta-protons would be resolved into two separate doublets. Both nitrogens in the ring are equivalent and can both bond to tin. It is possible then, that the pyrimidine ring rotates around and each nitrogen in turn is bonded to the tin in equilibrium (L). It is likely that at a lower temperature the pyrimidine ring would stop rotating and a solution of (30) would show a pair of resolved doublets for the meta-protons in the nmr experiment.



(XXXXIX)



(L)

The ^{13}C data are presented in Table 34. All the chemical shift data for the *i* carbons on the phenyl rings are below 138 ppm and this, according to the ranges set by Holecek *et al.*[100], is consistant with a 4-coordinate structure. This would be expected for the tetraorganotin compounds (22-25) and (32), but it is unexpected for the triorganotin compounds (26-31), which are presumed to have a 5-coordinate nature as discussed above. These results reinforce the fact that $\delta(^{13}C)$ values for the *i* carbon on phenyl rings cannot be used as a definitive, but only a tentative guide to the coordination number at tin. Typically, the $^{1}J(^{119}Sn, ^{13}C)$ coupling constant values for 4-coordinate R_4Sn compounds are in the range 300-340 Hz [100] and for 5-coordinate R_3SnX compounds, the range is 450-480 Hz [100]. The $^{1}J(^{119}Sn, ^{13}CH_2)$ coupling constant values for the tetraorganotin compounds (22-25) and (32) are in the range 344.2-412.4 Hz. These values are somewhat higher than other tetraorganotin compounds, e.g. Me_4Sn $^{1}J(^{119}Sn, ^{13}C)=335.6$ Hz, Et_4Sn $^{1}J(^{119}Sn, ^{13}C)=307.4$ Hz and Bu_4Sn $^{1}J(^{119}Sn, ^{13}C)=310$ Hz. Presumably (22-25) and (32) are 4-coordinate, and the high coupling constant values represent some artefact in the system.

The triorganotin derivatives, (26-29) and (31), have $^{1}J(^{119}Sn, ^{13}C)$ values in the range 433.8-528.6 Hz and these values would suggest that the compounds have a degree of 5-coordinate character. An examination of the ^{13}C chemical shift values for the heterocycles permits a speculation as to which of the donor atoms is associated with the tin atom. It would be expected that the chemical shifts of the carbon atoms adjacent to the donor hetero atom would be observed to vary from the δ values of the same carbons in the parent tetraorganotin. For example, in (26), $\delta(^{13}C)$ for C(3) is 141.1 ppm, whereas in the parent,

Table 34: ^{13}C nmr studies on $Ph_2Sn(X)CH_2S(Het)$ ^{a,b}

Aromatic Organotin carbons

Compound	*i*	*o*	$^2J(C-Sn)$ ^{c}	*m*	$^3J(C-Sn)$ ^{c}	*p*	$^4J(C-Sn)$
Het=Benzothiazole							
(22)	137.0	136.7	37.4	128.4	51.4	129.0	12.8
(26)	136.0	135.6	-	128.6	-	129.5	-
(27)	136.2	135.6	-	128.7	-	129.5	-
(31)	137.1	136.2	45.3	127.9	55.7	129.6	14.4
Het=Benzoxazole							
(23)	137.1	136.8	38.7	128.5	50.8	129.2	12.1
(28)	135.9	135.6	52.9	128.6	76.2	129.6	14.8
(29)	136.0	135.6	50.6	128.6	-	129.6	15.5
(32)	-	-	-	-	-	-	-
Het=1-methylimidazole							
(24)	136.8	135.8	-	128.3	-	129.1	-

Table 34 continued,

Het=Pyrimidine

(25)	136.9	136.6	36.1	128.3	49.7	128.7	11.2
(30)	135.8	135.5	47.8	128.8	71.7	129.6	16.9

Methyl and Heterocyclic carbons

Compound	C1	^1J(C-Sn)	C2	C3	C4	C5	C6	C7	C8
Het=Benzothiazole									
(22)	12.13	328.5 344.2	152.6	138.1	121.0	128.0	123.7	120.7	129.1
(26)	17.83	-[d]	152.3	141.1	121.5	126.7	125.0	119.9	129.4
(27)	16.41	-[d]	152.4	139.2	121.6	126.8	125.1	120.0	129.3
(31)	12.13	412.7 433.8	152.3	140.4	121.5	126.4	125.0	120.7	129.3
Het=Benzoxazole									
(23)	10.54	389.4 410.7	152.7	137.5	109.6	123.5	124.0	118.1	129.3
(28)	19.64	473.6 492.5	152.7	140.5	110.8	125.0	125.4	116.7	129.5
(29)	18.00	505.6 528.6	152.3	140.7	110.8	125.0	125.5	116.7	129.7

Table 34 continued,

(32)	16.54	393.8 412.4	152.3	141.3	109.9	123.7	124.2	117.9	129.2

Het=1-methylimidazole

(24)	20.36	-	161.3	125.0	124.0	-	* Me at 32.88		

Het=Pyrimidine

(25)	10.50	367.1 385.1	156.6	115.6	128.6	-	-	-	-
(30)	12.77	340.9 348.6	140.9	116.3	128.3	-	-	-	-

[a] All the chemical shift data given in ppm.

[b] All the coupling constant data given in Hz. All of the spectra were recorded as CDCl$_3$ solutions at 298K and TMS was used as a reference

[c] Refers to $^{117/119}$Sn-^{13}C coupling constant values respectively.

[d] Coupling constants not observed due to weak spectrum.

(22), $\delta(^{13}C)$ C(3) is only 138.1 ppm. The carbon adjacent to the sulphur, C(8), hardly varies at all from **(22)** to **(26)**. This simplistic approach would suggest that it is the nitrogen in benzothiazole that is associated to the tin, not the sulphur. The same effect is found for the benzoxazole and the pyrimidine compounds, again, it is the chemical shifts of the carbon atoms adjacent to the nitrogen atoms that vary. It is surprising that the carbon chemical shift values for C(2) in **(26-31)**, the compounds presumed to be 5-coordinate, do not change from the parent 4-coordinate tetraorganotin compounds. Such a change, if there is one, must be too small to be resolvable.

The ^{119}Sn nmr data are presented in Table 35. The tetraorganotin ^{119}Sn chemical shift values are in the range -82 to -128 ppm. and are typical of Ph_3SnR species, e.g. Ph_3SnMe, Ph_3SnEt, Ph_3Sn^nBu etc, $\delta(^{119}Sn)$= -93.0 [217], -111.1, -110.5 [197] ppm. respectively. Taylor *et al.* [216] have measured the chemical shift for $Ph_3SnCH_2SC_6H_4Me$-*p* by a double resonance technique and gave $\delta(^{119}Sn)$ as -118.0 ppm. This is quite consistent with the values found here.

The organotin halide derivatives, **(26-29)**, show $\delta(^{119}Sn)$ values in the range -171.7 to -204.4 ppm and are more negative than typical Ph_3SnX compounds, e.g. Ph_3SnI $\delta(^{119}Sn)$= -114.5 ppm. The values strongly suggest that these compounds are 5-coordinate.

Compound **(30)** is rather anomalous. It is rather surprising that **(30)** has the least negative $\delta(^{119}Sn)$ value of the triorganotin derivatives (-138.8 ppm), since it would be expected that in this compound the electronegative chlorine attached to the tin would generate the most Lewis acidic metal center and therefore would form the strongest $N\!:\!\rightarrow Sn$

Table 35: ^{119}Sn nmr [a] and Mossbauer [b] parameters for $Ph_2Sn(X)CH_2S(Het)$

Compound	X	$\delta(^{119}Sn)$	I.S. (δ)	ΔEq	Γ_1, Γ_2 [c]
Het=Benzothiazole					
(22)	Ph	-121.08	1.25	0.00	1.06, (-)
(26)	I	-194.90	1.32	2.73	0.84, 0.83
(27)	Br	-171.74	1.27	2.73	0.90, 0.85
(31)	$SCSNEt_2$	-203.46	1.28	2.05	0.92, 0.93
Het=Benzoxazole					
(23)	Ph	-118.63	1.25	0.22	0.87, 0.82
(28)	I	-204.38	1.36	2.79	0.88, 0.88
(29)	Br	-178.96	1.33	2.85	0.92, 0.92
(32)	(-)	-82.40	1.26	0.00	0.99, (-)
Het=1-methylimidazole					
(24)	Ph	-126.45	1.24	0.00	1.12, (-)
Het=Pyrimidine					
(25)	Ph	-128.72	1.29	0.49	1.04, 0.92
(30)	Cl	-138.87	1.23	2.66	0.88, 0.85

[a] All samples recorded as $CDCl_3$ solutions at 298K using Me_4Sn as a reference. Values in ppm.

[b] Mossbauer experiments recorded at 78K and values are given in mmsec^{-1}.

[c] Refers to maximum width at half height of the high and low velocity spectral components in mmsec^{-1}.

bond. It is also interesting to note that (30) has the lowest $^1J(^{119}Sn, ^{13}C)$ value (348.6Hz) of the triorganotin compounds. The only solid evidence that suggests that (30) has enhanced coordination rests with the ^1H nmr spectrum, i.e. a relatively large $^2J(^{119}Sn, ^1H)$ and the pyrimidinyl proton signals are much broader in (30) than in (25). The N:→Sn interaction is certainly not as strong as the N:→Sn interactions found for the 2-pyridyl compounds in Chapter 3. One possible reason for the weakness of the interaction could be due to the competition between the two equivalent nitrogens on the pyrimidine group.

The dithiocarbamate derivative, (31), also has a $\delta(^{119}Sn)$ value that would suggest that it is 5-coordinate in solution, however caution has to be exercised, since although the $\delta(^{119}Sn)$ value is a large negative number (-203.4 ppm), regular $R_3SnSCSNR'_2$ 4-coordinate compounds e.g. $Ph_3SnSCSNEt_2$ also have similar values, in this case $\delta(^{119}Sn)=-191.0$ ppm.

4.3.3 Mossbauer Spectroscopy

The Mossbauer data are presented in Table 35. The tetraorganotin compounds yield ΔEq values of close to zero, suggesting only very small electric field gradients in these molecules and showing that these molecules are essentially discrete, tetrahedral entities in the solid state. The isomer shift (δ) values are in the range 1.25-1.29 $mmsec^{-1}$ and as such are very similar to the δ values found for the tetraorganotin compounds described in Chapter 3. Taylor *et al.* [215] reported the Mossbauer parameters for $Ph_3SnCH_2SC_6H_4Me$-*p* to be: $\Delta Eq=0.00\ mmsec^{-1}$ and $I.S.(\delta)=1.30\ mmsec^{-1}$.

The triorganotin halide derivatives, (26-30), have ΔEq values in the range 2.66-2.85 mmsec^{-1}. This range is intermediate between discrete tetrahedral molecules (typically 1.00-2.40 mmsec^{-1}) and the 5-coordinate trans-tbp R_3SnX_2 (typically 3.00-4.00 mmsec^{-1}). For example, Ph_3SnBr has $\Delta Eq=2.48$ mmsec^{-1} and the molecule has a distorted tetrahedral structure, whilst Me_3SnBr has $\Delta Eq=3.45$ mmsec^{-1} and the molecule has a 5-coordinate trans-tbp structure. The ΔEq values found for the compounds under discussion probably relate to a distorted trans-tbp type geometry. It has been shown through the $\delta(^{119}Sn)$, $^{2}J(^{119}Sn, ^{1}H)$ and $^{1}J(^{119}Sn, ^{13}C)$ values that these compounds are weakly 5-coordinate in solution and that it is likely that the nitrogens on the heterocycles intramoleculaly chelate to the tin. Since, these compounds are 5-coordinate in solution the possibility that the ΔEq values are generated by intermolecular interactions, e.g. halide bridging, can be ruled out. It is therefore reasonable to speculate that (26-30) have discrete intramolecular trans-tbp type structures, similar to the $Ph_2Sn(X)CH_2CH_2Py$-2 (X=Br, I) compounds discussed in Chapter 3.

It is interesting to note that (31) has the second largest $\delta(^{119}Sn)$ value and therefore it seems reasonable to assume that this compound has at least 5-coordination at the metal center in solution. The ΔEq value for this compound is significantly different from (26-30) and the Mossbauer parameters suggest that (31) has a near 5-coordinate cis-tbp R_3SnX_2 structure in which the dithiocarbamate ligand probably has a long Sn----S(2) contact distance, but within the Van der Waals radii for the respective atoms. It is uncertain as to whether or not the benzothiazole plays any role in the coordination sphere around the tin in this case. Although it is worth remembering that the carbon chemical shift for C(3) on the heterocyclic ring changes from that of the parent tetraorganotin compound (22), suggesting some form of interaction, at least in the solution state.

4.4 Experimental

Triphenyl(iodomethyl)tin and *tetrakis*(iodomethyl)tin were prepared as described in Appendix I. The mercapto heterocycles were of commercial origin (Aldrich) and were used without further purification. Analytical data for all the compounds are presented in Table 32.

Synthesis of (Benzothiazolyl-2-thiomethyl)triphenyltin (22)

Sodium metal (0.21g, 9 mmol) was dissolved in absolute ethanol (50 ml) and stirred for 15 minutes at room temperature. 2-Mercapto benzothiazole (1.51g, 9 mmol) was added to the flask and stirred for 15 minutes to form a yellow solution. Triphenyl(iodomethyl)tin (4.41g, 9 mmol) was added to this mixture and the resulting pale yellow solution was refluxed for 12 hours. The solution was allowed to cool and the ethanol removed under reduced pressure. The solid residue was partially dissolved in diethyl ether (50 ml) and the insoluble inorganic by-product was filtered off. The diethyl ether was removed under reduced pressure and the crude product was redissolved in the minimum quantity of hot ethanol, which upon cooling yielded white needles (3.43g, 72%, mp=103°C)

The following compounds were prepared following the same basic procedure:

Synthesis of (Benzoxazolyl-2-thiomethyl)triphenyltin (23)

Mixture refuxed for 12 hours and product isolated as a brown oil and recrystallised from 80-100° petroleum ether to yield small, white, florets, (2.03g, 38%, mp=60-60.5°C)

Synthesis of (1-methylimidazole-2-thiomethyl)triphenyltin **(24)**

Mixture refluxed for 24 hours and product recrystallised as white florets from 80-100° petroleum ether (3.17g, 65%, mp=72°)

Synthesis of (Pyrimidinyl-2-thiomethyl)triphenyltin **(25)**

Mixture refluxed for 24 hours and product recrystallised from 80-80° petroleum ether and collected as white florets (6.12g, 76%, mp=81-2°C)

Synthesis of (Benzothiazolyl-2-thiomethyl)diphenyltin iodide **(26)**

Compound **(22)** (0.60g, 1.13mmol) was dissolved in $CHCl_3$ (20 ml) and stirred at room temperature. Iodine (0.29 g, 1.13 mmol) was also dissolved in $CHCl_3$ (30 ml) and added dropwise to the solution of **(22)** over a period of 30 minutes, during which time the iodine solution was completely decolourised. The solvent was removed under reduced pressure to yield a brown oil. The oil was redissolved in hot 60-80° petroleum ether/ethyl acetate mixture (10:1) and allowed to cool to yield the product as white needles (0.41 g, 64%, mp=166°C)

The following compounds were prepared following the same basic procedure.

Synthesis of (Benzothiazolyl-2-thiomethyl)diphenyltin bromide **(27)**

Bromine was used instead of iodine and the product was recrystallised from 80-100° petroleum ether as white needles (0.79 g, 79%, mp=169-70°C)

Synthesis of (Benzoxazolyl-2-thiomethyl)diphenyltin iodide **(28)**

Following the preparation described above for **(26)**, but using compound **(23)** as a starting material. The crude product was recrystallised from hot 60-80° petroleum ether to yield the product as white prisms (0.51 g, 92%, mp=159°C)

Synthesis of (Benzoxazolyl-2-thiomethyl)diphenyltin bromide **(29)**

Preparation as **(28)** above, but bromine used instead of iodine. The product was recrystallised from 60-80° petroleum ether and yielded white needles (0.41 g, 81%, mp=153°C)

Synthesis of (Pyrimidinyl-2-thiomethyl)diphenyltin chloride **(30)**

Chlorine gas was bubbled through CCl_4 until the solution was saturated. The concentration of Cl_2 was determined by density measurements. Compound **(25)** (2.09 g, 4.4 mmol) was dissolved in CCl_4 (30 ml) and stirred at room temperature. CCl_4 (28.81 ml) saturated with Cl_2 (0.31 g, 4.4 mmol) was added dropwise over 30 minutes, the crude product precipitated as it formed. The crude solid was filtered off and recrystallised from hot 60-80° petroleum ether as white prisms (1.73 g, 90%, mp=150-1°C)

Synthesis of (Benzothiazolyl-2-thiomethyl) N,N-diethyldithiocarbamato diphenyltin **(31)**

(26) (1.00 g, 1.7 mmol) was dissolved in ethanol (50 ml) and stirred at room temperature. Sodium N,N-diethyldithiocarbamate (0.38 g, 1.7 mmol) was added to the solution and refluxed for 12 hours.

The solution was allowed to cool and the ethanol removed under reduced pressure. The crude solid was partially redissolved in diethyl ether and the insoluble inorganic by-product removed by filtration. The ether was removed under reduced pressure and the crude solid recrystallised from hot ethyl acetate to yield white needles (0.87 g, 86%, mp=154°C)

Synthesis of tetrakis(Benzoxazolyl-2-thiomethyl)tin (32)

Sodium metal (0.134 g, 5.86 mmol) was dissolved in absolute ethanol (50 ml) and stirred at room temperature for 15 minutes. 2-mercaptobenzoxazole (0.88 g, 5.86 mmol) was added to the solution to form a deep brown solution and stirred for 15 minutes. *Tetrakis*(iodomethyl)tin (1.00 g, 1.46 mmol) was added and the solution refluxed for 12 hours. The solution was allowed to cool and the solvent removed under reduced pressure. The crude solid was partially dissolved in diethyl ether, the insoluble inorganic material filtered off and the filtrate reduced in volume to dryness. The crude product was recrystallised from hot 60-80° petroleum ether to yield white florets (0.71 g, 62%, mp=89°C)

CHAPTER 5

THE SYNTHESIS AND CHARACTERISATION OF SOME *N*- AND *C*- STANNYL TETRAZOLES

5.1. Introduction

Tetrazole compounds are important in medicinal chemistry and have uses in several fields including, antiinflammatory [219], hypocholesterolemic [219], antiinfective [220] and antiallergic [221] areas. The utility arises for two reasons: (i) a close similarity between the acidity of the tetrazole group ($-CN_4H$) and the carboxylic acid group ($-CO_2H$) [222], and (ii) the fact that the tetrazole function appears to be metabolically the more stable of the two [223]. Tetrazoles have also been used in agricultural preparations, e.g. tetrazolo [1,5-a] quinolines (fungicide) [224], 5-aryl (or heteroaryl)-2-alkanoic acid derivatives (plant growth inhibitors) [225] and benzodiazepines 1-(1H-tetrazole) acetic acids (plant growth regulators) [226].

Bicyclo molecules containing the tetrazole nucleus have also been formulated and have also found uses in medicinal chemistry, so much so that pentamethylene tetrazole (or PMT), $(CH_2)_5CN_4$ has been manufactered under the trade name "Metrazole" as an anticonvulsant. Two other molecules, 4,5-cyclononamethylene tetrazole, $(CH_2)_9CN_4$ and 4,5-cycloundecamethylene tetrazole, $(CH_2)_{11}CN_4$ have been patented as circulatory and repiratory analeptic agents. [227]

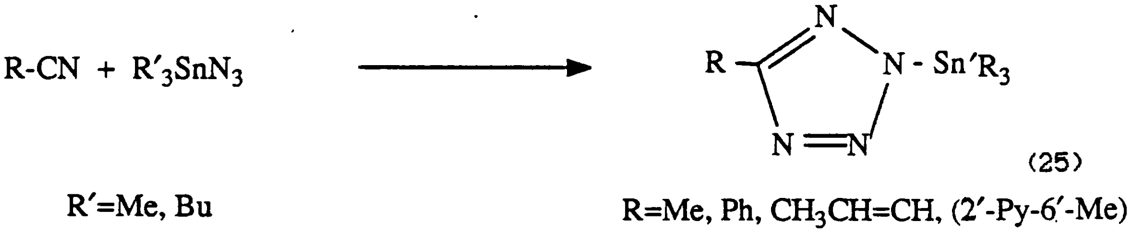
Various *N*-organotin heterocycles have been described in Chapter 1 and several novel *C*-organotin heterocycles have been described in Chapters 2-4. In this chapter both types of molecule are synthesised and a new variation is examined, that in which the tin atom is part of the heterocycle itself. The preparation of these latter compounds probably involves a thermal rearrangement mechanism and for this reason several simple N-triorganotin tetrazole compounds previously synthesised by other workers have been re-examined by variable temperature ^{119}Sn, ^{13}C and ^{15}N nmr and variable concentration ^{13}C nmr to yield some clues as to the structural dynamics of organotin tetrazole compounds.

The chemistry discussed in the previous chapters involved simply attaching the organotin moiety onto a preformed heterocycle, however, in this chapter the tetrazoles are formed *in situ* by ring building reactions. Tetrazoles are generally formed by condensing the appropriate nitrile with an azide ion and usually inorganic azide salts are used. An excellent review of azide chemistry has recently been published by Scriven and Turnbull [228] in which the preparation of several unusual organotin tetrazoles are described. Pereyre *et al.*[229] describe the synthetic uses of organotin azides and the preparation of triorganotin N-tetrazoles.

5.2 Synthesis

(A) Synthesis of 2-(Triorganostannyl)-5-Organotetrazoles

Four 2-(tributylstannyl)-5-R-tetrazoles , (R=Me-, Ph, $CH_3CH=CH$- and 6'-Me-2'-Py-) **(34-37)** and 2-(trimethylstannyl)-5-methyltetrazole **(33)** were synthesised. The preparative route followed parallels that described by Sisido *et al.*[230] in which the triorganotin azide is heated with an excess of the chosen nitrile. Sisido *et al.* prepared similar compounds by heating the mixtures in a sealed glass tube at 100°C for up to 14 hours. However, the cycloaddition reactions attempted here were performed at slightly elevated temperatures (approx 120°C) and under these conditions the reactions had reached completion in 5-7 hours. The reactions can be followed by the disappearance of the IR bands due to CN at 2250 cm^{-1} and N_3 at 2060 cm^{-1}. The crude, oily products were purified by distillation under reduced pressure and the crystalline solids were purified by recrystallisation from acetonitrile or methanol (equation 25).



(25)

(B) Synthesis of C-bonded Organostannyl Tetrazoles

Since azides will cyclise with nitriles to produce tetrazoles, it was reasoned that a suitable azide may possibly react with molecules such as $Ph_3Sn(CH_2)_nCN$ (n=2 or 3). The product would be a triphenyltin moiety linked by an passive alkyl chain to a tetrazole nucleus. A convenient source of the azide group is tributyltin azide and therefore equivalent amounts of the two materials were heated together, with stirring, at between 130-140°C for 3 hours, at room pressure, after which time the bands attributable to CN and N_3, 2250 and 2060cm^{-1} respectively, had disappeared from the IR spectrum. The cycloaddition product, 2-(tributylstannyl)-5-[n'-(triphenylstannyl)$(CH_2)_n$]tetrazole (n=2 or 3) **(38,39** respectively), both clear viscous oils, were fully characterised by the usual techniques (Scheme 14).

If these oils are heated at 140°C for a further 21 hours a thermal cyclisation reaction occurs in which Bu_3SnPh is eliminated with simultaneous ring closure to yield a bicyclo product. When n=2, the molecule is systematically named 2,3,4,5-tetraza-6-diphenylstannyl-[3,3]-bicycloocta-1,3-diene, **(40)**, and for n=3 ..-[3,4]-bicyclonona-1,3-diene, **(41)**, figure 13.

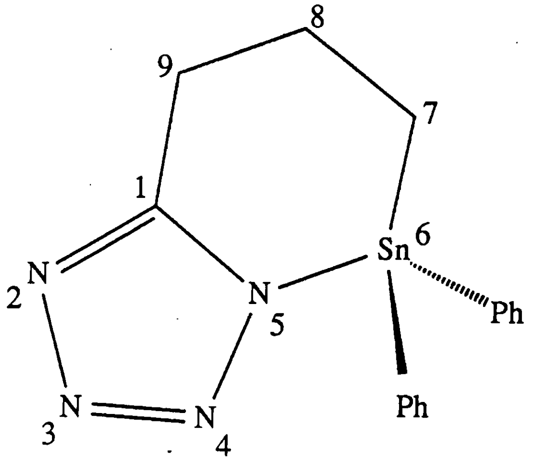
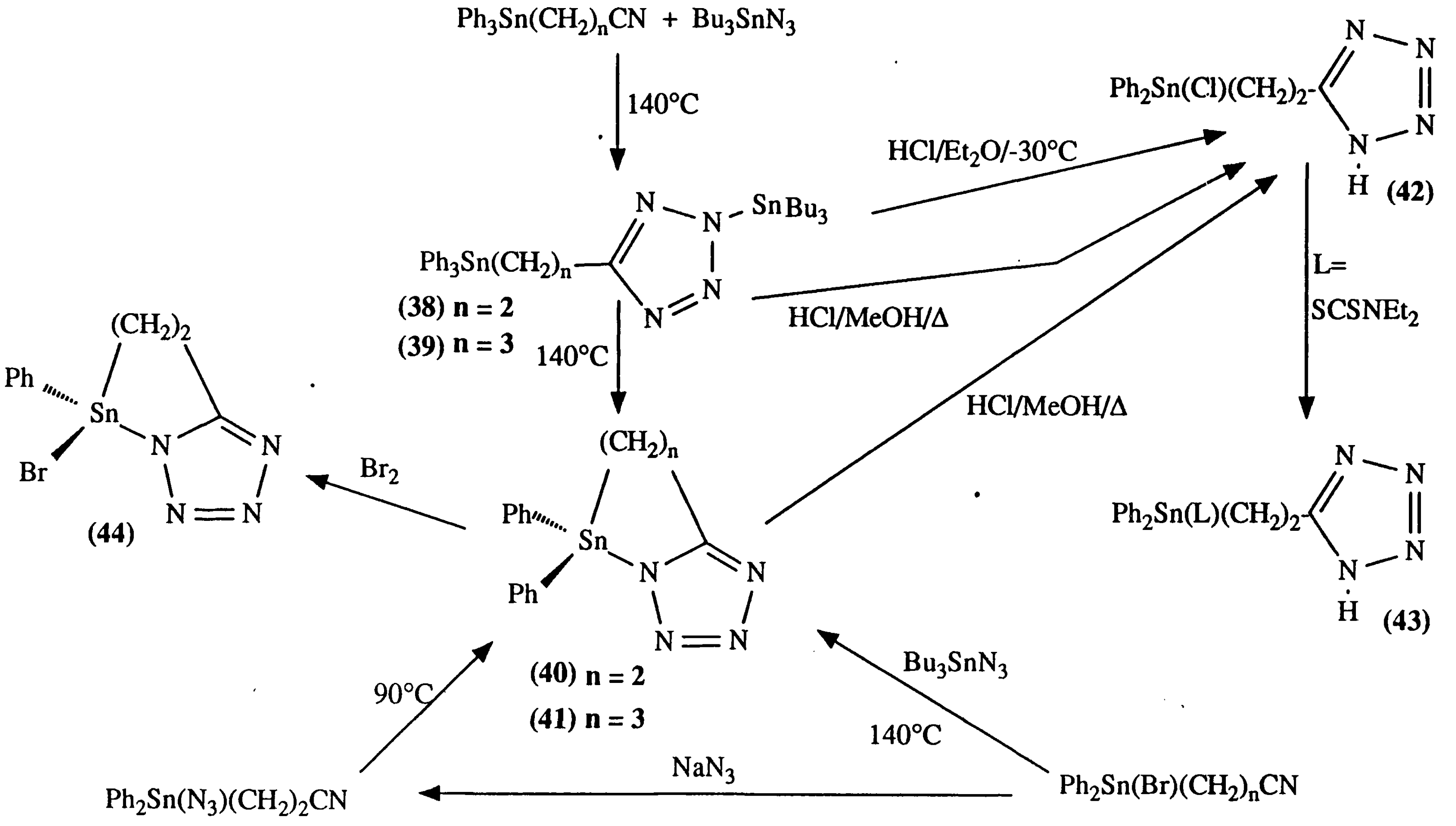


Figure 13.



Ph3Sn(CH2)nCN + Bu3SnN3
140°C
N
N
SnBu3
Ph3Sn(CH2)n
N
N
(38) n = 2
(39) n = 3
140°C
HCl/Et2O/-30°C
HCl/MeOH/Δ
HCl/MeOH/Δ
Ph2Sn(Cl)(CH2)2
N
N
N
N
H
(42)
L=
SCSNEt2
Ph2Sn(L)(CH2)2
N
N
N
N
H
(43)
(CH2)2
Ph
Sn
Br
N
N
N
N
(44)
Br2
(CH2)n
Ph
Sn
Ph
N
N
N
N
(40) n = 2
(41) n = 3
90°C
Bu3SnN3
140°C
NaN3
Ph2Sn(N3)(CH2)2CN
Ph2Sn(Br)(CH2)nCN

Scheme 14

These bicylo products are white crystalline, polymeric materials with very high melting points and can be readily separated from the oily by-product Bu_3SnPh by extraction of the latter with Et_2O. The solid materials are only sparingly soluble in common organic solvents, but they may be recrystallised from boiling $MeOH/CS_2$ mixtures. It is interesting to note that CS_2 can insert itself between Sn-N bonds in some tin amine compounds, e.g. $Me_2Sn(Cl)NEt_2$, to yield the dithiocarbamate [231], $Me_2Sn(Cl)SCSNEt_2$, however no such insertion occurs with the bicyclic tetrazoles. Two alternative routes are also available that yield the bicyclo product in shorter reaction times. One method involves the starting material $Ph_2Sn(Br)CH_2CH_2CH_2CN$ (from selective bromination of $Ph_3SnCH_2CH_2CH_2CN$ reacting with Bu_3SnN_3. The bicyclo product and tributyltin bromide are formed very quickly (≈5 minutes) and in very high yield (>96%). The other method involves heating at reflux a solution of $Ph_2Sn(N_3)CH_2CH_2CN$ (from treating $Ph_2Sn(Br)CH_2CH_2CH_2CN$ with NaN_3) in 60-80° petroleum ether for 30 minutes during which time the bicyclo product precipitates from solution.

The preparation of 2,3,4,5-tetraza-6-dibutylstannyl-[3,3]-bicycloocta-1,3-diene was attempted using a similar thermal cyclisation reaction by heating $Bu_3SnCH_2CH_2CN$ and Bu_3SnN_3 together at 140°C, however, no measurable decreases in the intensities of the -CN and $-N_3$ absorption bands in the IR spectrum were observed, and no bicyclo compound was collected.

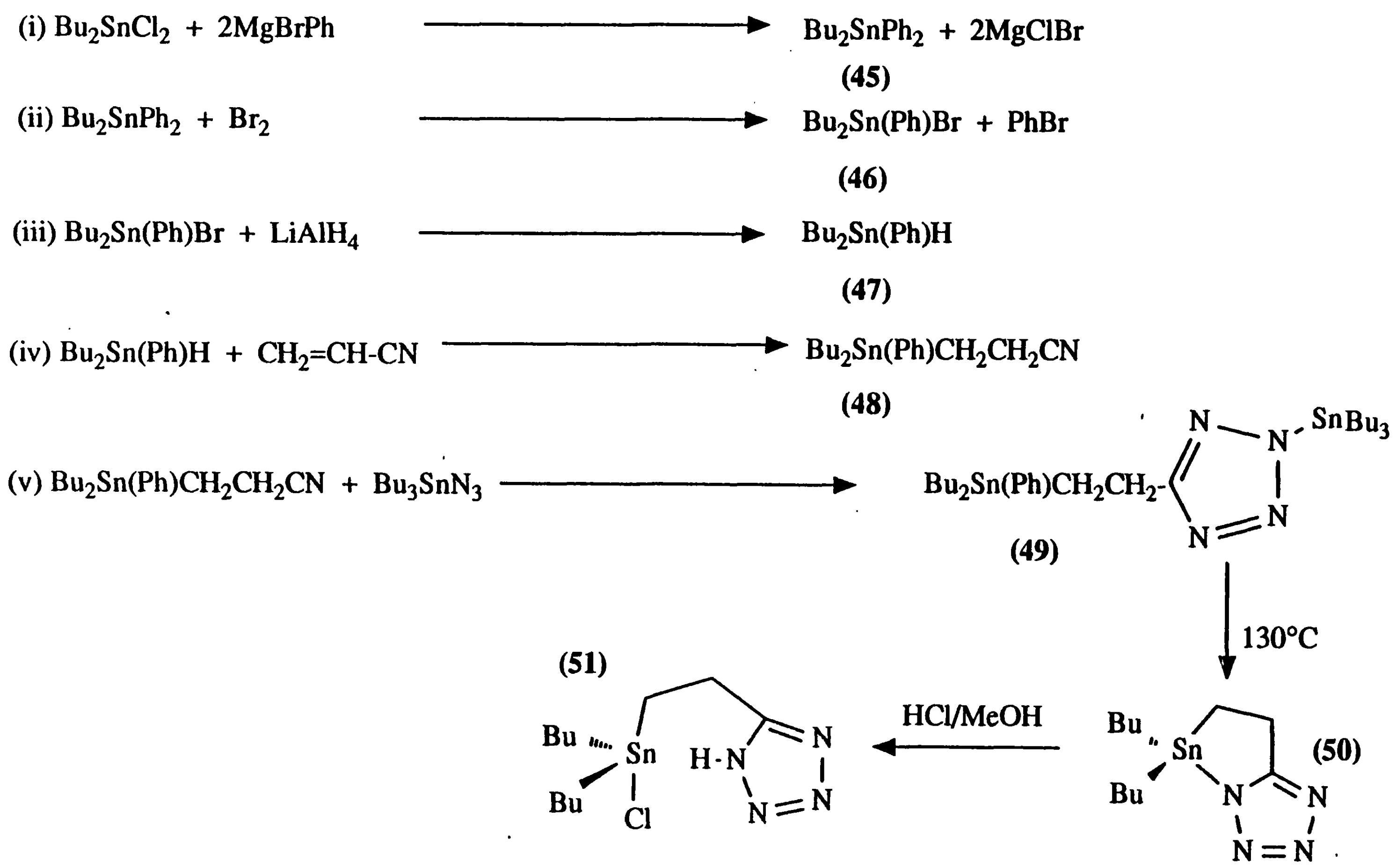
The same compound, 2,3,4,5-tetraza-6-dibutylstannyl-[3,3]-bicycloocta-1,3-diene, (50), however, could be prepared from

$Bu_2Sn(Ph)CH_2CH_2CN$, **(48)**, by a series of reactions involving the compounds **(45-49)** shown in Scheme 15.

A similar series of reactions to produce the dimethylstannyl-analogue, i.e. 2,3,4,5-tetraza-6-dimethylstannyl-[3,3]-bicycloocta-1,3-diene, were attempted, but failed at step (iv) in Scheme 16, due to the reaction producing a large number of products. However, the intermediate compounds **(52-54)** were fully characterised for completeness. It is also worth noting that the attempted cyclisation of Ph_3SnCN with Bu_3SnN_3 did not yield a tetrazole and only starting materials were recovered.

The two different tin-nitrogen bonds in the initial cycloaddition product **(38)** and the bicyclo product **(40)** can be cleaved by HCl to yield the same product, (2-[1'H-5'-tetrazolyl]ethyl)diphenyltin chloride, **(42)**, with the cycloaddition product also unexpectedly losing Bu_3SnPh in the process. **(42)** can be further derivatised by reactions with ligands such as dithiocarbamates, **(43)**, to yield tetrazole analogues of the compounds described in Chapters 3 and 4 (Scheme 14).

The bicyclo compounds do not react with iodine, even in refluxing MeOH, but react slowly with bromine at room temperature, decolourising the bromine solution over 24 hours. Bromobenzene was recovered from the reaction mixture along with a white, insoluble, polymeric powder. This material is probably 2,3,4,5-tetraza-6-monophenylstannyl bromide-[3,3]-bicycloocta-1,3-diene, **(44)**, but full structural characterisation was not possible due to its insolubility and the sample size (Scheme 14). All analytical data are presented in Table 36.


(i) Bu2SnCl2 + 2MgBrPh → Bu2SnPh2 + 2MgClBr
(45)
(ii) Bu2SnPh2 + Br2 → Bu2Sn(Ph)Br + PhBr
(46)
(iii) Bu2Sn(Ph)Br + LiAlH4 → Bu2Sn(Ph)H
(47)
(iv) Bu2Sn(Ph)H + CH2=CH-CN → Bu2Sn(Ph)CH2CH2CN
(48)
(v) Bu2Sn(Ph)CH2CH2CN + Bu3SnN3 →
Bu2Sn(Ph)CH2CH2-
SnBu3
(49)
130°C
(50)
HCl/MeOH
(51)
Bu
Sn
Cl
H-N

Scheme 15

(i) $Me_2SnCl_2 + 2MgBrPh \longrightarrow Me_2SnPh_2 + 2MgBrCl$

(52)

(ii) $Me_2SnPh_2 + Br_2 \longrightarrow Me_2Sn(Br)Ph + PhBr$

(53)

(iii) $Me_2Sn(Br)Ph + LiAlH_4 \longrightarrow Me_2Sn(H)Ph$

(54)

(iv) $Me_2Sn(H)Ph + CH_2{=}CH\text{-}CN \longrightarrow$ Mixture of products

Scheme 16

Table 36: Analytical data for Organotin Tetrazole compounds [a]

Compound	Formula	Mp/*Bp* (°C)	C: Found (Calc),	H:	N: %
(33)	$C_5H_{12}N_4Sn$	213	24.60(24.32)	5.05(4.89)	23.30(22.69)
(34)	$C_{14}H_{30}N_4Sn$	43-7	45.01(45.06)	8.02(8.10)	15.07(15.01)
(35)	$C_{19}H_{32}N_4Sn$	72	52.11(52.46)	7.01(7.41)	13.01(12.88)
(36)	$C_{16}H_{32}N_4Sn$	*224/0.3*	47.89(48.14)	8.11(8.08)	14.43(14.03)
(37)	$C_{19}H_{33}N_5Sn$	217	50.65(50.69)	7.36(7.38)	15.55(15.55)
(38)	$C_{33}H_{46}N_4Sn_2$	[b]	53.70(53.84)	6.39(6.29)	6.88(7.61)
(39)	$C_{34}H_{48}N_4Sn_2$	[b]	53.89(54.43)	6.21(6.44)	7.32(7.46)
(40)	$C_{15}H_{14}N_4Sn$	290-5(dec)	48.33(48.82)	3.97(3.82)	15.18(15.18)
(41)	$C_{15}H_{16}N_4Sn$	310(dec)	50.20(50.17)	4.37(4.21)	14.60(14.62)
(42)	$C_{15}H_{15}N_4SnCl$	157	44.70(44.44)	3.78(3.72)	13.95(13.82)
(43)	$C_{20}H_{25}N_5S_2Sn$	163	46.87(46.34)	4.24(4.86)	13.77(13.51)
(44)	$C_9H_9N_4BrSn$	125(dec)	30.42(29.07)	2.99(2.43)	14.34(15.05)
(45)	$C_{20}H_{28}Sn$	*101/1.0*	61.88(62.04)	7.12(7.29)	- -
(46)	$C_{14}H_{23}BrSn$	*182/0.3*	43.01(43.12)	5.65(5.94)	- -
(47)	$C_{14}H_{24}Sn$	*175/1.0*	54.08(54.06)	7.74(7.77)	- -
(48)	$C_{17}H_{27}NSn$	*194/0.3*	56.23(56.07)	7.56(7.47)	3.82(3.84)
(49)	$C_{29}H_{54}N_4Sn_2$	[b]	49.82(50.03)	7.72(7.81)	8.10(8.04)
(50)	$C_{11}H_{22}N_4Sn$	[b]	40.02(40.15)	6.71(6.73)	17.24(17.02)
(51)	$C_{11}H_{23}N_4SnCl$	57	36.71(36.15)	6.21(6.34)	15.24(15.33)
(52)	$C_{14}H_{16}Sn$	*140/0.5*	55.98(55.50)	5.24(5.28)	- -
(53)	$C_8H_{11}SnBr$	*175/0.5*	32.12(31.42)	3.81(3.62)	- -
(54)	$C_8H_{12}Sn$	*122/0.5*	42.71(42.35)	5.32(5.33)	- -

Table 36 continued,

[a] The structural formulae for compounds (**33-37**) are given on page 278
The struuctral formulae for compounds (**38-54**) are given in schemes 14-16

[b] These compounds are high boiling point oils that could not be distilled or purified by conventional chromatography.

5.3 Spectroscopy

The five triorganostannyl-N-tetrazole compounds were synthesised in order to examine the thermal dynamics of the N-bonded triorganotin group and a large quantity of variable temperature nmr data has been collected. It would be inappropriate to include the study here, since all mechanistic arguments concerning these reactions are discussed in Chapter 6.

5.3.1. Infra-red Spectroscopy

The infra-red data regarding the -CN and $-N_3$ bands at 2250cm $^{-1}$ and 2060cm^{-1} respectively were invaluable in following the extent of the reactions. The tetrazole ring generally shows IR absorption bands in the region 1000-1100 cm^{-1} and an absorption band between 1095-1120 cm^{-1} has been reported for many tetrazole derivatives. Other absorptions which have been ascribed to the ring appear at 1000-1030 cm^{-1} and 1045-1085 cm^{-1} [232]. The cyclic C=N of the tetrazole ring generally absorbs at 1590-1600 cm^{-1}. The infra-red data for the C-bonded organotin tetrazole are presented in Table 37. It is interesting to note that the cyclic C=N band at 1590-1600 cm^{-1} is only apparent for the two cycloaddition products (38) and (39). Compounds (42) and (51) both show ν(N-H) stretches at 3150 cm^{-1}. This N-H stretching frequency is quite low and therefore might suggest considerable association through H-bonding. Secondary amine groups can also show an N-H deformation which occurs around 1500 cm^{-1}, and indeed both compounds (42) and (51) do show absorption bands in this region.

Table 37. Infra-red data for the Organostannyl-C-Tetrazole compounds[a, b]

Compound	Ring stretches						Other
(38)	1580m	1300s	1100m	1080vs	1030s	1005s	-
(39)	1575m	1295m	1100w	1070s	1020s	1000s	-
(40)	-	1300m	1100m	1080m	1030m	1000m	-
(41)	-	1260w	1100s	1090s	1025m	1010m	-
(42)	-	1300m	1100m	1080m	1020w	1000w	3150m (N-H)
(43)	-	1300m	1100s	1080m	1020m	1000m	-
(44)	-	1300m	1100w	1080s	1025m	1000m	-
(49)	-	1300m	-	1080s	1035m	1010m	-
(50)	-	1300s	1100s	1080s	1035m	1010m	3150m (N-H)
(51)	-	1300m	-	1080s	1035w	-	-

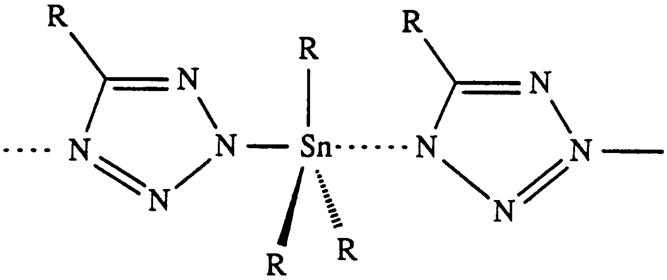
[a] Cm^{-1}

[b] Compounds (38), (39) and (49) were examined as liquid films on NaCl discs. All other data was collected as KBr discs.

w=weak, m=medium, s=strong, vs=very strong

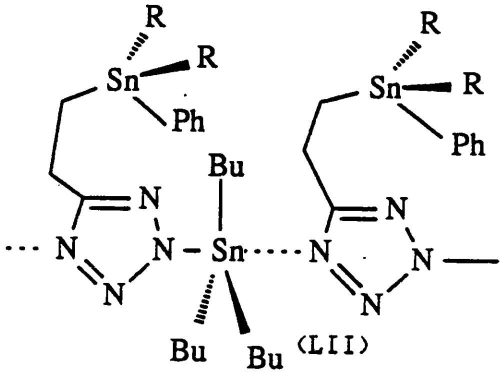
5.3.2. NMR

The ^1H, ^{13}C and ^{119}Sn nmr data are presented in Tables 38, 39 and 40 respectively. The ^1H nmr spectra of the cycloaddition products **(38)**, **(39)** and **(49)** are quite limited since the tributyltin protons obscure the more valuable data regarding the alkyl chain bridge, including the coupling constant data. The ^{13}C nmr data for these compounds are consistant with each other but no coupling constants were measured. The ^{119}Sn nmr data show two tin sites as expected. The tetraorganotin sites for **(38)** and **(39)** (both $Ph_3SnCH_2CH_2$--) would be expected to have chemical shifts similar to Ph_3SnEt [$\delta(^{119}Sn) = -111.1$ ppm. [197]], and indeed they do, at -101.1 and -102.2 ppm respectively. Similarly, the tetraorganotin site for **(49)** would be expected to have a $\delta(^{119}Sn)$ value very similar to that of its precursor compound **(48)**, [$Bu_2Sn(Ph)CH_2CH_2CN$ $\delta(^{119}Sn) = -40.9$ ppm], in fact it is almost identical [$\delta(^{119}Sn) = -40.8$ ppm.]. The tributyltin-N-tetrazole sites have chemical shifts that would suggest that they are 5-coordinate, even in chloroform solution. Sisido *et al.* [230] proposed that, when the C-substituent on the tetrazole is aliphatic the structure of these compounds is polymeric, even in solution, (LI).



(LI)

In accordance with this, compounds **(38)**, **(39)** and **(49)** probably have a structure similar to that depicted below, (LII).



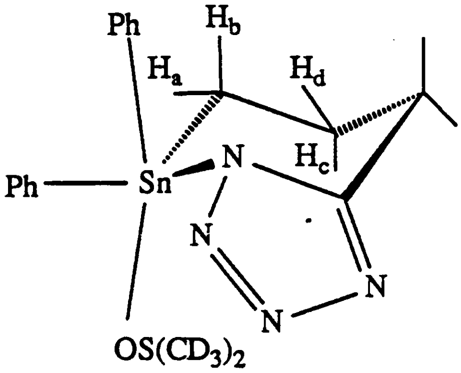
(LII)

R=Ph, Bu

Because **(40)** and **(41)** are insoluble in non-coordinating solvents it was presumed that the three bicyclo compounds **(40)**, **(41)** and **(50)** were polymeric in the solid state. This suggestion was later vindicated by the X-ray diffraction study, (see 5.4). For **(40)** and **(41)**, the strongly coordinating solvent d_6-DMSO was used to break-up the polymeric chains before any nmr data could be collected. The ^{1}H nmr data are of poor quality and the signals are broad (approx 14 Hz width at half height). The broadening is due to the fact that the methylene units forming the alkyl bridges are an integral part of a saturated heterocyclic ring and hence form non-equivalent protons, (LIII). This would also explain the lack of resolvable $^{117/119}$Sn satellites.

^{2}J(^{119}Sn, ^{1}H) coupling constant values for compounds **(40)** and **(41)** were estimated to be in the order of 94 and 79 Hz. respectively and such values reflect the 5-coordinate character of the solution species, either as oligomers or DMSO adducts. The ^{13}C nmr data for **(40)** and **(41)** shows the *i* carbons on the phenyl rings to be above 140 ppm, which can tentatively be taken as a guide to indicate

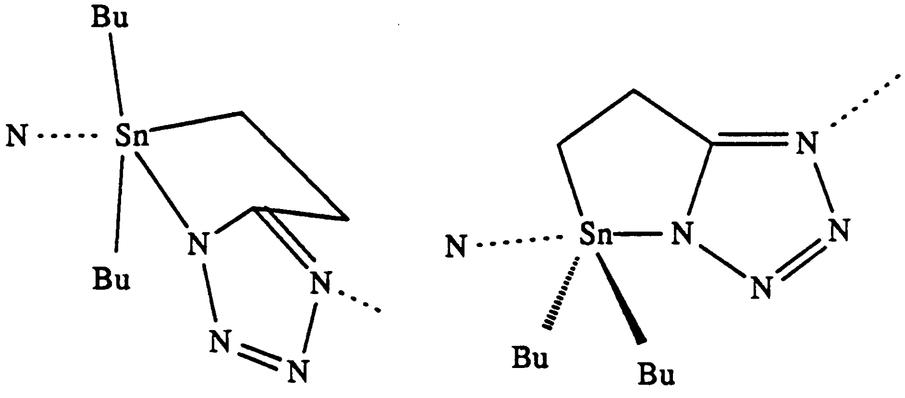
5-coordination at tin.



(LIII) $H_a \neq H_b \neq H_c \neq H_d$

The ^{13}C nmr data for the alkyl chains are consistent with each other as are the data for the tetrazole ring carbons. The ^{119}Sn nmr data shows 5-coordination for all three bicyclo compounds, the chemical shift values are -195.9 ppm and -224.3 ppm for (**40**) and (**41**) respectively and -83.4 ppm for (**50**). Compounds (**40**) and (**41**) were dissolved in d_6-DMSO and might be expected to form 5-coordinated DMSO adducts anyway, (LIII), however, (**50**) was soluble in $CDCl_3$ but still shows 5-coordination. Therefore one must propose either a polymeric R_3SnX_2 cis-tbp adduct or a polymeric trans-tbp structure, (LIV), existing in solution, but it is not possible to distinguish which one actually exists from the available data. It is of course possible, recognising the polymeric nature of the tetrazole compounds, that (**40**) and (**41**) are also short-chain polymers in solution, possibly end-capped with DMSO.

Compounds (**42**) and (**51**), the chlorinated organotin species show much sharper ^1H nmr signals, since these molecules have a freely rotating alkyl chain bridge. The methylene protons on the same carbon atoms become equivalent and the $^{117/119}Sn$ satellites are resolved.



cis-tbp

trans-tbp

(LIV)

The $^{2}J(^{119}Sn, ^{1}H)$ and $^{3}J(^{119}Sn, ^{1}H)$ values for **(42)** were measured as 78.8, 75.4 Hz respectively. Similarly, for **(51)**, these two parameters were measured to be 76.0 and 68.0 Hz respectively. The N-H tetrazole proton signals at 14.35 and 14.37 ppm. respectively are broad and this would suggest either rapid motion between the nitrogens, a certain degree of association *via* H-bonding, an artefact of the quadrupolar nitrogen atoms or a combination of these effects. Compound **(42)** was only soluble in DMSO, hence a 5-coordinate DMSO adduct might be expected. Indeed, the ^{13}C nmr data show a chemical shift for the *i* carbons on the phenyl rings to be 143 ppm, well inside the range for 5-coordinate tin set by Holecek *et al.* [100]. The large negative ^{119}Sn chemical shift for this compound, [$\delta(^{119}Sn) = -162.3$ ppm.], confirms the suggestion that the DMSO does indeed form an adduct with **(42)**. Compound **(51)** was soluble in $CDCl_3$ and therefore need not necessarily show a 5-coordinate nature. The $\delta(^{119}Sn)$ value of 14.25 ppm would suggest that this molecule is 5-coordinate and this value can be compared to that of the 5-coordinate adduct $Bu_3SnCl.DMSO$,

δ(^{119}Sn)= 5.27 ppm. The structure of **(51)** in solution could be a trans-tbp polymer or a discrete intramolecular chelate, however the data available here are insufficient to decide which proposed structure is correct.

The dithiocarbamate derivative, **(43)** was only soluble in DMSO and as a result forms the 5-coordinated solvent adduct. This designation is confirmed by the coupling constant, $^2J(^{119}Sn, ^1H)$, measured as 118 Hz, the δ(^{119}Sn) nmr value of -204.3 ppm. and the ^{13}C nmr δ value of the *i* carbons on the phenyl rings of 142 ppm.

Compound **(44)** was extremely insoluble, even in solvents such as DMSO and DMF, precluding solution state nmr. One can only speculate that the molecule must exist in a highly stable polymeric arrangement, that is very resistant to cleavage by solvent. The nmr data for compounds **(45-48)**, i.e. the precursors to **(49)**, and **(52-54)**, the dimethyltin compounds synthesised in the abortive preparation of 2,3,4,5-tetraza-6-dimethylstannyl-[3,3]-bicyclooocta-1,3-diene, have been recorded and included for completeness.

Table 38: ^{1}H nmr Studies of Organotin Tetrazole compounds ^{a,b,c}

Cpd	Arom.	CH$_2^{(\alpha)}$	CH$_2^{(\beta)}$	CH$_2^{(\gamma)}$	Butyl	Other
(33)	-	-	-	-	-	Me$_3$= 0.90 5-Me=2.60 (2xs,9H & 3H)
(34)	-	-	-	-	1.24-0.74 (m,27H)	5-Me=2.45 (s,3H)
(35)	7.84-7.21 (m,5H)	-	-	-	1.32-0.68 (m,27H)	-
(36)	-	-	-	-	1.27-0.68	CH=6.7(d,1H) CH=5.9(m,1H) Me=1.7(s,3H)
(37)	8.14-7.25 (m, 3H)	-	-	-	1.76-0.81 (m, 27H)	Me=2.7(s,3H)
(38)	7.60-7.26 (m,15H)	3.01 (t,2H)	2.55 (t,2H)	-	1.45-0.68 (m, 27H)	-
(39)	7.58-7.20 (m,15H)	2.28 (t,2H)	2.00-1.70(unresolved) (broad 4H)		1.45-0.68 (m, 27H)	-
(40)	7.80-7.30 (m,10H)	3.23 (m,2H)	2.20 (m,2H)	-	-	-
(41)	7.80-7.30 (m,10H)	2.94 (m,2H)	2.15 (m,2H)	1.90 (m,2H)	-	-
(42).	7.90-7.30 (m,10H)	3.41 (t,2H)	2.03 (t,2H)	- -	- -	N-H=14.35 (s,1H)

Table 38 continued,

(43)	7.87-7.26 (m,10H)	3.33 (t,2H)	2.06 (t,2H)	- -	- -	CH_2=1.55 (q,4H) CH_3=1.23 (t,6H) N-H=14.23 (s,1H)
(44)	Material not soluble					
(45)	7.70-7.22 (m,10H)	-	-	-	1.76-0.82 (m, 18H)	-
(46)	7.70-7.24 (m,5H)	-	-	-	1.76-0.81 (m, 18H)	-
(47)	7.70-7.14 (m,5H)	-	-	-	1.77-0.76 (m, 18H)	Sn-H=7.15 (s,1H)
(48)	7.64-7.33 (m,5H)	2.62 (t,2H)	1.85 (t,2H)	-	1.76-0.81 (m, 18H)	-
(49)	7.64-7.34 (m,5H)	3.09 (t,2H)	2.53 (t,2H)	-	1.64-0.86 (m,45H)	-
(50)	-	3.21 (t,2H)	1.96 (t,2H)	-	1.54-0.68 (m,18H)	-
(51)	-	3.41 (t,2H)	1.90 (t,2H)	-	1.70-0.85 (m,18H)	N-H=14.37 (s,1H)
(52)	7.68-7.22 (m,10H)	-	-	-	-	Me=0.98 (s,6H)
(53)	7.88-7.52 (m,5H)	-	-	-	-	Me=0.75 (s,6H)

Table 38 continued,

(54)	7.52-7.23 (m,5H)	-	-	-	-	Me=0.32 (d,6H) H=5.53 (sept,1H)

[a] All chemical shift data given in ppm. with TMS as a reference.

[b] All spectra recorded as $CDCl_3$ solutions at 25°C except for those marked below.

[c] Compounds **(40)**, **(41)**, **(42)** and **(43)** were dissolved in d_6-DMSO.

Table 39: ^{13}C nmr Studies of Organotin Tetrazole Compounds

Aromatic Organotin Carbons ^{a,b}

Compound	*i*	*o*	$^{2}J(C-Sn)$	*m*	$^{3}J(C-Sn)$	*p*	$^{4}J(C-Sn)$
(33)	-	-	-	-	-	-	-
(34)	-	-	-	-	-	-	-
(35)	137.1	136.5	-	128.2	-	129.7	-
(36)	-	-	-	-	-	-	-
(37) ^{c}							
(38)	138.9	136.9	34.56	128.7	50.51	129.3	11.96
(39)	138.4	136.8	-	128.4	-	129.1	-
(40)	140.7	136.1	48.42	128.8	67.79	129.7	14.52
(41)	141.3	136.3	44.83	128.6	65.61	129.4	14.21
(42)	143.5	135.8	-	128.2	-	128.8	18.71
(43)	142.4	135.7	-	128.3	58.93	128.9	-
(44)	-	-	-	-	-	-	-
(45)	-	-	-	-	-	-	-
(46)	-	-	-	-	-	-	-
(47)	-	-	-	-	-	-	-
(48)	139.3	136.3	-	128.3	-	128.7	-
(49)	136.9	136.3	-	128.3	-	128.6	-
(50)	-	-	-	-	-	-	-
(51)	-	-	-	-	-	-	-
(52)	136.1	135.0	-	128.7	-	129.8	-
(53)	140.5	136.1	37.5	128.2	-	128.5	-
(54)	137.3	136.6	-	128.4	-	128.6	-

Table 39 continued,

Alkyl Chain Carbon atoms

Compound	C_1	C_2	C_3	$C_{5'}$	C_α	C_β	C_γ	C_δ
(33) [d]	-	-	-	158.9	-	-	-	-
(34) [e]	-	-	-	157.9	18.4	28.5	27.4	13.9
(35)	-	-	-	159.1	18.3	28.4	27.3	13.9
(36)	-	-	-	160.1	18.4	28.6	27.5	13.8
(37)	-	-	-	160.5	18.5	28.0	26.8	13.4
(38)	9.4	26.8	-	163.2	18.0	28.0	27.3	13.6
(39)	16.8	23.1	25.9	161.5	18.2	28.1	27.0	13.7
(40)	14.9	19.2	-	166.1	-	-	-	-
(41)	16.8	23.7	25.1	160.9	-	-	-	-
(42)	18.7	19.5	-	158.2	-	-	-	-
(43) [f]	14.5	20.1	-	159.2	-	-	-	-
(44)	-	-	-	-	-	-	-	-
(45)	-	-	-	-	-	-	-	-
(46)	-	-	-	-	-	-	-	-
(47)	-	-	-	-	-	-	-	-
(48)	9.5	14.7	-	-	18.1	28.9	27.2	13.6
(49)	5.0	9.6	-	161.3	14.6	28.8	27.2	13.5
(50)	13.3	18.1	-	166.2	17.6	28.1	28.0	13.5
(51)	13.3	19.5	-	160.8	17.6	27.8	27.6	13.3
(52) [g]	-	-	-	-	-	-	-	-
(53) [h]	-	-	-	-	-	-	-	-
(54) [i]	-	-	-	-	-	-	-	-

Table 39 continued,

[a] Chemical shift data given in ppm. Coupling constants given in Hz.

[b] All samples recorded as $CDCl_3$ solutions at 25°C, except **(40)**, **(41)**, **(42)** and **(43)** which were recorded as d_6-DMSO solutions.

[c] Pyridine carbons are at the following chemical shifts:

2'	157.8 ppm.
3'	124.0 ppm.
4'	137.2 ppm.
5'	120.0 ppm.
6'	146.3 ppm.

[d] 5'-Me at 10.36 ppm, Me_3 at-0.9 ppm.

[e] 5'-Me at 11.23 ppm.

[f] SCS at 201.8 ppm., CH_2 at 48.5 ppm., CH_3 at 12.1 ppm.

[g] Me carbons at -2.11 ppm, $^{1}J(^{119}Sn, ^{13}C)=1191.9$ Hz.

[h] Me carbons at -10.15 ppm, $^{1}J(^{119}Sn, ^{13}C)=1374.5$ Hz.

[i] Me carbons at -11.71 ppm.

Table 40 ^{119}Sn nmr [a] and Mossbauer [b] Studies of Organotin Tetrazole compounds

Compound	$\delta(^{119}Sn)$ [c]	I.S.(δ)	ΔEq	Γ_1,	Γ_2 [d]
(33)	-59.5	1.33	3.56	0.96,	0.95
(34)	-74.9	1.23	3.45	0.94,	0.98
(35)	-40.7	1.22	3.23	0.97,	0.96
(36)	-65.4	1.23	3.44	0.96,	0.98
(37)	-0.5	1.49	3.69	0.83,	0.88
(38)	-101.1	1.27	0.00	1.01,	-
	-43.2	1.40	3.45	0.87,	1.08
(39)	-102.2	1.26	0.00	1.03,	-
	-55.4	1.42	3.54	0.87,	0.96
(40)	-195.9	1.32	3.28	0.92,	0.99
(41)	-224.3	1.29	3.26	0.90,	0.93
(42)	-162.3	1.39	3.32	0.94,	1.11
(43)	-204.3	1.28	3.27	0.98,	0.99
(44)	-	1.39	3.30	0.99,	0.97
(45)	-	-	-	-	-
(46)	-	-	-	-	-
(47)	-	-	-	-	-
(48)	-	-	-	-	-
(49)	-41.0	1.34	0.00	1.20,	-
	-43.8	1.45	3.53	0.93,	0.96
(50)	-83.5	1.43	3.48	1.09,	1.14

Table 40 continued,

(51)	14.2	1.46	3.42	0.99,	0.98
(52)	-59.4	-	-	-	-
(53)	68.0	-	-	-	-
(54)	-121.9	-	-	-	-

[a] All spectra recorded as $CDCl_3$ solutions at 25°C using Me_4Sn as a reference except (40), (41), (42) and (43) which were run in d_6-DMSO.

[b] Mossbauer experiments run at 78K and data given in $mmsec^{-1}$

[c] Values given in ppm.

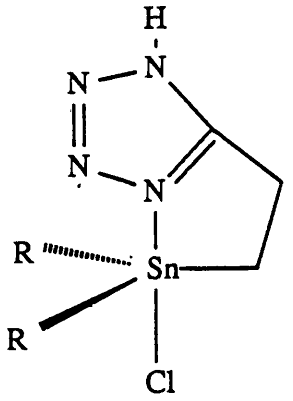
[d] Refers to maximum width at half height of the high and low velocity spectral components in $mmsec^{-1}$.

5.3.3 Mossbauer Spectroscopy

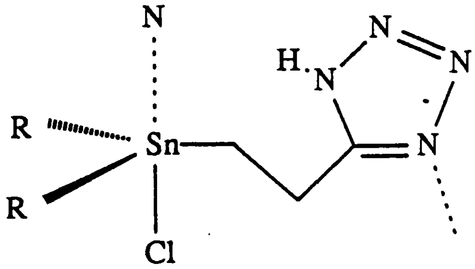
The Mossbauer data are presented in Table 40. Compounds **(38)**, **(39)** and **(49)** each have a tetraorganotin site in the molecule, and each show a broad singlet in the Mossbauer spectrum. For the simplicity of fitting the data it was assumed that for each of the broad singlets, $\Delta Eq=0.00$ mmsec^{-1}. The isomer shifts (δ) for these same sites fall in the range 1.26-1.34 mmsec^{-1} and are typical values for tetraorganotin molecules. The tributyltin sites attached to the tetrazoles have ΔEq values in the range 3.45-3.54 mmsec^{-1} and δ values in the range 1.40-1.45 mmsec^{-1}. These figures are consistent with a trans-R_3SnN_2-tbp type structure, and the structure proposed for these compounds in section 5.2.2, i.e. (LII), seems to be valid for the solid as well as the solution state. Barbieri *et al.*, using the point charge model, have calculated the quadrupole splitting parameters for trans-R_3SnN_2 systems [201] and the results for R=alk give $\Delta Eq=3.25$ mmsec^{-1} and R=Ph gives $\Delta Eq=2.80$ mmsec^{-1}. The theoretical result for R=alk seems a little low, however, the model is probably too simplistic since it does not distinguish between types of alkyl groups and hence this figure is only a general guide.

The bicyclo compounds, **(40)**, **(41)** and **(50)** have ΔEq in the range 3.28-3.48 mmsec^{-1} and δ in the range 1.29-1.43 mmsec^{-1}. The ΔEq values suggest trans-tbp type symmetry again, (and this proposition is borne out by the X-ray crystal structure in section 5.4.). The dibutyltin bicyclo compound has a larger δ value than the diphenyl- examples, due to the reduced 5s-electron withdrawing properties of the butyl groups.

The chlorinated species, **(42)** and **(51)** have ΔEq values in the range 3.32-3.42 mmsec^{-1} and δ in the range 1.39-1.46 mmsec^{-1}. The figures again are consistent with a trans-tbp structure. There are two possible structures, an intramolecular chelate, (LV), and a intermolecular polymer, (LVI).



(LV)



(LVI)

(R=Ph, Bu)

It is difficult to decide which of the two structures is correct, however, since **(42)** is insoluble in non-coordinating solvents, this might suggest a polymeric character. It must be noted that as similar chelate structures formed by the compounds discussed in Chapters 3 and 4 were generally very soluble in $CDCl_3$, this lends credence to the proposed polymeric structure (LVI).

The dithiocarbamate product, **(43)** and the mono bromo product, **(44)** both have Mossbauer parameters which indicate that they have trans-tbp geometry. Since both compounds do not readily dissolve, it might suggest that they both have a high degree of polymeric character.

The bromide may have a structure similar to that of compound **(41)**, discussed in the next section.

5.4 The Crystal and Molecular Structure of 2,3,4,5-Tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene **(41)**

Suitable crystals for X-ray diffraction were grown by very slow crystallisation from a methanol/carbon disulphide mixture (10:1). Details of the crystallographic analysis are given in Appendix II. The atomic coordinates and thermal parameters are given in Table 41, the bond lengths in Table 42 and the bond angles in Table 43. Figure 14 shows the local geometry about tin and figure 15 gives a view of the unit cell.

An examination of figure 14 reveals that there are two distinct molecules in the asymmetric cell. The stucture is polymeric and figure 15 shows the two polymers running side by side. The tin atom is carbon bonded through an alkyl chain to the tetrazole group and the tin atom is also an integral part of a stanna-piperidine ring, confirming the ring closure reactions described above.

The local geometry about tin is best described as a moderately distorted trans-tbp type structure. Two phenyl rings and the alkyl chain lie in the equatorial positions, whilst the axial positions are occupied by a intramolecular bonded nitrogen,[N(4) and N(5)], and a intermolecular bonded nitrogen,[N(1') and N(8')]. The four Sn-N bond lengths are nearly equivalent: in the first molecule, [Sn(1)-N(4)]=2.339(15) Å and [Sn(1)-N(1')]=2.37 Å and in the second molecule [Sn(2)-N(5)]=2.343 Å and [Sn(2)-N(8')]=2.36 Å. Table 44 lists bond distances of analogous compounds for comparison. The nitrogens bonded to the tin form part of an aromatic, completely planar, tetrazole ring. The sum of the internal angles being 540°, exactly the sum for

Table 41. Fractional Atomic Coordinates and Thermal Parameters (Å) for 2,3,4,5-Tetraza-6-Diphenylstannyl-[3,4]-bicyclonona-1,3-diene

Atom	X	Y	Z	U_{iso} or U_{eq}
Sn(1)	-0.51987(6)	0.10331(9)	0.23881(5)	0.0394(6)
N(1)	-0.53867(8)	-0.22861(11)	0.24933(6)	0.0546(9)
N(2)	-0.62633(8)	-0.20041(13)	0.26139(7)	0.0542(10)
N(3)	-0.63759(8)	-0.10773(12)	0.25228(7)	0.0503(9)
N(4)	-0.55918(8)	0.06798(12)	0.23509(7)	0.0563(9)
Sn(2)	0.01305(7)	-0.01929(9)	0.73872(6)	0.0408(6)
N(5)	0.05181(8)	0.15130(11)	0.76679(7)	0.0536(9)
N(6)	0.14274(8)	0.19151(12)	0.78473(7)	0.0461(9)
N(7)	0.13617(8)	0.28379(14)	0.79440(7)	0.0554(10)
N(8)	0.03918(8)	0.31104(9)	0.78330(6)	0.0421(8)
C(1)	-0.5157(9)	0.1168(12)	0.3633(7)	0.040(3)
C(2)	-0.4360(11)	0.1577(15)	0.4226(9)	0.061(4)
C(3)	-0.4365(13)	0.1689(18)	0.5063(11)	0.081(5)
C(4)	-0.5192(15)	0.1451(18)	0.5238(12)	0.088(6)
C(5)	-0.5996(13)	0.1041(18)	0.4654(11)	0.081(5)
C(6)	-0.5969(10)	0.0924(14)	0.3831(9)	0.053(4)
C(7)	-0.6503(9)	0.1439(12)	0.1432(8)	0.043(3)
C(8)	-0.6478(12)	0.1420(15)	0.0630(10)	0.064(4)
C(9)	-0.7357(14)	0.1701(18)	-0.0044(11)	0.082(6)
C(10)	-0.8177(15)	0.1940(19)	0.0125(12)	0.090(6)
C(11)	-0.8197(13)	0.1996(18)	0.0924(11)	0.081(5)

Table 41 continued,

C(12)	-0.7349(11)	0.1693(15)	0.1580(9)	0.062(4)
C(13)	-0.4016(10)	0.0594(13)	0.1976(8)	0.050(4)
C(14)	-0.4138(12)	-0.0450(15)	0.1548(10)	0.065(5)
C(15)	-0.4083(12)	-0.1362(16)	0.2121(10)	0.066(5)
C(16)	-0.5023(9)	-0.1443(12)	0.2322(7)	0.033(3)
C(17)	0.0960(10)	-0.0574(13)	0.8628(9)	0.052(4)
C(18)	0.0499(12)	-0.0701(16)	0.9200(10)	0.069(5)
C(19)	0.1066(16)	-0.0971(21)	1.0038(13)	0.102(7)
C(20)	0.2027(16)	-0.1011(20)	1.0255(13)	0.100(7)
C(21)	0.2510(16)	-0.0952(21)	0.9701(13)	0.101(7)
C(22)	0.1970(13)	-0.0712(17)	0.8850(11)	0.075(5)
C(23)	0.0826(9)	-0.0326(12)	0.6471(7)	0.041(3)
C(24)	0.0503(12)	-0.1054(16)	0.5857(10)	0.070(5)
C(25)	0.0989(14)	-0.1156(18)	0.5256(11)	0.083(6)
C(26)	0.1757(13)	-0.0549(16)	0.5309(10)	0.071(5)
C(27)	0.2051(14)	0.0235(18)	0.5883(11)	0.082(5)
C(28)	0.1583(12)	0.0336(16)	0.6488(10)	0.068(5)
C(29)	-0.1383(10)	0.0228(13)	0.7068(8)	0.050(4)
C(30)	-0.1606(11)	0.1350(14)	0.6837(9)	0.057(4)
C(31)	-0.1171(10)	0.2107(14)	0.7523(9)	0.055(4)
C(32)	-0.0068(9)	0.2211(12)	0.7670(7)	0.035(3)

Table 42. Bond Lengths (Å) for (41)

Sn(1)-C(1)	2.124(14)	Sn(1)-C(7)	2.118(12)
Sn(1)-C(13)	2.148(17)	Sn(1)-N(4)	2.339(15)
C(1)-C(2)	1.371(19)	C(1)-C(6)	1.372(22)
C(2)-C(3)	1.45(3)	C(3)-C(4)	1.37(3)
C(4)-C(5)	1.37(3)	C(5)-C(6)	1.43(3)
C(7)-C(8)	1.389(23)	C(7)-C(12)	1.378(24)
C(8)-C(9)	1.454(22)	C(9)-C(10)	1.36(3)
C(10)-C(11)	1.38(3)	C(11)-C(12)	1.421(22)
C(13)-C(14)	1.55(3)	C(14)-C(15)	1.54(3)
C(15)-C(16)	1.521(24)	C(16)-N(1)	1.313(21)
C(16)-N(2)	2.160(20)	C(16)-N(3)	2.163(19)
C(16)-N(4)	1.319(21)	N(1)-N(2)	1.409(18)
N(1)-N(3)	2.166(20)	N(1)-N(4)	2.154(22)
N(3)-N(4)	1.375(19)	Sn(2)-C(17)	2.124(13)
Sn(2)-C(23)	2.142(15)	Sn(2)-C(29)	2.156(15)
Sn(2)-N(5)	2.343(15)	C(17)-C(18)	1.37(3)
C(17)-C(22)	1.401(24)	C(18)-C(19)	1.44(3)
C(19)-C(20)	1.32(3)	C(20)-C(21)	1.36(4)
C(21)-C(22)	1.44(3)	C(23)-C(24)	1.390(24)
C(23)-C(28)	1.401(24)	C(24)-C(25)	1.44(3)
C(25)-C(26)	1.35(3)	C(26)-C(27)	1.40(3)
C(27)-C(28)	1.43(3)	C(29)-C(30)	1.547(25)
C(30)-C(31)	1.514(23)	C(31)-C(32)	1.544(20)
C(32)-N(5)	1.259(20)	C(32)-N(6)	2.129(18)
C(32)-N(7)	2.140(18)	C(32)-N(8)	1.351(19)

Table 42 continued,

N(5)-N(6)	1.362(17)	N(5)-N(7)	2.105(22)
N(5)-N(8)	2.154(20)	N(6)-N(7)	1.243(24)
N(6)-N(8)	2.182(19)	N(7)-N(8)	1.406(17)

Intermolecular distances

Sn(1)-N(1')	2.37(1)	Sn(2)-N(8')	2.36(2)

Table 43. Bond Angles for (41)

C(7)-Sn(1)-C(1)	118.2(5)	C(13)-Sn(1)-C(1)	126.7(5)
C(13)-Sn(1)-C(7)	115.0(5)	N(4)-Sn(1)-C(1)	91.9(5)
N(4)-Sn(1)-C(7)	94.5(5)	N(4)-Sn(1)-C(13)	86.7(6)
C(2)-C(1)-Sn(1)	121(1)	C(6)-C(1)-Sn(1)	119.5(9)
C(6)-C(1)-C(2)	120(1)	C(3)-C(2)-C(1)	119(2)
C(4)-C(3)-C(2)	119(2)	C(5)-C(4)-C(3)	122(2)
C(6)-C(5)-C(4)	118(2)	C(5)-C(6)-C(1)	122(1)
C(8)-C(7)-Sn(1)	117(1)	C(12)-C(7)-Sn(1)	123(1)
C(12)-C(7)-C(8)	120(1)	C(9)-C(8)-C(7)	118(2)
C(10)-C(9)-C(8)	119(2)	C(11)-C(10)-C(9)	122(2)
C(12)-C(11)-C(10)	118(2)	C(11)-C(12)-C(7)	121(2)
C(14)-C(13)-Sn(1)	115(1)	C(15)-C(14)-C(13)	115(1)
C(16)-C(15)-C(14)	110(1)	N(1)-C(16)-C(15)	125(1)
N(2)-C(16)-C(15)	164(1)	N(2)-C(16)-N(1)	39.1(8)
N(3)-C(16)-C(15)	163(1)	N(3)-C(16)-N(1)	72.5(9)
N(3)-C(16)-N(2)	33.4(7)	N(4)-C(16)-C(15)	125(1)
N(4)-C(16)-N(1)	110(1)	N(4)-C(16)-N(2)	71(1)
N(4)-C(16)-N(3)	37.5(8)	N(2)-N(1)-C(16)	105(1)
N(3)-N(1)-C(16)	72(1)	N(3)-N(1)-N(2)	32.8(9)
N(4)-N(1)-C(16)	35.1(8)	N(4)-N(1)-N(2)	70(1)
N(4)-N(1)-N(3)	37.1(6)	N(1)-N(2)-C(16)	35.9(8)
N(3)-N(2)-C(16)	73(1)	N(3)-N(2)-N(1)	109(1)
N(4)-N(2)-C(16)	35.8(6)	N(4)-N(2)-N(1)	71.7(9)
N(4)-N(2)-N(3)	37.7(8)	N(1)-N(3)-C(16)	35.3(6)
N(2)-N(3)-C(16)	73(1)	N(2)-N(3)-N(1)	37.8(8)

Table 43 continued,

N(4)-N(3)-C(16)	35.7(8)	N(4)-N(3)-N(1)	71.0(9)
N(4)-N(3)-N(2)	109(1)	C(16)-N(4)-Sn(1)	127(1)
N(1)-N(4)-Sn(1)	159.2(6)	N(1)-N(4)-C(16)	34.9(8)
N(2)-N(4)-Sn(1)	157.0(8)	N(2)-N(4)-C(16)	73(1)
N(2)-N(4)-N(1)	38.4(6)	N(3)-N(4)-Sn(1)	125(1)
N(3)-N(4)-C(16)	107(1)	N(3)-N(4)-N(1)	72(1)
N(3)-N(4)-N(4)	33.5(9)	C(23)-Sn(2)-C(17)	117.7(6)
C(29)-Sn(2)-C(17)	120.2(6)	C(29)-Sn(2)-C(23)	121.9(5)
N(5)-Sn(2)-C(17)	90.4(5)	N(5)-Sn(2)-C(23)	95.1(5)
N(5)-Sn(2)-C(29)	87.5(5)	C(18)-C(17)-Sn(2)	120(1)
C(22)-C(17)-Sn(2)	120(1)	C(22)-C(17)-C(18)	121(1)
C(19)-C(18)-C(17)	119(2)	C(20)-C(19)-C(18)	119(2)
C(21)-C(20)-C(19)	123(2)	C(22)-C(21)-C(20)	119(2)
C(21)-C(22)-C(17)	118(2)	C(24)-C(23)-Sn(2)	119(1)
C(28)-C(23)-Sn(2)	120(1)	C(28)-C(23)-C(24)	121(2)
C(25)-C(24)-C(23)	119(2)	C(26)-C(25)-C(24)	119(2)
C(27)-C(26)-C(25)	123(2)	C(28)-C(27)-C(26)	118(2)
C(27)-C(28)-C(23)	119(2)	C(30)-C(29)-Sn(2)	115(1)
C(31)-C(30)-C(29)	116(1)	C(32)-C(31)-C(30)	109(1)
N(5)-C(32)-C(31)	127(1)	N(6)-C(32)-C(31)	164(1)
N(6)-C(32)-N(5)	37.3(8)	N(7)-C(32)-C(31)	162(1)
N(7)-C(32)-N(5)	71(1)	N(7)-C(32)-N(6)	33.9(7)
N(8)-C(32)-C(31)	122(1)	N(8)-C(32)-N(5)	111(1)
N(8)-C(32)-N(6)	73.9(9)	N(8)-C(32)-N(7)	40.0(8)

Table 43 continued,

C(32)-N(5)-Sn(2)	126(1)	N(6)-N(5)-Sn(2)	125(1)
N(6)-N(5)-C(32)	109(1)	N(7)-N(5)-Sn(2)	159.2(7)
N(7)-N(5)-C(32)	74(1)	N(7)-N(5)-N(6)	34.3(8)
N(8)-N(5)-Sn(2)	162.2(6)	N(8)-N(5)-C(32)	35.8(8)
N(8)-N(5)-N(6)	73(1)	N(8)-N(5)-N(7)	38.5(6)
N(5)-N(6)-C(32)	34.1(8)	N(7)-N(6)-C(32)	73.6(9)
N(7)-N(6)-N(5)	108(1)	N(8)-N(6)-C(32)	36.5(6)
N(8)-N(6)-N(5)	70.6(9)	N(8)-N(6)-N(7)	37.1(7)
N(5)-N(7)-C(32)	34.5(6)	N(6)-N(7)-C(32)	73(1)
N(6)-N(7)-N(5)	38.1(8)	N(8)-N(7)-C(32)	38.2(7)
N(8)-N(7)-N(5)	72.6(8)	N(8)-N(7)-N(6)	111(1)
N(5)-N(8)-C(32)	33.0(7)	N(6)-N(8)-C(32)	69.6(9)
N(6)-N(8)-N(5)	36.6(5)	N(7)-N(8)-C(32)	102(1)
N(7)-N(8)-N(5)	68.8(9)	N(7)-N(8)-N(6)	32.2(9)

Intermolecular Bond Angles

N(4)-Sn(1)-N(1')	173.43	N(8')-Sn(2)-N(5)	173.32

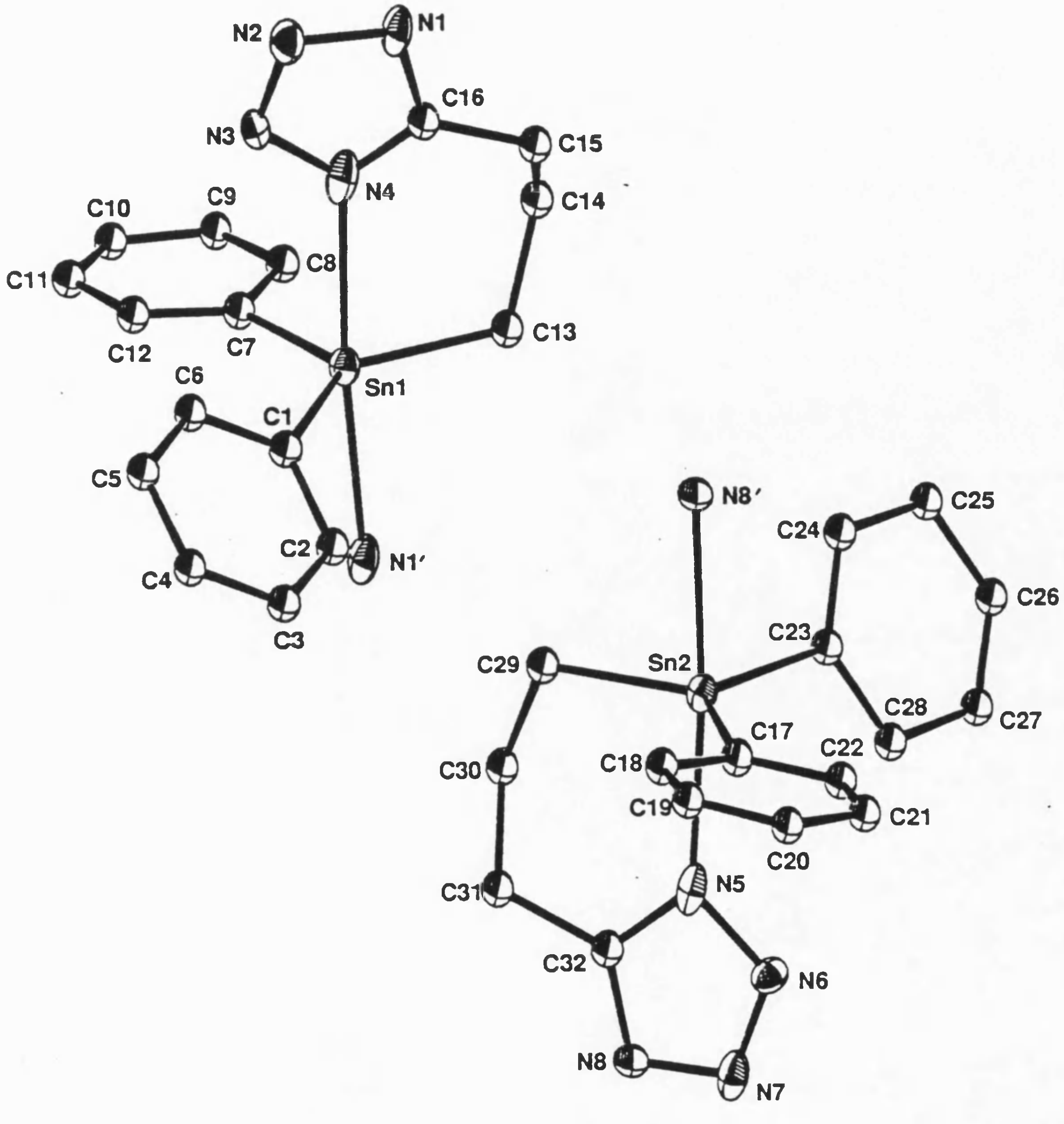

N2
N1
C16
N3
C15
N4
C14
C10
C9
C8
C11
C13
C12
C7
Sn1
C6
C1
C5
N8′
C25
C24
C2
N1′
C4
C26
C3
C23
C29
Sn2
C28
C27
C17
C22
C18
C30
C19
C21
C20
N5
C31
C32
N6
N8
N7

Figure 14: The Crystal Structure of

2,3,4,5-tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene.

Hydrogen atoms omitted for clarity.

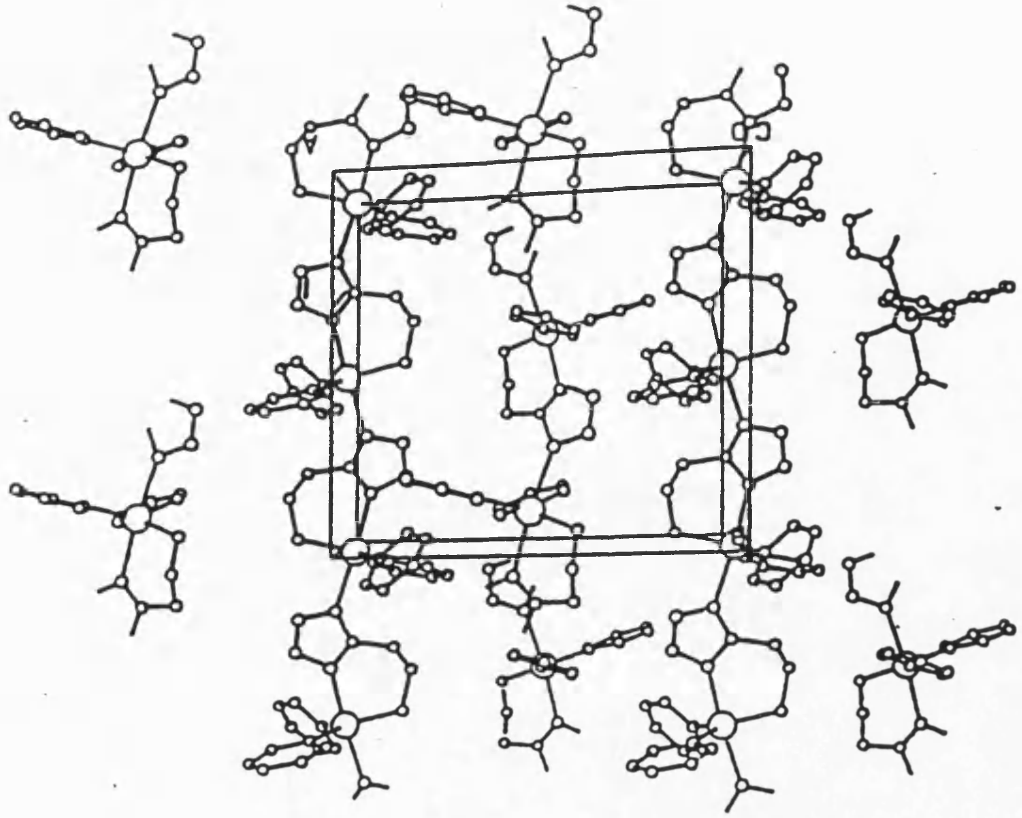
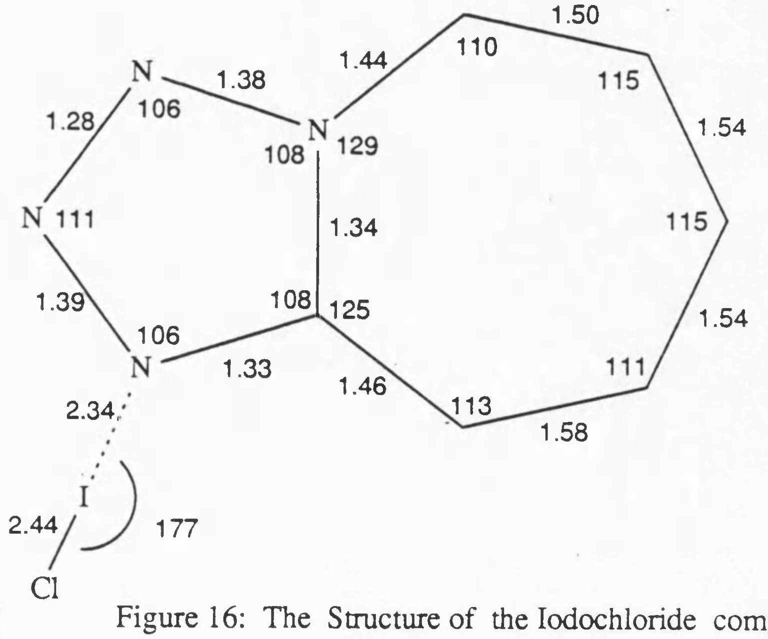


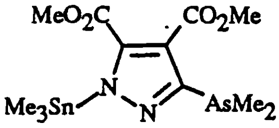
Figure 15: The Molecular Structure of 2,3,4,5-tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene.



N
N
N
N
I
Cl
1.50
1.44
110
115
1.38
106
1.28
108
129
1.54
N 111
1.34
115
1.39
108
125
1.54
106
1.33
1.46
111
113
1.58
2.34
2.44
177

Figure 16: The Structure of the Iodochloride complex of Pentamethylene tetrazole.

Table 44. Selected Sn-N bond distances for the compounds related to 2,3,4,5-tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene

Compound	CN[a]	d(Sn-N)[b,c]	d(Sn---N)[b,d]	Reference
(41)	5	2.339	2.37	[h]
$Me_3SnNSN{=}S{=}NSO_2$	5	2.218	[e]	238
Me_3SnN_3	5	2.390	2.390	239
	5	2.180	[f]	240
Me_3SnNCS	5	2.150	[g]	241
$Me_3SnN(CN)_2$	5	2.335	2.289	242
Me_3SnNCN	5	2.470	2.470	243
$Cy_3SnN{-}CH{=}N{-}CH{=}N$	5	2.29	2.350	244

[a] Coordination number

[b] Distances in angstroms (Å)

[c] Intramolecular Sn-N bond

[d] Intermolecular Sn-N bond

[e] d(Sn---O)=2.822 Å

[f] d(Sn---O)=3.32 Å

[g] d(Sn---S)=3.13 Å

[h] This work

an ideal planar 5-membered ring. It is interesting to note that the formal C=N double bonds [C(16)-N(1)]=1.313 Å and [C(32)-N(8)]=1.351 Å are significantly longer than a typical C=N bond length found in a discrete tetrazole compound, e.g. 5-bromotetrazole, in which the C=N bond is reported to be 1.290 Å [233]. The formal N=N double bonds [N(2)-N(3)]= 1.243 Å and [N(7)-N(6)]=1.243 Å are surprisingly shorter than the N=N bond length reported for 5-bromotetrazole, (1.283 Å). It might have been expected that due to the neighbouring nitrogens, N(1) and N(8), coordinating to the adjacent tin atoms, the extent of double bond character in N(2)-N(3) and N(7)-N(6) would be reduced, but this appears not to be the case.

The sum of the internal angles between the equatorial carbon atoms in the first molecule, C(7), C(1), C(13) and Sn(1) amounts to 359.9°, and similarly the sum of the angles between C(17), C(23), C(29) and Sn(2) in the second molecule amounts to 359.8°, both molecules displaying almost ideal equatorial planarity. Also, N(4) and N(5) are both almost directly above Sn(1) and Sn(2) respectively, thus giving rise to bond angles between N(4), Sn(1) and the equatorial carbons atoms of the first molecule,(and similarly between N(5), Sn(2) and the equatorial carbon atoms of the second molecule), of almost 90°. The <N(4)-Sn-N(1') and <N(5)-Sn-N(8') were measured to be 173.4° and 173.3° respectively, so the molecules are only moderately distorted from ideality (180°).

X-ray structures have been reported for a wide range of simple tetrazoles and these show the ring to be a planar resonance hybrid. The structure of the molecular complex pentamethylenetetrazole iodine monochloride has been reported [234] and is displayed in figure 16.

The structure of this compound is quite similar to that of compound **(41)** discussed here. A brief examination of figure 16 reveals that the ICl group is bonded to the tetrazole ring preferentially at N(1), (using consistent nomenclature). This preferential bonding site also occurs in the dichlorobis(1-methyltetrazole)zinc(II) complex [235]. However; in the reported crystal structure of nitratobis(pentamethylenetetrazole) silver(I), i.e. $[Ag(PMT)NO_3]_2$ [236], both N(1) and N(2) act as donor sites, the different bond lengths are given in figure 17.

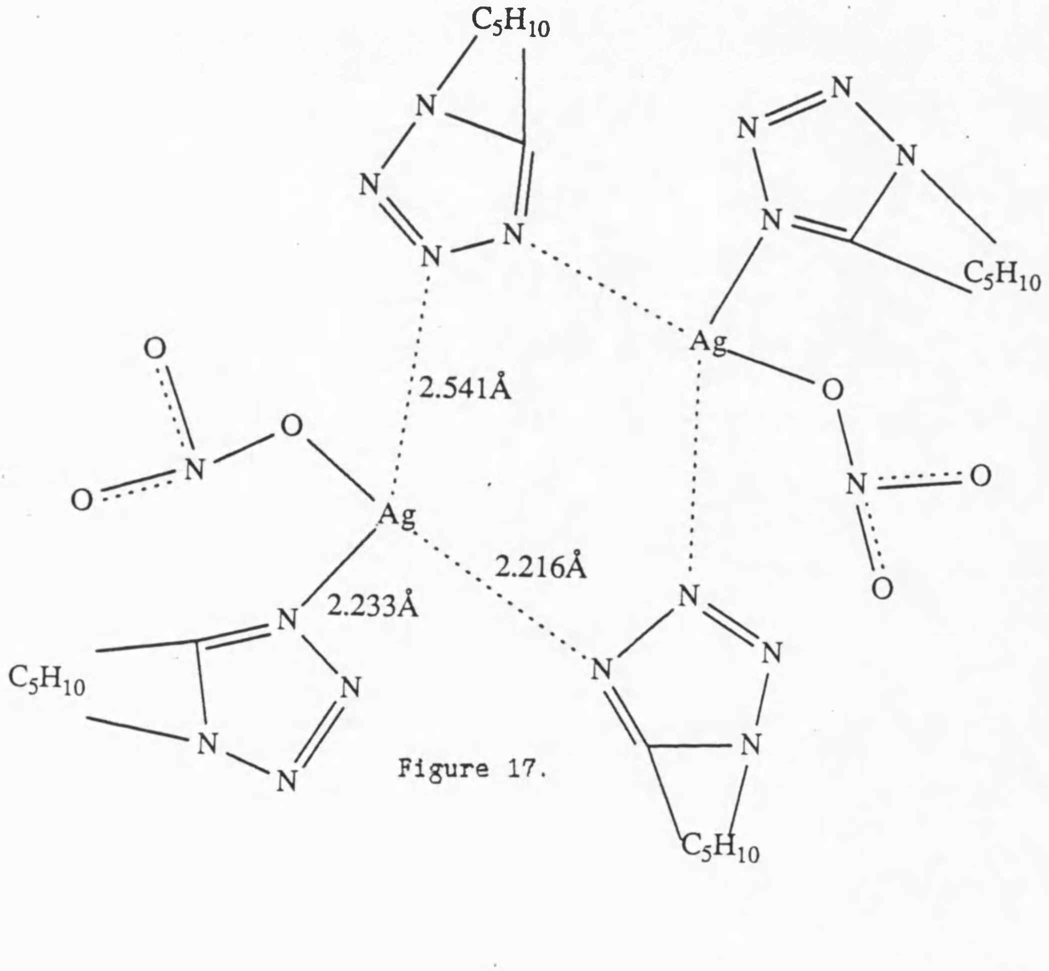

C5H10
N
N
N
N
N
N
N
N
C5H10
Ag
2.541Å
O
O
N
O
Ag
2.216Å
O
N
O
O
2.233Å
N
N
N
N
C5H10
N
N
N
N
C5H10

Figure 17.

It has been shown in this Chapter that organotin tetrazole compounds are very polymeric species. This would be expected for relatively Lewis acidic organotin centers e.g. Ph_3Sn- and Ph_2SnCl-, but it is apparent that even low Lewis acidic centers like Bu_3Sn- are 5-coordinate in the polymeric tetrazole compounds. The tetrazole ring is generally a weak base, and protonation occurs preferentially at N(4). A basic pK_a value of -3.0 has been quoted for tetrazole in aqueous H_2SO_4. However compounds like PMT have been observed to be reasonably strong monoprotic bases in formic acid [237].

The thermal cyclisation reactions are very interesting, both mechanistically and synthetically. The mechanisms of these reactions, to produce **(40)** and **(41)** will be dealt with more fully in the next Chapter. Synthetically, these reactions open up an exciting new field of organotin thermal cyclisation chemistry. Preliminary studies suggest, for example, that $Ph_3SnCH_2CH_2CH_2OH$ loses Ph-H on heating and possibly yields a cyclic entity $Ph_2\overline{SnCH_2CH_2CH_2O}$. In 1957 Van Der Kerk *et al* [211] reported the 'anomalous' reaction of Ph_3SnH with CH_2=CH-CO_2H, instead of the expected 2-(triphenyltin) propionic acid, the reaction at 70°C yields Ph-H and what they tentatively assign to be $Ph_2Sn^+CH_2CH_2CO_2^-$. Their suggestion that the organotin forms an inner salt may be somewhat incorrect, since it is possible that the tin is part of a ring, e.g. $Ph_2\overline{SnCH_2CH_2C(O)O}$. They also found that $Pr_3{}^nSnH$ reacted with CH_2=CH-CO_2H in a different way, yielding H_2 and $Pr_3{}^nSnO_2CCH$=CH_2. The fact that tripropyltin hydride does not react in a similar way, suggests that it is important for the tin to have a good leaving group to allow the cyclisation reaction to proceed.

Presumably, if a better leaving group were present in the hydride, e.g. $Pr_2{}^nSnPhH$, the reaction would procede in a similar manner to the triphenyltin hydride reaction.

Another area of possible interest are cyclisation reactions of species such as $Ph_3SnCH_2CH_2CH_2C\equiv CCH_3$ or $Ph_3SnCH_2CH=CHCH_3$ with Bu_3SnN_3. Preliminary studies with $Ph_3SnCH_2C\ CH$ and Bu_3SnN_3 were complicated by the thermal rearrangement of the organotin alkyne to the organotin allene, ($Ph_3SnCH=C=CH_2$), however, if the alkyne functionality could be placed further down the alkyl chain, away from the influence of the tin, the thermal rearrangement would be less likely.

The following Chapter looks at the simple model compounds (33-37) to help answer some of the questions posed by the synthesis of the bicyclic compounds described in this Chapter.

5.5 Experimental

Trimethyl- and tributyltin azides were prepared according to the methods of Thayer and West [245] and Reichle [245] respectively. The nitriles were commercial in origin (Aldrich) and were purified by distillation or recrystallisation prior to use. (2-Cyanoethyl)- and (3-cyanopropyl)triphenyltin were prepared according to Van der Kerk *et al.* [211]. Sodium diethyldithiocarbamate, iodine and bromine were commercial in origin (BDH) and were used as supplied.

Synthesis of 2-(Trimethylstannyl)-5-methyltetrazole (33)

A mixture of trimethyltin azide (0.51 g, 2.5 mmol) and freshly distilled acetonitrile (5 mmol) were heated together in a small sealed tube at 120°C for 2 hours. A solid material was formed after 5 minutes. The sealed tube was allowed to cool, opened and excess acetonitrile was removed under reduced pressure. The crude solid material was recrystallised from ethanol to yield the product as white prisms (0.58 g, 94%, mp 213°C, lit. [230] 215-216°C)

Synthesis of 2-(Tributylstannyl)-5-methyltetrazole (34)

Tributyltin azide (2.00 g, 6 mmol) and acetonitrile (12 mmol) were treated in an analogous fashion at 100°C for 7 hours. The crude oily product was vacuum distilled (210°C/0.3 mmHg) to give a white solid (1.73 g, 76%, mp 44°C, lit. [230] 43-47°C)

Synthesis of 2-(Tributylstannyl)-5-phenyltetrazole (35)

Tributyltin azide (1.16 g, 3.5 mmol) and benzonitrile

(0.50 g, 4.8 mmol) were treated in analogous fashion to **(33)** at 120°C for 4 hours. The crude oily solid was recrystallised from acetonitrile to give white needles (0.92 g, 60 %, mp. 72°C, lit. [230] 66-7°C)

*Synthesis of 2-(Tributylstannyl)-5-prop-1-enetetrazole **(36)***

Tributyltin azide (2.00 g, 6 mmol) and 1-cyanoprop-1-ene (0.90 g, 13 mmol) were treated in an analogous fashion to **(33)** at 100°C for 4 hours. The crude product was distilled under reduced pressure (224°C/0.3 mmHg) to yield a clear oil (1.10 g, 45 %)

*Synthesis of 2-(Tributylstannyl)-5-(2'-pyridyl-6'-Me)tetrazole **(37)***

Tributyltin azide (3.33 g, 10 mmol) and 2-cyano-6-methylpyridine (1.17 g, 10 mmol) were treated in an analogous fashion to **(33)** at 120 °C for 2 hours. The crude product was recrystallised from acetonitrile to yield white needles (3.21 g, 71 %, mp. 217°C)

Synthesis of

*2-(Tributylstannyl)-5-[2'-(Triphenylstannyl)ethyl]tetrazole **(38)***

Tributyltin azide (1.80 g, 5.4 mmol) and (2-cyanoethyl)triphenyltin (2.20 g, 5.4 mmol) were placed in a small round-bottomed flask and stirred at 130°C for 3 hours. The extent of the reaction was followed by monitoring the disappearance of the IR bands attributable to CN and N_3 at 2250 and 2060cm^{-1} respectively. The oil was dissolved in cold (0°C) 60-80° petroleum ether and filtered to remove excess (2-cyanoethyl)triphenyltin. The solvent was removed from the filtrate under reduced pressure to yield the product as a clear, viscous oil

(3.89 g, 97 %). The oil could not be distilled, recrystallised or chromatographied (Silica) without decomposition.

Synthesis of

2-(Tributylstannyl)-5-[3'-(Triphenylstannyl)propyl]tetrazole ***(39)***

Tributyltin azide (0.79 g, 2.4 mmol) and (3-cyanopropyl)triphenyltin (1.00 g, 2.4 mmol) were heated together with stirring at 140°C for 3 hours. The oil was washed with cold (0°C) 60-80° petroleum ether and filtered. The solvent was removed under reduced pressure to yield the product (1.78 g, 99%). The oil could not be purified by standard techniques.

Synthesis of

2,3,4,5-tetraza-6-diphenylstannyl-[3,3]-bicycloocta-1,3-diene ***(40)***

Method A.

(38), (3.00 g, 4.1 mmol) was placed in a small round-bottomed flask and stirred at 130°C for 21 hours. Following this period the contents of the flask had solidified. The solid material was washed with diethyl ether (4 x 50 ml) and dried in air. The diethyl ether washings were combined, reduced in volume to dryness and vacuum distilled (115°C/0.3 mmHg) to yield Bu_3SnPh (1.47 g, 97%). The solid material was dissolved in boiling $MeOH/CS_2$ (10:1) (200ml), and allowed to cool very slowly to yield the product (0.84 g, 83%, mp. 290-5°C) as white needles and powder.

Method B.

(2-Cyanoethyl)triphenyltin (2.00 g, 4.95 mmol) was dissolved in $CHCl_3$ (50 ml) and stirred at room temperature. Bromine (0.79 g, 4.95 mmol) was dissolved in $CHCl_3$ (50 ml) added to the solution in the stirred flask over a period of 30 minutes. Following this period, the solvent was removed by reduced vacuum, and the white solid residue was recrystallised from 80-100° petroleum ether to yield (2-Cyanoethyl) diphenyltin bromide as white needles (1.76g, 87%, mp. 157°C).

(2-Cyanoethyl)diphenyltin bromide (1.5g, 3.68 mmol) was dissolved in ethyl acetate (50 ml) and placed in a 500 ml separating funnel. Sodium azide (0.24 g, 3.68 mmol) was dissolved in distilled water (50 ml) and added to the solution in the separating funnel. The separating funnel was shaken for 20 minutes and then the water layer was removed. The organic layer was dried over $MgSO_4$, filtered and finally reduced in volume to a white powder. Recrystallisation of the (2-Cyanoethyl) diphenyltin azide was attempted from 60-80° petroleum ether, however **(40)** (0.92g, 67%), was precipitated from solution during a 30 minute reflux.

Synthesis of
2,3,4,5-tetraza-6-diphenylstannyl-[3,4]-bicyclonona-1,3-diene ***(41)***

Method A.

(39), (1.65 g, 2.2 mmol) was placed in a small round-bottomed flask and stirred at 140°C for 24 hours. Following this period the oil had solidified. The solid material was washed with diethyl ether (4 x 50 ml) and dried in air. The diethyl ether washings were combined, reduced in volume and vacuum distilled (116°/0.3 mmHg)to yield Bu_3SnPh

(0.69 g, 85%). The dried solid was slowly dissolved in boiling $MeOH/CS_2$ (10:1) (200ml) and allowed to cool very slowly to yield the product as white needles/prisms (0.64 g, 76%, mp. 310°C {dec})

Method B.

(3-Cyanopropyl)diphenyltin bromide (0.48 g, 1.1 mmol) and tributyltin azide (0.37 g, 1.1 mmol) were heated together in a round-bottomed flask at 140°C for 5 minutes. After this period the contents of the flask had totally solidified. The solid, **(41)**, (0.42 g, 96%, mp. 310°C) was washed with diethyl ether (4 x 50 ml), collected by filtration and dried in air. The diethyl ether washings were combined, reduced in volume and the oily residue vacuum distilled (100°C/0.3 mmHg) to yield Bu_3SnBr, (0.39 g, 96%)

Synthesis of (2-[1'H-5'-tetrazolyl]ethyl)diphenyltin chloride ***(42)***

Method A.

Powdered **(40)**, (1.00 g, 2.7 mmol) was suspended in boiling MeOH (30 ml). Aqueous HCl (1.4 ml, 2.8 mmol) was added dropwise over 5 minutes and, during the addition, the suspension became clear. Stirring was continued for a further 10 minutes and the solution was allowed to cool slowly to 0°C. The product was crystallised as white needles, collected by filtration and dried in air (0,98 g, 89%, mp. 157°C)

Method B.

(38), (3.64 g, 4.9 mmol) and aqueous HCl (3.3 ml, 4.9 mmol) were dissolved in MeOH (50 ml) and stirred at room temperature for 1 hour. The solution was reduced in volume to dryness and the crude oily material remaining was washed with diethyl ether (10 ml), whereupon a white crystalline material was precipitated. The solid material was collected by filtration and dried in air. The filtrate was reduced in volume and the residue vacuum distilled (115°C/0.3 mmHg) to yield Bu_3SnPh (0.92 g, 51%, 115°C/0.3 mmHg). The solid material, **(42)**, was recrystallised from methanol at 0°C to yield the product as white needles, (1.71 g, 85%, mp. 157°C)

Method C.

A similar reaction to method B was attempted with the following exceptions: the reactant, **(38)**, was dissolved in the non-protic solvent, dry diethyl ether (50 ml), stirred at -30°C and the HCl was added as a saturated diethyl ether solution. Both products were formed in similar yields.

Synthesis of

(2-[1'H-5'-tetrazolyl]ethyl)diphenyltin diethyldithiocarbamate ***(43)***

(42), (0.32 g, 0.79 mmol) was dissolved in a $CHCl_3$/THF mixture (1:1) (50 ml) and stirred at room temperature. Sodium diethyldithiocarbamate (0.18 g, 0.79 mmol) was added to the flask and the solution was refluxed for 2 hours. The solution was allowed to cool, reduced in volume to dryness, washed with hot ethyl acetate/ acetone (1:1) (30 ml) and the insoluble NaCl was filtered off. The filtrate was allowed to cool to 0°C and the product crystallised as white florets (0.12 g, 29%, mp. 163°C)

Synthesis of 2,3,4,5-tetraza-6-monophenylmonobromostannyl-[3,3]-bicycloocta-1,3-diene ***(44)***

(40), (1.0 g, 2.7 mmol) was suspended in $CHCl_3$ (50 ml) and stirred at room temperature. Bromine (0.43 g, 2.7 mmol) was dissolved in $CHCl_3$ (20 ml) and added dropwise to the flask. The bromine was very slowly decolourised to yield a white suspension. The solvent was removed under reduced pressure to yield a tacky oil that possessed a very strong odour of PhBr. The PhBr was removed under a high vacuum with mild warming to yield a white powder, (0.92 g, 92%, mp. 125°C(dec)). The powder was insoluble in all common organic solvents.

Synthesis of Diphenyldibutyltin ***(45)***

Magnesium turnings, (3.64 g, 150 mmol) were placed in a clean, dry flask and just covered with dry diethyl ether. Several drops of neat bromobenzene and one small iodine crystal were added to the flask to initiate the reaction. With the appearance of a milky suspension, bromobenzene (23.53 g, 150 mmol) dissolved in diethyl ether (200 ml) was added dropwise over the period of 1 hour. Following this period, the Grignard reagent was filtered through a glass wool plug into a clean addition funnel attached to a 1 litre flask. The flask contained dibutyltin dichloride (21.25 g, 70 mmol) dissolved in diethyl ether (200 ml). The Grignard solution was added dropwise to the flask over the period of 2 hours. Following this period the ether solution was filtered to remove MgClBr, extracted with distilled water (3 x 50 ml), dried over $MgSO_4$, filtered again, reduced in volume to a yellow oil and finally vacuum distilled to give the product as a colourless oil (23.11 g, 85%, bp. 101°C/1.0 mmHg)

Synthesis of Dibutylphenyltin bromide ***(46)***

(45) (23.00 g, 59 mmol) was dissolved in $CHCl_3$ (150 ml) and stirred at room temperature. Bromine (9.43 g, 59 mmol) was dissolved in $CHCl_3$ (100 ml) and added to the solution of **(45)** dropwise over 1 hour. Following the addition the solvent was removed and the residual oil was vacuum distilled to yield PhBr, (8.71 g, 94%) and the product, (17.22 g, 74%, bp. 182°C/0.3 mmHg) as colourless oils.

Synthesis of Dibutylphenyltin hydride **(47)**

Lithium aluminium hydride, (1.74 g, 44 mmol) was placed in a clean, dry 500 ml flask with a nitrogen atmosphere. Dry diethyl ether (80 ml) was added and the resulting slurry stirred at room temperature. **(46)** (17.22 g, 44 mol) was dissolved in diethyl ether (100 ml) and added dropwise to the slurry. Following the addition the solution was refluxed for 2.5 hours. After this period, quinol, (0.25 g) and distilled water (10 ml) were added to the flask to decompose the remaining lithium aluminium hydride. The ether suspension/slurry was quickly filtered *via* a Buchner funnel. The filtrate was reduced in volume to dryness and the residual yellow oil vacuum distilled at 175°C/1.0 mmHg to yield the product (9.21 g, 67%) as a colourless oil.

Synthesis of (2-Cyanoethyl)dibutylmonophenyltin **(48)**

(47) (5.0 g, 16 mmol) and cyanoethene, (1.70 g, 32 mmol) were stirred together under a dry nitrogen atmosphere at 80°C for 7.5 hours. The flask was then cooled to 40°C and stirred for a further 12 hours, after which time the IR band associated with Sn-H at 1850cm^{-1} had disappeared. Following this period excess cyanoethene was removed under reduced pressure to yield the crude product as a yellow oil. This was vacuum distilled at 194°C/0.3 mmHg to yield the product (3.81 g, 65%) as a slightly yellowish oil.

Synthesis of 2-[Tributylstannyl]-5-(2'-[Dibutylmonophenylstannyl)ethyl]tetrazole **(49)**

Tributyltin azide, (3.19 g, 9.6 mmol) and **(48)** (3.50 g, 9.6 mmol) were stirred together at 104 °C for 2 hours. After this period the IR bands attributable to -CN and -N_3 had disappeared. The product, **(49)**, (6.68 g, 99%), a slightly yellowish, viscous oil could not be purified by any of the standard methods.

Synthesis of

2,3,4,5-tetraza-6-dibutylstannyl-[3,3]-bicycloocta-1,3-diene (50)

The crude compound **(49)**, (6.50 g, 9.3 mmol) was heated in a small round-bottomed flask at 170°C for 12 hours. Following this period the flask was allowed to cool. The yellow oil was washed with 60-80° petroleum ether (10 x 10 ml). The washings were combined, reduced in volume and the oily residue was vacuum distilled to yield Bu_3SnPh, (2.20 g, 64%, 110°C/0.3 mmHg). The yellow oily residue left after the washing with the petroleum ether was subjected to a low pressure (<0.1 mmHg) and slight warming for 48 hours. During this treatment the oily residue slowly solidified to give the crude product (2.77 g, 90%, mp. 42-47°C). Several attempts to recrystallise the product failed as did an attempt to distill the product, which resulted in decomposition.

Synthesis of (2-[1'H-5'-tetrazolyl]ethyl)dibutyltin chloride (51)

(50) (0.34 g, 1 mmol) was dissolved in MeOH (20 ml) and stirred at room temperature. Aqueous HCl, (10 ml, 1 mmol) was added dropwise to the solution, whereupon a white solid was precipitated. The crude product was filtered off and air dried. The white solid was recrystallised from boiling methanol to yield the product, (0.15 g, 41%, mp. 57°C) as a white powder.

Synthesis of dimethyldiphenyltin **(52)**

Magnesium turnings, (7.29g, 300 mmol) were placed in a clean, dry flask and just covered with dry diethyl ether. Several drops of bromobenzene were added and the solution allowed to stand until a milky suspension was observed. Bromobenzene, (47.18 g, 300 mmol), dissolved in diethyl ether (300 ml) was then added dropwise to the flask over the period of 1 hour *via* a dropping funnel. Following this period the Grignard reagent was filtered through a glass wool plug into a clean addition funnel attached to a 1 litre flask. The flask contained dimethyltin dichloride (30g, 136 mmol), dissolved in dry diethyl ether (200 ml). The Grignard reagent was added dropwise to the flask over the period of 2 hours. Following this period the ether solution was filtered to remove MgClBr, extracted with distilled water (3 x 50 ml), dried over $MgSO_4$, filtered again, the solvent removed under reduced pressure and the crude yellow oil finally distilled under reduced pressure (140°/0.5 mmHg) to yield the product, **(52)** (23.03g, 75%) as a colourless oil.

Synthesis of dimethylphenyltin bromide **(53)**

(52) (22.91 g, 75.6 mmol) was dissolved in CCl_4 (100 ml) and stirred at 0°C. Bromine (12.09g, 75.6 mmol) was dissolved in CCl_4 and added to the solution of **(52)** dropwise over the period of 2 hours. Following the addition the solvent was removed and the residual oil was vacuum distilled (175°/0.5 mmHg) to yield the product **(53)** (18.22g, 78%) as a slightly yellowish oil.

Synthesis of dimethylphenyltin hydride **(54)**

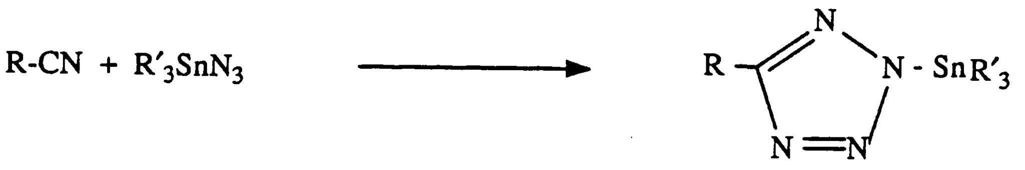
Lithium aluminium hydride (3.02 g, 75.6 mmol) was placed in a clean dry flask with a dry nitrogen atmosphere. Dry diethyl ether (100 ml) was added and the resulting slurry was stirred at room temperature. **(53)** (17.33g, 56.7 mmol) was dissolved in dry diethyl ether (100 ml) and added dropwise to the slurry over 1 hour. Following the addition the resulting suspension was refluxed for 2.5 hours. After this period, quinol (0.25 g) and distilled water (10 ml) were added to decompose the remaining $LiAlH_4$. The suspension was quickly filtered *via* a Buchner funnel and the ether filtrate was dried over $MgSO_4$. The filtrate was filtered once more and then reduced in volume to yield the crude oily product. The oil was distilled under reduced pressure (122°/0.5 mmHg) to yield the product **(54)** (7.48g, 43%) as a colourless oil.

CHAPTER 6

AN INVESTIGATION INTO THE THERMAL DYNAMICS OF *N*-TRIALKYLTIN-5-SUBSTITUTED TETRAZOLE COMPOUNDS

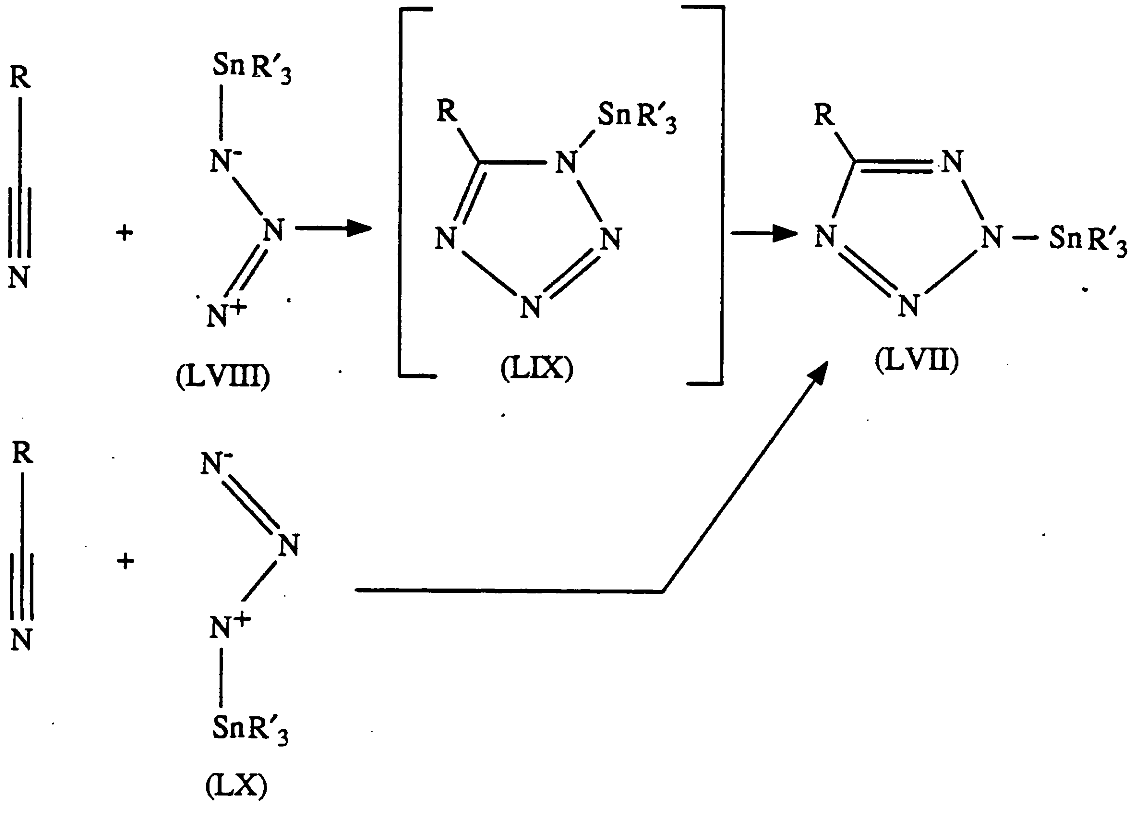
6.1 Introduction

In Chapter 5 the synthesis and structures of several *C*-organostannyl tetrazole compounds were discussed. The reactions of triorganotin azides with nitriles have been described elsewhere [230] and a full explanation need not be entered into here, suffice to say that trialkyltin azides and various nitriles cyclise in 1,3-dipolar addition reactions to yield *N*-trialkyltin-5-substituted tetrazoles and evidence from viscosity and nmr experiments have suggested that the tin is situated on the N(2) position of the tetrazole (equation 26).



(26)

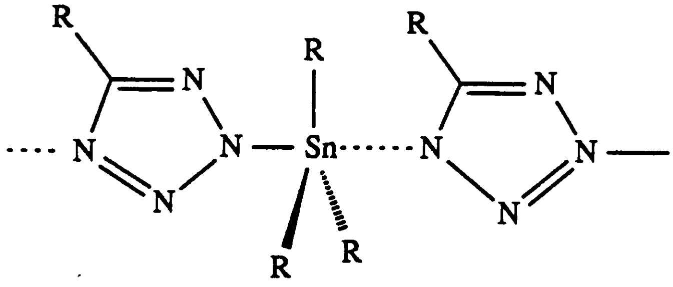
Two routes are possible for the formation of the tetrazole (LVII), (Scheme 17). When the trialkyltin azide has the 1,3-dipolar resonance structure shown in (LVIII), cycloaddition should give the 1-trialkyltin isomer (LIX). Migration of the trialkyltin group from 1-nitrogen (LIX) to 2-nitrogen (LVII) might be possible; Birkofer and Wegner [247] reported a similar migration of the trimethylsilyl group in the reaction of trimethylsilyl azide with acetylene compounds to give 2-(trimethylsilyl)-1,2,3-triazoles. When the trialkyltin azide has the 1,3-dipolar resonance shown in (LX), cycloaddition with the nitrile gives the N(2) isomer, (LVII), directly.



Scheme 17.

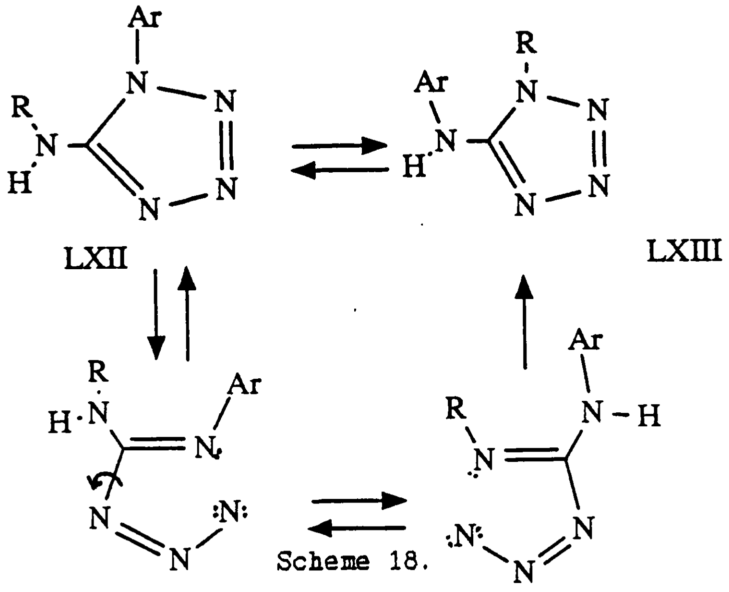
Sisido *et al.* [230] have shown that solutions of N-tributyltin-5-alkyltetrazoles display high viscosities even in non-coordinating solvents like toluene and this would indicate that these compounds have polymeric structures containing pentacoordinated tin atoms. The polymeric structure they proposed is depicted below (LXI).

In Chapter 5 it was shown that compounds **(40)**, **(41)** and **(50)** were formed by thermal cyclisation reactions resulting in the irreversible loss of tributylphenyltin or tributyltin bromide.



(LXI)

Several thermal rearrangements of tetrazoles have been reported [248-250], but the best-known is that of substituted 5-aminotetrazoles (LXII). In general 1-aryl-5-alkylaminotetrazoles rearrange to 1-alkyl-5-arylaminotetrazoles (LXIII) when heated, (Scheme 18).



Scheme 18.

In this Chapter various spectral data regarding the structure and thermal behaviour of *N*-trialkyltin-5-substituted tetrazoles (33-37) are discussed and resulting from this, a mechanism for the thermal cyclisation reactions that result in compounds (40), (41) and (50) being formed is proposed.

6.2 The Structures of N-Trialkyltin-5-Substituted Tetrazoles.

Compounds (33-37) were used as model systems to explore the thermal properties associated with a trialkyltin moiety attached *via* a nitrogen atom to a tetrazole ring. It was hoped that the behaviour of the model compounds would be similar to that of the more complex systems of compounds (38), (39) and (49). Several spectroscopic probes were used to examine the structures of (33-37), including variable concentration and variable temperature ^{13}C, ^{15}N and ^{119}Sn nmr.

6.2.1. Variable Concentration NMR.

Before one can explore the thermal properties of N-trialkylstannyl tetrazoles in solution one must initially examine the extent of polymeric character associated with these compounds in solution. Initial ^{119}Sn nmr measurements on (33-34) suggested that at moderate concentrations (≈1.0 M) the tin atoms in these compounds are 5-coordinate and this agrees with the viscosity experiments performed by Sisido *et al* [230]. Since the polymers are formed as the result of a intermolecular coordination effect, it was necessary to perform variable concentration ^{13}C nmr experiments. By measuring the $^{1}J(^{119}Sn, ^{13}CH_2)$ coupling constants for (34) and (35) in the concentration range 0.025 M to 1.0 M, the coordination number at tin could be estimated. The results are given in Table 45 and plotted in Figure 18. An examination of the figure reveals that (34) achieves 5-coordination in relatively dilute solutions at around 0.15 M. The $^{1}J(^{119}Sn, ^{13}C)$ value is still decreasing at the limit of resolution (0.025M), and it can be safely assumed that (34) is extremely polymeric over a wide concentration range. Compound (35) seems to be 4-coordinate in the

Table 45: Variable Concentration ^{13}C NMR Studies on (34) and (35)

Compound (34)

Concentration [a]	$^{1}J(^{119}Sn, ^{13}C)$ [b]
0.025	398.9
0.050	418.6
0.075	431.8
0.100	436.3
0.150	442.9

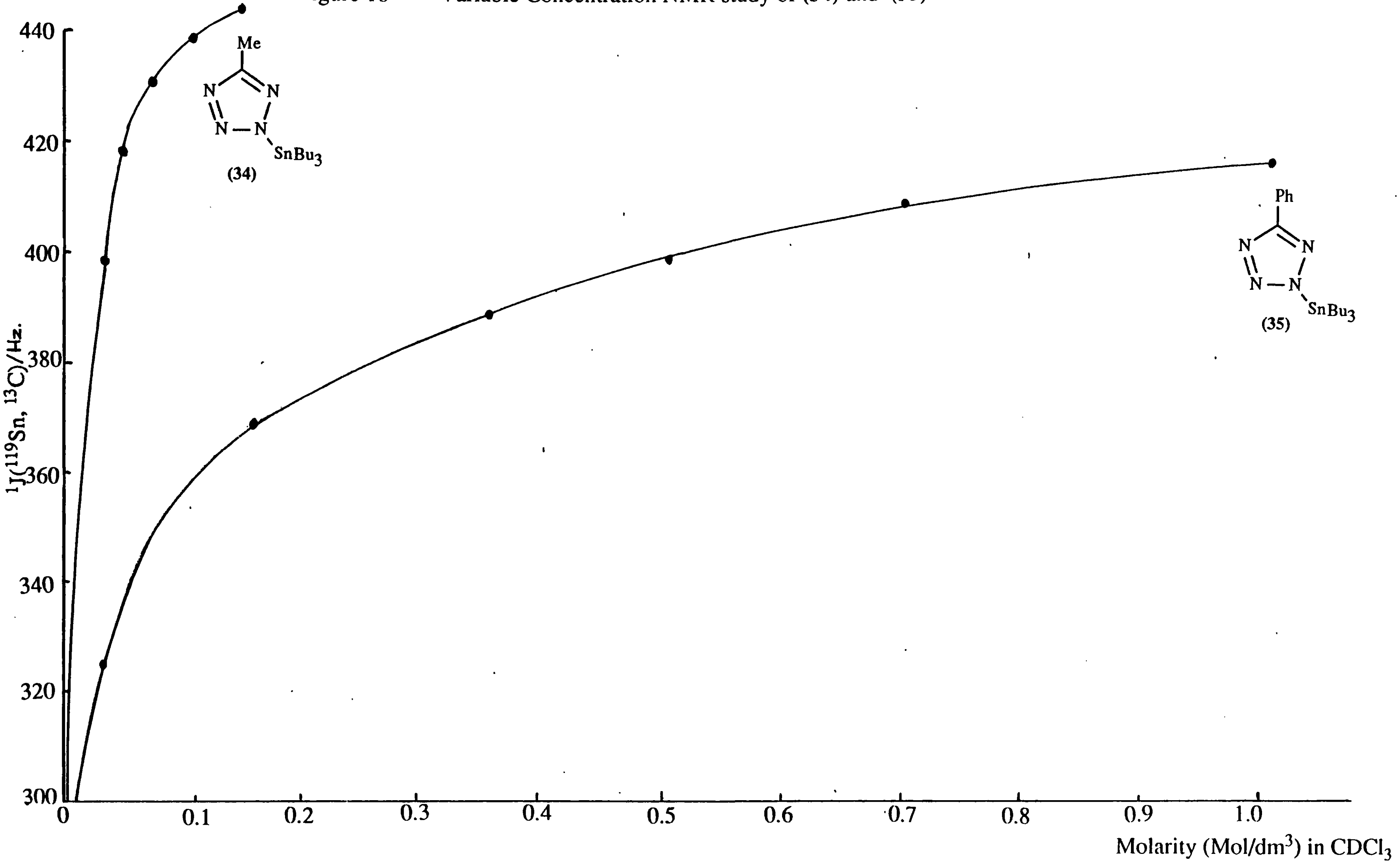
Compound (35)

Concentration [a]	$^{1}J(^{119}Sn, ^{13}C)$ [b]
0.050	326.4
0.150	352.3
0.350	387.5
0.500	398.8
0.750	413.5
1.000	425.3

[a] Concentration measured in mol/dm^3

[b] Spectra recorded as $CDCl_3$ solutions, $CDCl_3$ used as a reference.

Figure 18 Variable Concentration NMR study of (34) and (35)



range 0.05 M to 0.2 M, however it reluctantly achieves 5-coordination at higher concentrations, e.g. 1.0 M.

6.2.2 Variable Temperature NMR.

The ^{119}Sn nmr chemical shift values for (33) and (34) were recorded at 25°C as ≈ 1.0 M deuterated chloroform solutions and it was observed that the peaks were broad. The line widths at half height were measured to be 688 Hz and approximately 1000 Hz respectively. Although this line broadening might arise from the position of the tin adjacent to the quadrupolar nucleus ^{14}N, this seems unlikely since the ^{119}Sn nmr line width recorded for (37), containing a similar Sn-N bond, was only 170 Hz and in fact both of the 5-aryl substituted tetrazole compounds (35) and (37) displayed significantly sharper lines than the 5-alkyl substituted compounds.

Sisido *et al.* [230] have made the distinction between these two classes of compounds, (C-aryl vs. C-alkyl tetrazoles), when they observed that the 5-aryl tetrazole derivatives yielded much lower viscosities than the 5-alkyl compounds and proposed that, due to steric and inductive effects, the structures of the 5-aryl derivatives tended towards monomeric structures as opposed to the polymeric structures expected for the 5-alkyl derivatives. This has obviously been vindicated by the variable concentration experiments on (34) and (35).

The ^{119}Sn nmr chemical shift values for (34-37) were recorded in approximately 1.0 M $CDCl_3$ solutions in the temperature range -50° to +105 °C and the results are given in Table 46 and plotted in Figure 19. A brief examination of the figure reveals that there are clearly

Table 46. Variable Temperature ^{119}Sn NMR Data for N-tributyltin-5-R-Tetrazole Compounds. (34-37) [a]

	R=Me-, (34)		R=CH$_3$CH=CH-, (36)	
Temperature [b]	δ(^{119}Sn)[c]	L.W. [d]	δ(^{119}Sn)[c]	L.W. [d]
-50	-84.2	50	[e]	
-40	-82.7	60	-78.3	75
-20	-79.7	140	-75.7	105
0	-77.7	≃450	-73.2	115
20	-65.0	≃1000	-67.7	325
40	[e]	-	-52.0	≃450
50	[e]	-	-46.5	≃450
60	-11.5	-	[e]	-
70	[e]	-	-39.7	270
80	-5.9(-12.5 [f])	300	-36.6	270
90	[e]	-	-32.6	250
95	-0.6(-12.5 [f])	130	[e]	-
100	[e]	-	-28.6	170
105	4.4(-12.5 [f])	90	[e]	-

	R=Ph-, (35)		R=6-Me-2-pyridyl-, (37)	
Temperature	δ(^{119}Sn)	L.W.	δ(^{119}Sn)	L.W.
-40	-56.3	65	-66.2	45
-20	-52.7	26	-62.8	20

Table 46 continued,

0	-48.6	32	-59.3	15
20	-42.8	65	-55.5	15
30	-38.6	50	[e]	-
40	-34.4	40	-47.2	10
50	-29.2	22	-43.9	10
60	-22.1	16	-39.8	10
70	-11.9	14	[e]	-
90	22.4	10	-17.6	10

[a] All concentrations at 25% w/w (≈1.0 M) in toluene

[b] Temperature measured in °C

[c] $\delta(^{119}Sn)$ values given in ppm. relative to Me_4Sn

[d] L.W.= Line widths given in Hz.

[e] Peak not recorded.

[f] Extra peak corresponds to a small quantity of Bu_4Sn formed by a decomposition reaction.

Variable Temperature NMR study of compounds (34-37)

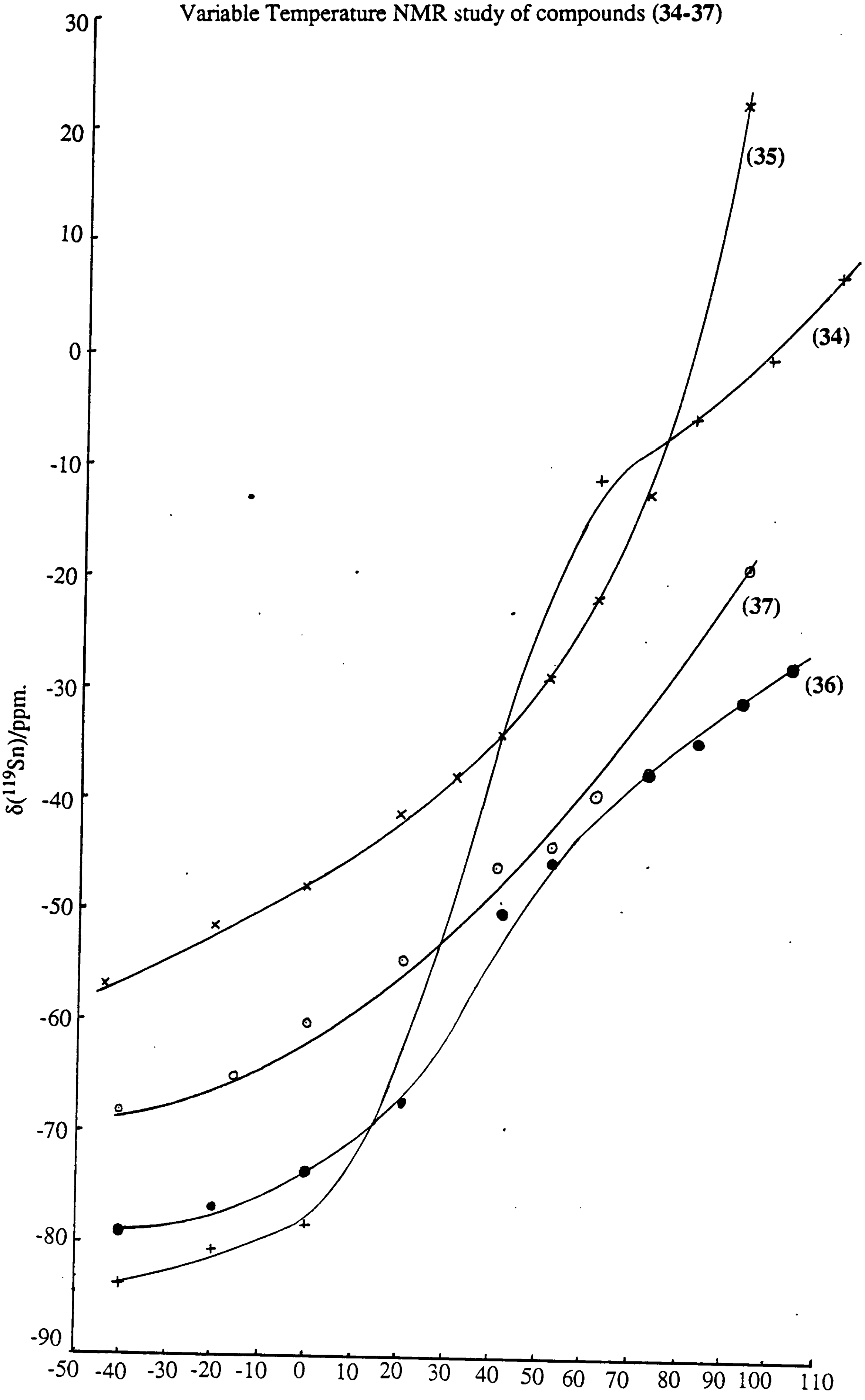


Figure 19

different processes operating for the 5-alkyl and the 5-aryl substituted tetrazoles in solution. The 5-aryl substituted compounds (35) and (37), display smooth curves relating $\delta(^{119}Sn)$ values with temperature, wheras the 5-alkyl substituted compounds (34) and (36) show marked 'steps', beginning around +20° and ending around +60°C. As the temperature decreases from 0°C, all of the compounds (34-37) become more and more progressively locked into a polymeric structure containing pentacoordinated tin atoms, until finally the frozen solution state is reached. Figure 19 shows this effect clearly and the ^{119}Sn chemical shifts tend toward values in the range -50 to -80 ppm. It is worth noting that compounds (34) and (36) with the less sterically demanding 5-substituent have the lowest $\delta(^{119}Sn)$ nmr values and hence can be assumed to be the most polymeric.

The Mossbauer parameters for the compounds (34-37) are given in Chapter 5, Table 40. The ΔEq values lie in the range 3.23-3.69 $mmsec^{-1}$ and the isomer shifts are in the range 1.22-1.49 $mmsec^{-1}$. It is clear from these values that these compounds all have trans-tbp 5-coordinate geometry, and their structures are not likely to differ when the compounds are in the frozen toluene solution state.

As the temperature is raised above 0°C, the $\delta(^{119}Sn)$ values of the 5-aryl derivatives, (35) and (37), smoothly increase and the line widths become sharper until at around 80°C for (35) and 110°C for (37) the $\delta(^{119}Sn)$ values become positive. Whilst the temperature is increasing the polymeric nature of these species is decreasing, until eventually the molecules are largely 4-coordinate monomers, even at relatively high concentrations, e.g. 1.0M. For comparison, a typical 4-coordinate tributyltin-nitrogen bonded compound e.g. Bu_3SnNEt_2, has $\delta(^{119}Sn)$=+36 ppm. [135].

In the temperature range of 20° to 60° the solutions of **(34)** and **(36)** display anomalous $\delta(^{119}Sn)$ values. The chemical shift values rapidly increase for a small change in temperature. In addition, the line widths during this 'step' rapidly increase until the line is so broad that it becomes unobservable. Such a marked deviation from the behaviour of the two 5-aryl compounds, **(35)** and **(37)**, is indicative of a dynamic process taking place, as well as polymer cleavage. Above 60°C the gradients of the $\delta(^{119}Sn)$ vs. Temp. curves for **(34)** and **(36)** are reduced to the initial values between -60° and 0°C.

In order to be certain that at elevated temperatures, (≈ 100°C), the 1.0 M solutions of the 5-alkyl substituted tetrazole compounds still contain 5-coordinate tin atoms, a variable temperature ^{13}C nmr study was conducted on **(34)**. The results for this experiment are given in Table 47. An examination of the data reveals that there are no significant changes in any of the ^{13}C δ values, even over the temperature range for the anomalous 'step' found in the v.t. ^{119}Sn nmr experiments. However, it must be noted that at -40° and -20°C the ^{13}C nmr signals due to the α-CH_2-'s on the butyl chains were very broad and no $^{117/119}Sn$ satellites could be resolved, hence no $^{1}J(^{119}Sn, ^{13}C)$ values could be calculated. This is presumably caused by the inability of the butyl chains to move freely in the highly viscous solutions, making them non-equivalent. Fortunately, at 0°C and 100°C the ^{13}C signals due to the α-CH_2's were much sharper and the $^{117/119}Sn$ satellites were sufficiently resolved at 100°C to be able to measure $^{1}J(^{119}Sn, ^{13}C)$ which was 437 Hz. If compared to the data plotted in figure 18, this value is indicative of a fully saturated 5-coordinate

Table 47: Variable Temperature ^{13}C NMR Data for N-tributyltin-5-Methyltetrazole (34).

Temperature [a]	α CH$_2$ [b]	β-CH$_2$	γ-CH$_2$	δ-CH$_3$	C(5)	5-Me
-40	18.46	28.58	27.51	14.01	157.87	10.20
-20	18.40	28.53	27.46	13.95	157.92	10.31
0	18.35	28.47	27.35	13.85	157.92	10.36
100	18.38 [c]	28.58	27.19	13.58	158.30	10.63

[a] Temperature in °C

[b] Spectra were recorded as toluene solutions and figures given in ppm. relative to TMS.

[c] $^1J(^{119}Sn, ^{13}C)$ measured at 437 Hz.

Table 48: ^{15}N Natural Abundance NMR Results for (34) at 20°C and 90°C.

Temperature [a]	δ(^{15}N) [b,c]
20	-12.62, -79.61
90	-12.07, -78.99

[a] Temperature in °C.

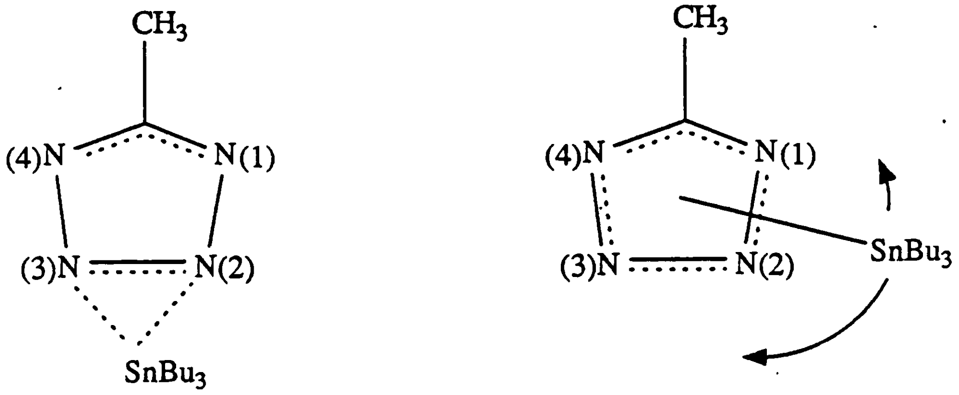
[b] Recorded as CDCl$_3$ solutions with 20 hour accumulation times.

[c] Figures given in ppm. relative to CH$_3$NO$_2$.

tin atom, and therefore the structure of **(34)** in a 1.0 M $CDCl_3$ solution has been proved to be polymeric even at 100°C.

Since it has been confirmed that compound **(34)** has 5-coordinate geometry between -60° and 100°C, (LXI), and contains 4 chemically different nitrogen atoms, the ^{15}N nmr spectra should, in principle, show four peaks. ^{14}N nuclear quadrupole resonance studies on tetrazole [251] have not proved useful and have shown that the molecule is piezoelectric and only two resonances could be observed. ^{14}N nmr studies have been conducted on 1,5-disubstituted tetrazole compounds similar to PMT and only 4,5-cyclotrimethylene tetrazole shows four well resolved, but broad, signals [252]. In general, the signal of the singly bonded nitrogen is sharper and at higher field than that of the doubly-bonded nitrogen. Two natural abundance ^{15}N nmr experiments were performed on **(34)** at 20°C and 90°C and the results are presented in Table 48. The recorded spectra reveal only two nitrogen environments, the slightly broader peak at lower field may be assigned to be the sp^2 nitrogens and the one at higher field to be the sp^3 hybridised nitrogen. There are no significant differences in the chemical shifts of the spectra over the two temperatures which incidentally span the same temperature region as the anomalous 'step' in the v.t. ^{119}Sn nmr experiments on the same compound. The ^{15}N nmr evidence is inconclusive. It is apparent that at both extremes of temperature there are significant amounts of both sp^2 and sp^3 nitrogens and the chemical natures of the nitrogens with similar hybridisation modes must be very similar, or are involved with a dynamic tributyltin moiety. If the tributyltin moiety is moving around the ring, then at

20°C it may be moving between N(2) and N(3), Scheme 19. This generates two nitrogens, N(2) and N(3), with a significant amount of sp^3 character and two nitrogens, N(1) and N(4), mainly sp^2 in character. At higher temperatures, e.g. 90°C, the tributyltin moiety can move all around the ring from N(1) to N(4)), this would cause, N(2) and N(3), to have a significant amount of sp^2 character associated with them, and conversely N(1) and N(4) would have a significant amount of sp^3 character associated with them (Scheme 19).



Scheme 19.

Sisido *et al.* [230] performed several U.V. and viscosity experiments on various trialkylstannyl tetrazole compounds and from their results deduced that the trialkyltin unit resides on the N(2) of the tetrazole ring. The results from the variable concentration nmr or variable temperature nmr presented here do not unambiguosly show that this original postulation is correct, however a recent X-ray crystal structure of $(PhMe_2Si)_3CSiMe_2\overline{N\text{-}N=C(Me)\text{-}N=N}$ reported by Eaborn et al. [253] has shown that in this discrete monomeric compound the bulky silicon ligand resides on the N(2) of the tetrazole ring (using consistant numbering schemes) (figure 20). No fluxionality was reported for this compound but this is possibly due to the steric hindrance caused by the bulky silicon ligand. It is perhaps reasonable then to assume that Sisido *et al.'s* proposed site of attachment of the trialkyltin group, e.g. on N(2) is correct and that therefore in the light of this new X-ray data it is likely that the structures proposed here for the tetrazole compounds are correct also.

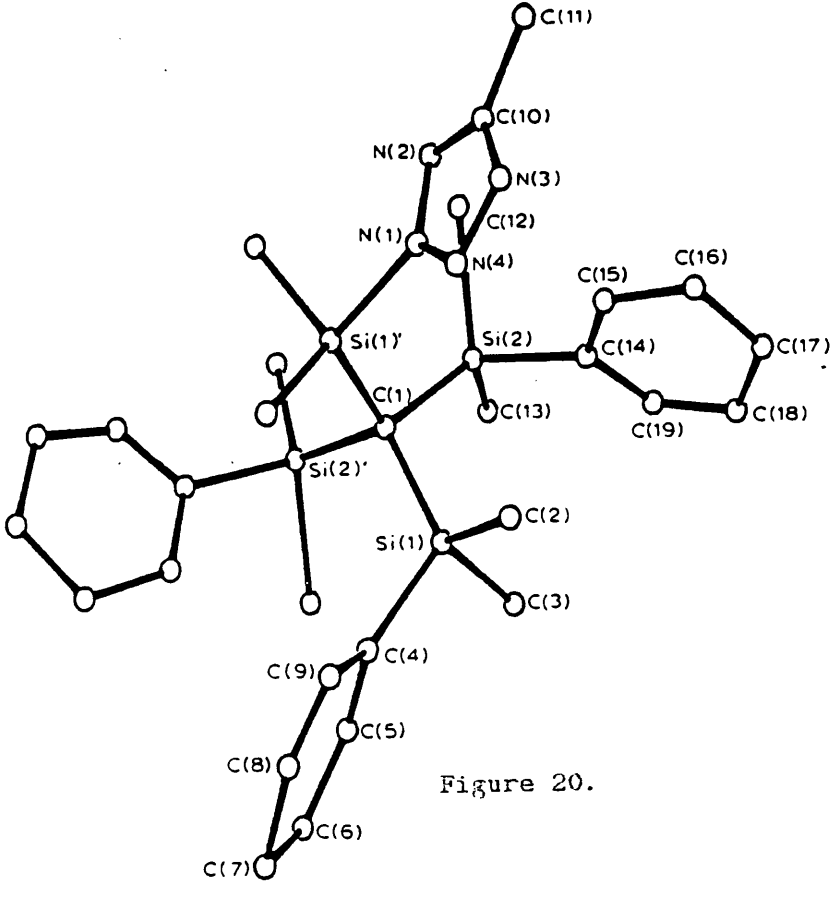
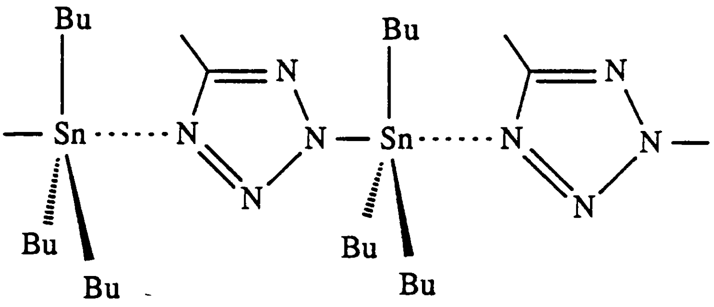


Figure 20.

6.3 The Thermal Behaviour of N-Tributyltin-5-alkyltetrazoles

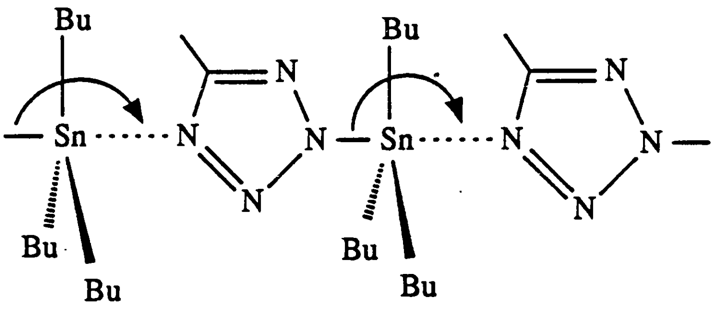
To rationalise the variable temperature nmr data for **(34)** and **(36)** and to account for the bicyclic products **(40)** and **(41)** synthesised in Chapter 5, it is proposed that the tributyltin moiety initially attached to the tetrazole ring at N(2) is engaged in a dynamic process in which the triorganotin oscillates between N(2) and N(1) at higher temperatures. This can occur in two possible ways: (1) in an intermolecular fashion *via* a covalent/dative bond exchange mechanism, or (2) an intramolecular N(2) to N(1) shift. Whichever mechanism is correct it is apparent that very little energy is required for the shift, since it occurs below 60°C. A structural rationalisation of the intermolecular exchange is depicted below, for a 1.0M toluene solution of **(34)**, which at -60°C is so viscous as to be a semi-solid. The series of diagrams below follows the changes as the temperature is increased. In (i), the solution of **(34)** is a semi-solid. The tributyltin is firmly bonded to the N(2) of the tetrazole and N(1) of a neighbouring tetrazole is coordinated to the tin *via* a longer bond.

(i) -60°C



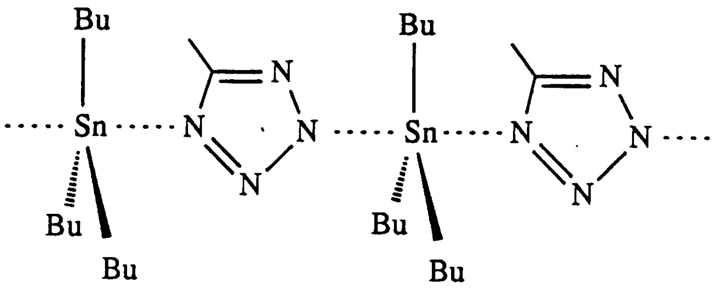
Between 20° and 40°C, (ii), the tributyltin moiety begins slowly exchanging from N(2) to N(1), this has the effect of causing the ^{119}Sn peak to broaden. The nmr sees both ^{119}Sn-N(2) and ^{119}Sn-N(1) signals and as the temperature increases the signals blur together until finally at 40°C the line width is so broad that the signal is lost altogether.

(ii) 20-40°C

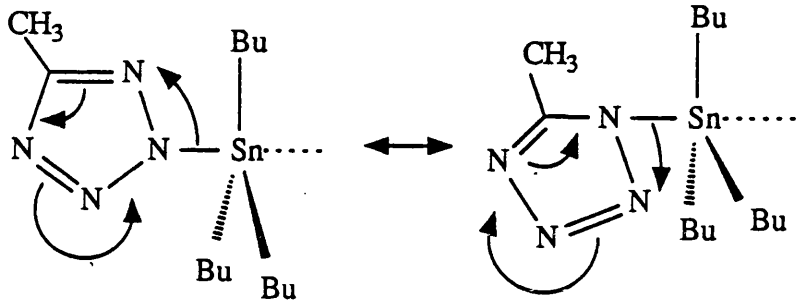


At +60°C, (iii), the bonds are exchanging so rapidly that the nmr 'sees' an average signal and the line width sharpens again. The compound is still 5-coordinate and the triorganotin spends an appreciable amount of time on N(1) of the neighbouring tetrazole as well as N(2) of the original tetrazole. As the temperature is increased still further the geometry around the tin becomes steadily more and more 4-coordinate.

(iii) +60°C



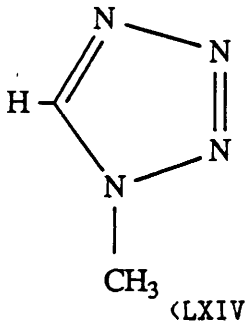
The second scenario involves the direct intramolecular transfer of Bu$_3$Sn- from N(2) to N(1) on the tetrazole ring. Scheme 20.



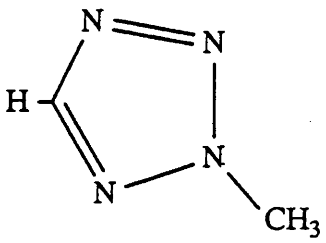
Scheme 20.

The same arguments as for the intermolecular mechanism cover the line broadening effects and from these data is it not possible to distinguish which mechanism is dominant. One such experiment which could differentiate the two would be to perform a variable temperature ^{119}Sn nmr experiment on an extremely dilute solution of (**34**), e.g. perhaps 0.001 M, although at such dilutions the spectra of low abundance nuclei are hard to observe.

The ^{119}Sn nmr chemical shift values for (**34**), i.e. those in the range -84.2 to 4.4 ppm, all suggest that (**34**) is 5-coordinate over the temperature range of -50° to +105°. Therefore one cannot rationalise the large increases in the δ(^{119}Sn) values as simply a 5- to 4-coordination change alone, but rather the effect on the δ(^{119}Sn) value as the N(2) to N(1) exchange sets in. If one examines similar N-substituted tetrazole systems, e.g. tetrazole isomers with methyl groups at the 1- and 2-positions, an appreciation of the differences in the ^{1}H and ^{13}C nmr spectra can readily distinguish the two isomers. Methyl groups bonded to N(1), e.g. (LXIV) are more shielded by *ca.* 0.15-0.35 ppm in the ^{1}H spectra and by *ca.* 2-6 ppm in the ^{13}C spectra relative to the N(2) isomers, e.g. (LXV). If these figures are considered to be percentage shifts of the total chemical shift range, for the ^{1}H spectra this represents an approximately 2.5% difference in the δ value and for the ^{13}C nmr spectra an approximately 2% difference in the δ value. Therefore the difference between an N(2)-$SnBu_3$ and an N(1)-$SnBu_3$ group would be expected to be about 2% of the ^{119}Sn nmr chemical shift range(≈3000 ppm). This yields the figure of approximately 60 ppm, which is indeed in the order of the differences in the shifts observed, for the N(2) to N(1) exchange.



(LXIV)



(LXV)

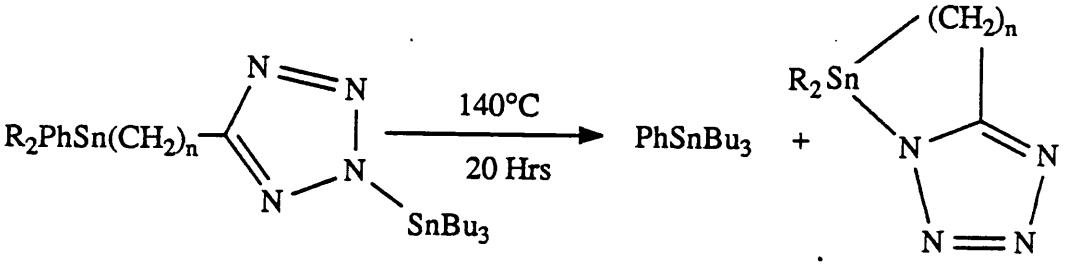
When the C-substituent on the tetrazole is small or flexible, like a methyl group or an alkyl chain, this exchange occurs readily. However, with bulky or inflexible C-substituents, like the 6-Me-2-pyridyl group, the formation of the polymer is more difficult and 5-coordinate tin is only formed in relatively concentrated solutions. This implies that the formation of the intermolecular N(1)-Sn bond is difficult. Therefore the N(2) to N(1) shift would also be disfavoured on similar steric grounds.

It is perhaps for this reason that the δ(^{119}Sn) values of the 5-aryl compounds, (35) and (37), do not display a 'step' with increasing temperature, since in these cases the Sn---N(1) bond lengths simply increase until the temperature is high enough for the molecules to exist largely as monomers.

6.4 The Thermal Cyclisation of 5-Organostannyl-2-Tributylstannyl-Tetrazoles.

In Chapter 5, using various spectral evidence, the structures of (38), (39) and (49) were described as polymeric materials containing pentacoordinated tin atoms. The structures are very similar to the N-tributyltin-5-alkyltetrazoles discussed earlier in this chapter.

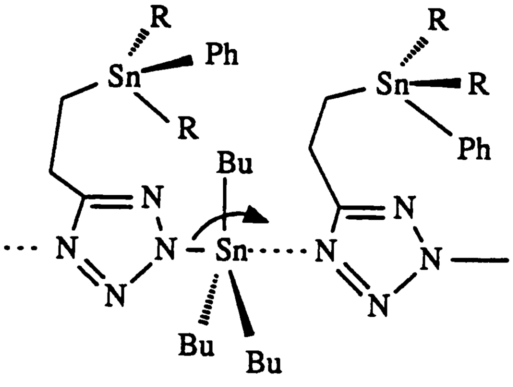
To recap, the thermal cyclisations of (38), (39) and (49) were initiated by heating each compound, without solvent, at around 140°C for about 20 hours. In each case, tributylphenyltin was liberated along with a bicyclic diorganostannyl tetrazole compound, (Equation 27).



(27)

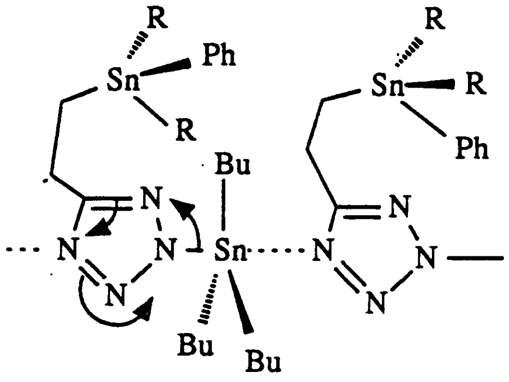
(R=Ph, Bu n=2,3)

In accordance with the mechanism proposed earlier, (Sec. 6.3), at an elevated, but not excessively high temperature, e.g. *ca.* 70°, the N-tributyltin moiety is in equilibrium between the N(2) and the N(1) positions on the tetrazole ring, the rate of site exchange, either intra- or intermolecularly, increases with temperature to enhance the number of N(1)-$SnBu_3$ moieties, Scheme 21.



R=Ph, Bu

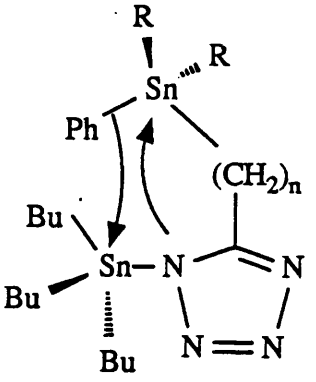
Intermolecular transfer



Intramolecular transfer

Scheme 21.

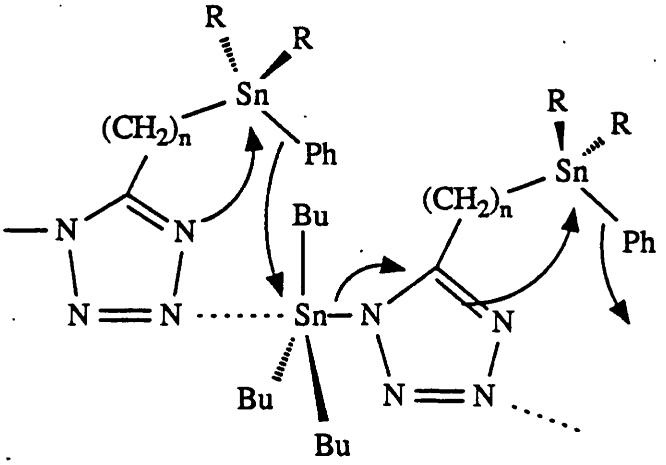
In this new configuration the organotin moieties are very close. The reaction can now proceed in either of two ways. The first route involves an intramolecular attack of N(1)-$SnBu_3$ on the $R_2PhSn(CH_2)_n$-group. This releases a Ph (or in Ph_2BrSn- a Br) group which attacks the departing $SnBu_3$ moiety, the tetraorganotin is no longer coordinated to the tetrazole and becomes a discrete tetrahedral unit, Scheme 22. The argument against this mechanism is as follows. Since it has been shown that when bulky 5-substituents are present the N(1) is not readily available for the -$SnBu_3$, then presumably, when the -$SnBu_3$ unit does transfer to N(1) the $R_2PhSn(CH_2)_n$- unit will be pushed away from N(1) to reduce steric hindrance, and therefore the $R_2PhSn(CH_2)_n$- group is further away and less likely to be attacked by N(1). It must however be recognised that N(1) has become tetrahedral to a certain degree and this does aid attack.



Scheme 22.

The second possible route involves an intermolecular attack. Since Bu_3Sn-N(1) has pushed the $R_2PhSn(CH_2)_n$- group away, the $R_2PhSn(CH_2)_n$- group now is in close proximity to N(4). A concerted mechanism then follows in which the sp^2 nitrogen, N(4), previously noted for its willingness to act as a weak base at this position, (see Chapter 5, section 5.4), attacks the adjacent tin releasing a Ph group. The released Ph group then intermolecularly attacks the Bu_3Sn-N(1) on a neighbouring tetrazole. The tetraorganotin is released from the tetrazole and the ring re-aromatises, Scheme 23. The argument against this mechanism is as follows. If a model is made of the system it can be shown that the intermolecular distance between the attacking Ph group and the Bu_3Sn-N(1) group is quite large, however this distance can be reduced with larger values of n on $R_2PhSn(CH_2)_n$-.

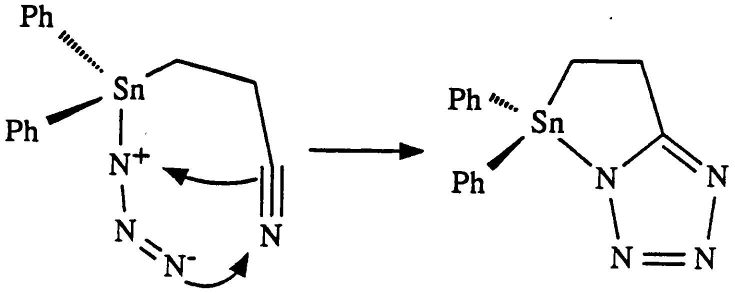
One can only speculate as to which mechanism is correct, either nucleophilic attack on Sn(2) from N(1) or nucleophilic attack from N(4), and there are valid arguements for both, however, due to the noted weak basicity of N(4) and the reduced nucleophilicity of N(1) (due to the attached Bu_3Sn- moiety), it is felt that the second route is the more likely.



Scheme 23.

Since these thermal cyclisation reactions only occur at elevated temperatures (≃ 140°C), it is apparent that the rate limiting step is not the transfer of Bu_3Sn- from N(2) to N(1), since this has been shown to occur for 5-alkyl substituted tetrazoles at temperatures below 60°. It has also been shown that if a Ph is substituted by a Br in the $R_2PhSn(CH_2)_n$- substituent exocyclic from the tetrazole, the reaction proceeds in about five minutes compared to the twenty four hours required for the Ph analogue. It is also worthwhile noting that the cyclisation reaction of $Bu_3SnCH_2CH_2CN$ with Bu_3SnN_3 does not occur at all and no bicyclic product or Bu_4Sn are formed either. This is reasonable since a butyl chain is not regarded as a good leaving group from tin. Therefore the rate limiting step appears to involve the cleavage of the leaving group from Sn(2), i.e. Ph vs. Br.

A third route to the bicyclic compound **(40)** is available, however, which does not involve a thermal rearrangement, but rather centers upon an intramolecular cyclisation reaction of $Ph_2Sn(N_3)CH_2CH_2CN$. (2-Cyanoethyl)diphenyltin azide rapidly cyclises in refluxing 60-80° petroleum ether to give **(40)** in virtually quantitative yields, (Equation 28.)



(28)

CONCLUSIONS

The primary aim of this work was to prepare a selection of novel C-organostannyl heterocyclic compounds that might show biological activity. Several novel compounds have indeed been synthesised, however, none as yet have been tested. Unfortunately, it has now become less likely to find maunfacturers willing to test new organotin biocides due to pollution concerns created by the use of heavy metals in the environment.

The secondary aim of the project, the exploration of new avenues in organotin chemistry, has been much more successful. It has been shown that there are a variety of ways that heterocyclic ligands can be attached to an organotin moiety. Some of the compounds were air/moisture sensitive and some quite stable.

In Chapter 2, the X-ray structure of 2-(triphenyltin)benzothiazole will prove a useful addition to the scant structural data reported for these type of compounds. The small ΔEq values for the tetraorganotin compounds reported here are very interesting and perhaps would provide a starting point for some studies into the organisation of the hybrid orbitals on tin.

Chapters 3 and 4 have shown that it is possible to prepare virtually any number of C-organostannyl heterocyclic compounds, although further work needs to be conducted into hydrostannylation reactions, i.e. why some vinyl groups can be hydrostannylated and some cannot.

Chapter 5 shows some very exciting new organotin chemistry. Thermal cyclisation reactions could yield some very exotic new compounds. The chemistry can be conducted on a relatively simple level using quite cheap organotin materials, ideal for a final year undergraduate student, or on more complicated multi-stage synthetic level. The possibilities for this new chemistry are vast. For example: the cyclisation rates could be studied by altering the leaving groups on the tin, hitherto unknown structures could be prepared (e.g. a 'butterfly'-type structure using starting materials like $Ph_2Sn(CH_2CH_2CN)_2$) and another area of interest would be to experiment with other cyclisable functionalities on the alkyl chain pendant to tin, the possibilities are endless.

Finally Chapter 6 has illuminated some interesting thermal activity of tributyltin attached to a tetrazole nucleus. It would be interesting to explore this phenomenon on other heterocyclic systems.

APPENDIX I

Synthesis of organotin starting materials

Ph_3SnCl, Ph_2SnCl_2, Bu_3SnCl, Bu_2SnCl_2, Me_2SnCl_2 and Me_4Sn were purchased from Aldrich Chemical Co. Ltd and were generally used without further purification. The following materials were synthesised in our laboratory prior to use.

(a) Me_3SnCl: Trimethyltin chloride was obtained from the disproportionation reaction of tetramethyltin with anhydrous stannic chloride in the ratio 3:1 as indicated below (1). The reagents were heated under reflux together at approximately 150°C for two hours, and the product isolated and purified by sublimation under reduced static pressure at 30°C.

$$3\ Me_4Sn\ +\ SnCl_4 \longrightarrow 4\ Me_3SnCl \qquad (1)$$

(b) Ph_3SnH: Triphenyltin hydride was prepared according to G.J.M. Van der Kerk *et al.* [254] and the crude compound purified by distillation under reduced pressure (210°/0.3 mmHg).

(c) Ph_3SnCH_2I and $Sn(CH_2I)_4$: Triphenyl(iodomethyl)tin and *tetrakis* Iodomethyltin were prepared according to Seyferth and Andrews [255] and the compounds were purified by recrystallisation from 60-80° petroleum ether.

(d) $Ph_3SnCH_2CH_2CN$ and $Ph_3SnCH_2CH_2CH_2CN$ were prepared according to G.J.M. Van der Kerk *et al.* [211] and purified by recrystallisation from 60-80° petroleum ether.

APPENDIX II

(1) Crystallographic Analysis and Structural Refinement of 2-(Triphenyltin)benzothiazole

(a) Crystal Data:

$C_{25}H_{19}NSSn$ MW= 484.18, triclinic, space group= P1 with

$\underline{a}$ = 9.501(1)Å, $\underline{b}$ = 10.172(2)Å, $\underline{c}$ = 13.231(2)Å.

$\underline{\alpha}$ = 67.93(2)Å, $\underline{\beta}$ = 70.46(1)Å, $\underline{\gamma}$ = 69.71(1)Å.

V = 1082.8 Å^3, Z = 2, μ = 11.74 cm^{-1}, F000 = 484.0, Radiation Mo-Kα, λ=0.71069 Å.

For 2264 observed reflections with $I > 3\sigma I$, R = 0.0719 and R_w = 0.0719

(b) Crystallographic Analysis.

A crystal with the dimensions of 0.3 x 0.3 x 0.35 mm was glued to the top of a glass fibre and placed on the diffractometer. It was used for preliminary crystal analysis and final data collection performed on a Hilger and Watts Y290 Automatic 4 circle Diffractometer. Final cell dimensions were obtained for least square refinement of the angular settings of 12 accurately centered reflections. The intensities of all reflections with $2° < \theta < 22°$ were measured. One reflection was used as a standard and its intensity was monitored every 50 observations. No significant crystal decay was observed.

(C) Structure Solution and Refinement:

The structure was solved by using direct methods, SHELX86 [256] and refined by full matrix least squares using SHELX76 [257]. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atom positions were included in the calculation, (fixed V = 0.05Å^2, [d(C-H)=1.08Å]). The tin and the sulphur atoms were refined anisotropically, while the remaining atoms were refined isotropically. The atomic scattering factors and the anomalous dispersion correction factors for both hydrogen and non-hydrogen atoms were taken from the literature, [258-260]. The ORTEP program was used to obtain the drawings [261]. Fractional atomic coordinates given on Table 49, bond lengths and bond angles are given on Tables 50 and 51 respectively.

Table 49. Fractional Atomic Coordinates and Thermal Parameters (Å) for 2-Ph_3Sn-Bzt.

Atom	x	y	z	Uiso or Ueq.
Sn	0.38815(11)	0.24743(12)	0.33034(8)	0.0562(6)
S(1)	0.38624(5)	0.58348(5)	0.13499(3)	0.0778(3)
N(1)	0.1708(13)	0.4615(13)	0.1771(9)	0.061(3)
C(1)	0.5654(16)	0.3054(16)	0.3589(11)	0.055(4)
C(2)	0.6974(17)	0.3219(17)	0.2767(13)	0.069(4)
C(3)	0.8184(20)	0.3537(20)	0.2972(15)	0.083(5)
C(4)	0.8057(20)	0.3567(19)	0.4016(14)	0.081(5)
C(5)	0.6795(20)	0.3294(20)	0.4857(15)	0.085(5)
C(6)	0.5578(17)	0.3038(17)	0.4652(12)	0.063(4)
C(7)	0.4645(15)	0.0687(15)	0.2607(11)	0.051(3)
C(8)	0.5982(17)	-0.0339(17)	0.2752(12)	0.063(4)
C(9)	0.6472(19)	-0.1484(19)	0.2289(13)	0.075(4)
C(10)	0.5596(20)	-0.1615(22)	0.1698(15)	0.088(5)
C(11)	0.4275(21)	-0.0553(21)	0.1536(15)	0.091(5)
C(12)	0.3764(19)	0.0618(19)	0.1990(13)	0.074(4)
C(13)	0.2070(14)	0.2136(15)	0.4778(10)	0.048(3)
C(14)	0.1378(16)	0.3182(17)	0.5336(12)	0.060(4)
C(15)	0.0215(17)	0.2939(18)	0.6305(13)	0.068(4)
C(16)	-0.0284(18)	0.1728(18)	0.6692(13)	0.071(4)
C(17)	0.0377(19)	0.0637(20)	0.6145(14)	0.081(5)
C(18)	0.1562(17)	0.0873(17)	0.5173(12)	0.063(4)

Table 49 continued,

C(19)	0.2959(15)	0.4389(15)	0.2056(11)	0.050(3)
C(20)	0.2441(16)	0.6760(17)	0.0621(12)	0.060(4)
C(21)	0.2248(20)	0.8122(19)	-0.0159(14)	0.079(5)
C(22)	0.0978(21)	0.8650(23)	-0.0597(16)	0.091(5)
C(23)	-0.0045(20)	0.7832(20)	0.0499(14)	0.080(5)
C(24)	0.0101(20)	0.6432(20)	0.0499(14)	0.080(5)
C(25)	0.1376(16)	0.5876(16)	0.0969(11)	0.056(4)

Table 50. Bond Lengths (Å) of 2-Ph$_3$Sn-Bzt.

Sn-C(1)	2.147(14)	Sn-C(7)	2.141(14)
Sn-C(13)	2.135(12)	Sn-C(19)	2.159(13)
S(1)-N(1)	2.553(12)	S(1)-C(19)	1.755(14)
S(1)-C(20)	1.718(15)	S(1)-C(25)	2.560(14)
N(1)-C(19)	1.285(16)	N(1)-C(25)	1.340(17)
C(1)-C(2)	1.373(19)	C(1)-C(6)	1.382(19)
C(2)-C(3)	1.427(22)	C(3)-C(4)	1.359(22)
C(4)-C(5)	1.365(22)	C(5)-C(6)	1.396(21)
C(7)-C(8)	1.354(19)	C(7)-C(12)	1.384(20)
C(8)-C(9)	1.385(21)	C(9)-C(10)	1.384(22)
C(10)-C(11)	1.362(23)	C(11)-C(12)	1.400(23)
C(13)-(14)	1.376(19)	C(13)-C(18)	1.384(19)
C(14)-C(15)	1.391(19)	C(15)-C(16)	1.331(21)
C(16)-C(17)	1.403(22)	C(17)-C(18)	1.404(21)
C(19)-C(25)	2.205(19)	C(20)-C(21)	1.377(21)
C(20)-C(25)	1.433(19)	C(21)-C(22)	1.367(22)
C(22)-C(23)	1.359(23)	C(23)-C(24)	1.410(23)
C(24)-C(25)	1.393(20)		

Table 51. Bond Angles (°) of 2-Ph_3Sn-Bzt.

C(7)-Sn-C(1)	115.8(5)	C(13)-Sn-C(1)	111.0(5)
C(13)-Sn-C(7)	111.1(5)	C(19)-Sn-C(1)	104.1(5)
C(19)-Sn-C(7)	106.1(5)	C(19)-Sn-C(13)	108.1(5)
C(20)-S(1)-N(1)	27.6(5)	C(20)-S(1)-N(1)	62.5(6)
C(20)-S(1)-C(19)	90.0(7)	C(25)-S(1)-N(1)	30.4(4)
C(25)-S(1)-C(19)	57.9(5)	C(25)-S(1)-C(20)	32.1(6)
C(19)-N(1)-S(1)	39.2(7)	C(25)-N(1)-S(1)	75.1(8)
C(25)-N(1)-C(19)	114.0(1)	C(2)-C(1)-Sn	120.0(1)
C(6)-C(1)-Sn	120.0(1)	C(6)-C(1)-C(2)	119.0(1)
C(3)-C(2)-C(1)	120.0(1)	C(4)-C(3)-C(2)	119.0(2)
C(5)-C(4)-C(3)	121.0(2)	C(6)-C(5)-C(4)	121.0(2)
C(5)-C(6)-C(1)	120.0(1)	C(8)-C(7)-Sn	120.0(1)
C(12)-C(7)-Sn	119.0(1)	C(12)-C(7)-C(8)	121.0(1)
C(9)-C(8)-C(7)	120.0(1)	C(10)-C(9)-C(8)	121.0(2)
C(11)-C(10)-C(9)	118.0(2)	C(12)-C(11)-C(10)	121.0(2)
C(11)-C(12)-C(7)	118.0(2)	C(14)-C(13)-Sn	120.0(1)
C(18)-C(13)-Sn	120.0(1)	C(18)-C(13)-C(14)	119.0(1)
C(15)-C(14)-C(13)	120.0(1)	C(16)-C(15)-C(14)	121.0(2)
C(17)-C(16)-C(15)	121.0(2)	C(18)-C(17)-C(16)	118.0(2)
C(17)-C(18)-C(13)	121.0(1)	S(1)-C(19)-Sn	121.7(7)
N(1)-C(19)-Sn	125.0(1)	N(1)-C(19)-S(1)	113.0(1)
C(25)-C(19)-Sn	158.6(8)	C(25)-C(19)-S(1)	79.7(6)
C(25)-C(19)-N(1)	33.7(7)	C(21)-C(20)-S(1)	129.0(1)
C(25)-C(20)-S(1)	108.0(1)	C(25)-C(20)-C(21)	122.0(1)
C(22)-C(21)-C(20)	118.0(2)	C(23)-C(22)-C(21)	121.0(2)

Table 51 continued,

C(24)-C(23)-C(22)	123.0(2)	C(25)-C(24)-C(23)	117.0(2)
N(1)-C(25)-S(1)	74.5(8)	C(19)-C(25)-S(1)	42.4(4)
C(19)-C25)-N(1)	32.1(7)	C(20)-C(25)-S(1)	39.6(7)
C(20)-C(25)-N(1)	114.0(1)	C(20)-C(25)-C(19)	82.0(9)
C(24)-C(25)-S(1)	158.0(1)	C(24)-C(25)-N(1)	128.0(1)
C(24)-C(25)-C(19)	160.0(1)	C(24)-C(25)-C(20)	118.0(1)

(2) Crystallographic Analysis and Structural Refinement of [2-(2'-Pyridyl)ethyl]diphenyltin(IV) N,N-dimethyldithiocarbamate

(a) Crystal data:

$C_{22}H_{24}N_2S_2Sn$ MW= 499.28, triclinic, space group = p1, with

a = 9.611(4)Å, b = 10.255(3)Å, c = 12.896(9)Å

α = 75.35(4)Å, β = 70.97(4)Å, γ = 68.09(3)Å

V = 1102.19 $Å^3$, Z = 2, μ = 12.42 cm^{-1}, F000 = 504.0, Radiation Mo-Kα λ=0.71069 Å. For 2134 observed reflections with $I > 3\sigma I$, R = 0.0492 and R_w = 0.0542.

(b) Crystallographic Analysis:

A crystal of dimensions 0.2 x 0.2 x 0.1 mm was used for data collection. The crystal was glued onto a glass fibre and placed on the diffractometer. The intensities of all reflections with $2° < \theta < 22°$ were measured.

(c) Structure Solution and Refinement.

The structure was solved using a Patterson search, SHELX86 [256] and refined by full matrix least squares using SHELX76 [257]. Data were corrected for Lorentz and polarization effects, but not for absorption. Hydrogen atom postions were included in the calculation, [d(C-H)=1.08Å]. The tin, sulphur, nitrogen and carbon atoms (C(1)-C(5)) were refined anisotropically, while the remaining atoms were refined isotropically. The atomic scattering factors and the anomalous dispersion correction factors for both hydrogen and non-hydrogen atoms were taken from the literature [258-260]. The ORTEP program was used to obtain the drawings [251]. The cell packing diagram was obtained using PLUTO.

(3) Crystallographic Analysis and Structural Refinement of 2,3,4,5-tetraza-6-diphenylstannyl-[3.4]-bicyclonona-1,3-diene.

(a) Crystal Data:

$C_{16}H_{16}N_4Sn$ MW= 383.00, monoclinic, space group = $P2_1/C$, with

a = 14.544(3)Å, b = 13.267(7)Å, c = 17.147(4)Å.

β = 109.63(1) α = β.

V = 3116.36 $Å^3$, Z = 8, μ = 15.01 cm^{-1}, F000 = 1520.0, Radiation Mo-Kα

λ=0.71069 Å.

For 2844 unique and observed reflections with $I > 3\sigma I$ R = 0.0653 and

R_w = 0.0653.

(b) Crystallographic analysis:

A crystal with the approximate dimensions 0.38 x 0.2 x 0.2 mm was used for the data collection. The crystal was mounted on a glass fibre and placed on the diffractometer. The intensities of all reflections in the range 2° < θ < 22° were measured.

(c) Structure solution and refinement:

The structure was solved using a Patterson search, SHELX86 [256], and refined by full matrix least squares using SHELX76 [257]. Data were corrected for Lorentz and polarization effects and also for absorption. The hydrogen atoms were not included in the calculation.

The tin and the nitrogen atoms were refined anisotropically and the remaing atoms refined isotropically. the atomic scattering factors and the anomalous dispersion correction factors for non-hydrogen atoms were taken from the literature [258-260]. The ORTEP program was used to obtain the drawings [261]. The cell packing diagrams were obtained using PLUTO.

APPENDIX III

Instrument Details

(a) Infra-red Spectroscopy

Infra-red spectra were recorded as KBr discs or nujol mulls on KBr, CsI or NaCl plates using either a Perkin Elmer 599B or 597 spectrometer in the region 4000-200cm^{-1}. Calibration was with polystyrene film.

(b) N.M.R. Spectroscopy

^{1}H and ^{13}C nmr spectra were recorded on a JEOL GX 270 spectrometer using TMS as an internal standard. ^{119}Sn and ^{15}N spectra were recorded on a JEOL GX 400 (^{1}H decoupled) spectrometer and variable temperature ^{119}Sn spectra recorded at the International Tin Research Institute on a JEOL FX60 Q spectrometer. Chemical shifts [δ(^{119}Sn)] for the tin spectra are relative to Me_4Sn.

(c) Mass spectrometry

Mass spectra were collected on a V.G. 70-70E instrument with a DS2025 data system under electron ionisation (70eV) or chemical ionisation (iso-butene) conditions.

(d) Microanalysis

Carbon, hydrogen and nitrogen were analysed for using a Carlo Erba Strumentazione E.A. mod 1106 analyser at the University of Bath.

(e) Mossbauer

Mossbauer spectra were recorded on a constant acceleration Mossbauer spectrometer (Cryophysics) fitted with a 10mCi calcium stannate-^{119m} source (Amersham Int.) and operated in sawtooth wave mode. The sample temperature was controlled using a continuous flow liquid nitrogen cryostat linked to a DTC-2 digital variable temperature controller (Oxford Instruments). Temperature stability was +/- 0.1K of the set temperature. The source was at room temperature. Samples were prepared as finely ground powders. Calibration was based on the spectrum of natural iron with ^{119}Sn chemical shifts quoted relative to SnO_2 (zero velocity). Spectra were fitted to Standard Lorenzian line shapes, with a correction for parabolic background curvature using a conventional least squares fit technique.

References

(1) V.P. Neuman, 'The Organic Chemistry of Tin', Wiley, London, 1970

(2) R.C. Poller, 'The Chemistry of Organotin Compounds'. Logos London, (1970).

(3) 'Organotin Compounds', ed. A.K. Sawyer, Dekker, New York, 1971.

(4) A.G. Davies and P.J. Smith, *Adv. Inorg. Chem. Radiochem.* 23, 1, (1980).

(5) A.G. Davies and P.J. Smith,'Comprehensive Organometallic Chemistry' eds. G. Wilkinson; F.G.A Stone and E.W. Abel, Permagon Press, Oxford, (1982) ,p.519

(6) P.G. Harrison, *Coord. Chem. Rev.* 75, 200, (1986)

(7) R.J. Hulme, *J. Chem. Soc.* 1524, (1963)

(8) J.D. Cotton; P.J. Davidson; M.F. Lappert; J.D. Donaldson; and J.J. Silver, *J. Chem. Soc.; Dalton Trans.* 2286, (1976).

(9) J.A. Zubieta and J.J. Zuckerman, *Prog. Inorg. Chem.* 24, 251, (1978)

(10) P.A. Cusack; P.J. Smith; J.D. Donaldson and S.M. Grimes, "A Biblography of X-ray Structures of Tin Compounds", I.T.R.I, London, (1981), Publication no.588.

(11) A. Karipides; C. Forman; R.H.P. Thomas and A.T. Reed, *Inorg. Chem.* 13, 811, (1974).

(12) A. Karipides and K. Wolfe, *Acta. Crystallogr. Sect B.* 31, 605, (1975).

(13) A. Karapides; A.T. Reed; D.A. Haller and F. Hayes, *Acta Crystallogr. Sect B.* **33**, 950, (1977).

(14) C.J. Cardin; D.J. Cardin; J.M. Kelley; R.J. Norton; Abhijit Roy; B.J. Hathaway and T.J. King, *J. Chem. Soc. Dalton Trans.* 671, (1983)

(15) P.G. Harrison and K.C. Molloy, *J. Organometal. Chem.* **152**, 53, (1978).

(16) J.E. Weidenborner; R.B. Larrabee and A.L. Bednowitz, *J. Amer. Chem. Soc.* **94**, 4140, (1972).

(17) A.G. Davies; M.-W. Tse; J.D. Kennedy; W. McFarlane; G.S. Pyne, ; M.F.C. Ladd and D.C. Povey, *J. Chem. Soc.; Chem. Commun.* 791, (1978).

(18) M.J.S. Gyanne; M.F. Lappert; S.J. Miles; A.J. Carty and N.J. Taylor, *J. Chem. Soc. Dalton Trans.* 2009, (1977).

(19) P.L. Clarke; M.E. Cradwick and J.L. Wardell, *J. Organomet. Chem.* **63**, 279 (1973).

(20) H. Puff; R. Galtmeyer; R. Hundt and R. Zimmer, *Angew. Chem. Int. Ed. Engl.* **16**, 547, (1977)

(21) B. Menzebah and P. Bleckman, *J. .Organometal. Chem.* **91**, 291, (1975).

(22) D. Kobelt; E.F. Paulus and H. Scherer, *Acta. Crystallogr. Sect. B.* **28**, 2323, (1972).

(23) J.S. Tse; M.J. Collins; F.L. Lee and E.J. Gabe, *J. Organometal. Chem.* **310**, 169, (1986)

(24) S.W. Ng.; C. Wei; V.G. Kumar Das and T.C.W. Mak, *J. Organometal. Chem.* **326**, C61, (1987)

(25) S.W. Ng.; C. Wei; V.G. Kumar Das and T.C.W. Mak, *J.*

Organometal. Chem. **334**, 283, (1987)

(26) V.S. Petrosyan and O.A. Reutov, *Pure. Appl. Chem.* **147**, 37, (1974).

(27) A. Tzschach and K. Jurkschat, *Pure. Appl. Chem.* **58**, 639, (1986).

(28) E.O. Schlemper and D. Britton, *Inorg. Chem.* **5**, 507, (1966).

(29) D.W. Allen; D.J. Derbyshire; I.W. Nowell and J.S. Brooks, *J. Organomet. Chem.* **260**, 263, (1984).

(30) G.Van Noten; J.G. Noltes and A.L. Spek, *J. Organometal. Chem.* **118**, 183, (1978).

(31) K.C. Molloy and K. Quill, *J. Chem. Soc. Dalton. Trans.* 1417, (1985).

(32) T.J. King and P.G. Harrison, *J. Chem Soc. Dalton Trans.* 2298, (1974).

(33) P.G. Harrison; K. Lambert; T.J. King and B. Majee, *J. Chem. Soc. Dalton Trans.* 363, (1983).

(34) F.W.B Einstein and B.R. Penfold, *J. Chem. Soc. (A).* 3019, (1968).

(35) D.L. Evans and B.R. Penfold, *J. Cryst. Molec. Struct.* 5, 93, (1975).

(36) M. Webster; K.R. Mudd and D.J. Taylor, *Inorg. Chim. Acta.* **20**, 231, (1976).

(37) A. Tzschach; K. Ponicke; L. Korecz and K.J. Burger, *J. Organometal. Chem.* **59**, 199, (1973).

(38) V.G. Kumar Das; L.K. Mun; C. Wei and T.C.W. Mak, *Organometallics.* **6**, 10, (1987).

(39) K.C. Molloy; T.G. Purcell; K. Quill and I.W. Nowell, *J. Organometal. Chem.* **267**, 237, 1984.

(40) B.K. Nicholson, *J. Organometal. Chem.* **265**, 153, (1984).

(41) E.O. Schlempler and W.C. Hamilton; *Inorg. Chem.* **5**, 995, (1966).

(42) A.G. Davies; H.J. Milledge; D.C. Puxley and P.J. Smith, *J. Chem. Soc. A.* 2862, (1970).

(43) N.W. Alcock and J.F. Sawyer, *J. Chem Soc. Dalton Trans.* 1090, (1977).

(44) Y.M. Chow, *Inorg. Chem.* **9**, 794, (1970)

R.A. Forder and G.M. Sheldrick, *J. Organometal. Chem.* **22**, 611, (1970).

(45) N.G. Bokii; Yu. T. Struckov.and A.K. Prokof'ev, *J. Struct. Chem.* . **13**, 619, (1972).

(46) P.T. Green and R.F. Bryan, *J. Chem. Soc. A.* 2549, (1971).

(47) K.C. Molloy; G. Tagliavini; P. Ganis and D. Furlani, *Inorganica Chemica. Acta.* **141**, 7, (1988).

(48) K.C. Molloy; K. Quill and I.W. Nowell, *J. Organometal. Chem.* **289**, 271, (1985).

(49) P. Ganis; G. Valle; D. Furlani and G. Tagliavini, *J. Organometal. Chem.* **301**, 165, (1986).

(50) G.A. Miller and E.O. Schlemper, *Inorg. Chem.* **12**, 677, (1973).

(51) P.G. Harrison; T.J. King and M.A. Healy, *J. Organometal. Chem.* **182**, 17, (1979).

(52) T. Kimura; T. Ueki; N. Yasuoka; N. Kasai and M. Kakudo, *Bull. Chem. Soc. Japn.* **42**, 2479, (1969).

(53) E.O. Schlemper, *Inorg. Chem.* **6**, 2012, (1967).

(54) P.F. Lindley and P. Carr, *J. Cryst. Molec. Struct.* **4**, 173, (1974).

(55) P.G. Harrison and A. Mangia, *J. Organometal. Chem.* **120**, 211, (1976).

(56) L.A. Aslanov; V.M. Ionov; W.M. Attiya and A.B. Permin, *J. Struckt. Chem.* **19**, 166, (1978).

(57) G.S. Brownlee; A. Walker; S.C. Nyberg and J.T. Szymanski, *J. Chem. Soc.; Chem. Commun.* 1073, (1971).

(58) C. Pelizzi; G. Pelizzi and G. Predieri, *J. Organometal. Chem.* **263**, 9, (1984).

(59) T. Tanaka, *Organometal. Chem. Rev. (A)*, **5**, 1, (1970).

(60) Y. Limouzin and J.C. Maire, *Adv. Chem. Ser.* **157**, 227, (1976)

(61) A.G. Davies; A.J. Price; H.M. Dawes and M.B. Hursthouse, *J. Chem. Soc.; Dalton Trans.* 297, (1986).

(62) K.C. Molloy, *Inorganica Chemica Acta.* **141**, 151, (1988).

(63) R.K. Harris; P. Reams and K.J. Packer, *J. Molec. Struct.* **141**, 13 (1986).

(64) A.G. Davies and S.D. Slater, *Silicon, Germanium, Tin and Lead Compounds, IX,* **87**, (1986).

(65) R.R. Holmes; R.O. Day; V. Chandrasekhar; J.F. Vollano and J.M. Holmes, *Inorg. Chem.* **25**, 2490, (1986).

(66) R. Barloutard; E. Cotton; J.-L. Picou and J. Quidort, *C.R. Hebd. Seances. Acad. Sci.* **250**, 319, (1960).

(67) J. J. Zuckerman, *Adv. Organometal. Chem.* **9**, 21, (1970).

(68) J. R. Ruddick, 'A Review of ^{119m}Sn Mossbauer Data Published in the Period 1970-74'.

(69) G.M. Bancroft and R.H. Platt, *Adv. Inorg. Radiochem.* **15**, 59, (1976).

(70) J.J. Zuckerman, in "Chemical Mossbauer Spectroscopy". ed. R.H. Herber, Plenum. New York. 267-293. (1984).

(71) R.V. Parish, "Mossbauer Spectroscopy and Chemistry", 1 & 2 *Chem. in Brit.* June/Aug 1985.

(72) N.N. Greenwood and T.C. Gibb, " Mossbauer Spectroscopy", Chapman and Hall, London (1971).

(73) A. Vertes, L. Korecz and K. Burger, "Mossbauer Spectroscopy", Elsevier, (1979).

(74) V.I. Goldanski and R.H. Herber, "Chemical Applications of Mossbauer Spectroscopy", Academic Press (1968), London.

(75) G.M. Bancroft, "Mossbauer Spectroscopy-An Introduction for Chemists and Geochemists", Mcgraw-Hill (London), (1973).

(76) P.J. Smith, *Organometal. Chem. Rev. (A).* **5**, 373, (1970).

(77) R.V. Parish, *Prog. Inorg. Chem.* **15**, 101, (1972).

(78) B.W. Fitzsimmons, N.J. Seeley and A.V. Smith, *J. Chem. Soc. (A).* 143, (1969).

(79) R.V. Parish and R.H. Platt, *J. Chem. Soc. (A).* 2145, (1969).

(80) T.K. Sham and G.M. Bancroft, *Inorg. Chem.* **14**, 2281, (1975).

(81) P.G. Harrison, *Adv. Chem. Ser.* **157**, 258, (1976).

(82) K.C. Molloy and K. Quill, *J. Chem. Soc.; Dalton Trans.* 1417, (1985)

(83) P.J. Smith and P. Tupciauskas, Annu. Rev. N.M.R. Spec. **8**, 291, (1978).

(84) V.S. Petrosyan, *Prog. N.M.R. Spec.* **11**, 115, (1977).

(85) B. Wrackmeyer, *Ann. Rep. N.M.R. Spec.* **16**, 73, (1985).

(86) J.D. Kennedy and W. Mc.Farlane, *Rev. Si. Ge. Sn. Pb.* **1**, 235, (1974)

(87) R.K. Harris and B.E. Mann, "N.M.R. and the Periodic Table", Academic Press (1978).

(88) J. Mason, ed. "Multinuclear N.M.R.", Plenum press, New York and London, (1987).

(89) B.K. Hunter and L.W. Reeves, *Can. J. Chem.* **46**, 1399, (1968).

(90) P.J. Smith and L. Smith, *Inorganic Chem. Reviews*, ed. Groatto, U. **7**, 11, (1973).

(91) A.A. Cheremisin and P.V. Schastnev, *J. Magn. Reson.* **40**, 459, (1980).

(92) J.J. Burke and P.C. Lauterbur, *J. Amer. Chem. Soc.* **83**, 326, (1961).

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

(94) W. McFarlane and R.J. Wood, *J. Organometal. Chem.* **40**, C17, (1972)

(95) J. Otera, *J. Organomet. Chem.* **221**, 57, (1981).

(96) J. Otera; A. Kusaba; T. Hinoishi and Y. Kawasaki, *J. Organometal. Chem.* **228**, 223, (1982).

(97) J.D. Kennedy; W. McFarlane and G.S. Pyne, *Bull. Soc. Chim. Belge.* **84**, 289, (1975).

(98) T.P. Lockhart and W.F. Manders, *Inorg. Chem.* **25**, 892, (1986).

(99) T.P. Lockhart; W.F. Manders and J.J. Zuckerman, *J. Am. Chem. Soc.* **107**, 4546, (1985).

(100) J. Holecek; M. Nadvornik; K. Handir and A. Lycka, *J. Organometal. Chem.* **241**, 177, (1983).

(101) R.A. Cummins and P. Dunn, "The Infra-red spectra of organotin compounds", *Aust. Def. Sci. Ser. Report No. 266.* (1963).

(102) R. Okawara and M. Wada, *Adv. Organometal. Chem.* **5**, 137, (1967).

(103) R. Okawara; D.E. Webster and E.G. Rochew, *J. Amer. Chem. Soc.* **82**, 3287, (1960).

(104) R. Mathias-Noel; M. Lesbre and I. Seree de Roche, *C.R. Rebd. Seances Acad. Sci.* **243**, 257, (1956).

(105) M.C. Henry and J.G. Noltes; *J. Amer. Chem. Soc.* **82**, 555, (1960).

(106) H. Kriegsmann and S. Pitschschan, *Z. Anorg. Allg. Chemie.* **308**, 212, (1961)

(107) F.W. Behnke and C. Tamborski, ASTIA AD 274995 Tech. Doc. Rep. No. ASD-TDR-62-224

(108) R.C. Poller, *J. Inorg. Nucl. Chem.* **24**, 593, (1962).

(109) D.B. Chambers; F. Glockling and M. Watson, *J. Chem. Soc. (A)* 1759, (1967).

(110) W.D. Jamieson; S. Safe and O. Hutzinger; Chemical Institute of Canada Conference, Halifax, N.S. Canada, June, (1971).

(111) E. Hartmann; M. Hardtmann and P. Kummel, *U.S. Pat. 1,744,633* (1930).

(112) G.J.M. van der Kerk and J.G.A. Luijten, *J. Appl. Chem.* **4**, 314, (1954).

(113) A.G. Davies and P.J. Smith, *Adv. Inorg. Chem. Radiochem.* **23**, 1, (1979).

(114) A. Tzschach and K. Ponicke, *Kem. Kozlem.* **41**, 141, (1974).

(115) G. van Koten; C.A. Schaap and J.G. Noltes, *J. Organometal. Chem.* **99**, 157, (1975).

(116) B. Svatun and A. Attramadel, *Acta Odontol. Scand.* **36**, 211, (1978)

(117) P.J. Smith and L. Smith, *Chem. Ber.* **11**, 208, (1975).

(118) F. Caujolle; M. Lesbre and D. Meynier, *C.R. Acad. Sci. Paris* **239**, 556, (1954).

(119) J.E. Cremer, *Biochem. J.* **68**, 685, (1958).

(120) W.N. Aldridge, p.186 in "Organotin Compounds: New chemistry and Applications", ed. J.J. Zuckerman, *Adv. Chem. Ser.* **157**, 227, (1976).

(121) P.J. Smith, "Toxicological Data on Organotin Compounds", Int. Tin. Res. Inst. Public. No. 538 (1978).

(122) R.F. Steiner, "Life Chemistry: An Introduction to Biochemistry" (1968).

(123) W.N. Aldridge and B.W. Street, *Biochem. J.* **91**, 287, (1964).

(124) M.J. Selwyn; A.P. Dawson; M. Stockdale and N. Gains, *Eur. J. Biochem.* **14**, 120, (1970).

(125) W.N. Aldridge and B.W. Street, *Biochem. J.* **118**, 171, (1970).

(126) B.M. Elliot and W.N. Aldridge, *Biochem. J.* **163**, 583, (1977)

(127) B.M. Elliot; W.N. Aldridge and J.W. Bridges, *Biochem. Soc. Trans.* **6**, 1252, (1978)

(128) B.M. Elliot; W.N. Aldridge and J.W. Bridges, *Biochem. J.* **177**, 461, (1979)

(129) B.G. Farrow and A.P. Dawson, *Eur. J. Biochem.* **86**, 85, (1978).

(130) R. Barbieri, G.Fis XXIII, 289, (1982).

(131) R.D. Barnes; A.T. Bull and R.C. Poller, *Pestic. Sci.* **4**, 305, (1973).

(132) A.M. Chapman and J.W. Price, *Int. Pest Control* **14**, 11, (1972).

(133) P. Cenci and B. Cremonini, *Ind. Sacc. Ital.* **62**, 313, (1969).

(134) H. Waggon and D. Jehle, *Nahrung* **19**, 271, (1975).

(135) P.J. Smith; A.J. Crowe; D.W. Allen; J. Brookes and R. Formstone, *Chem. Ind. (London)* 874, (1977).

(136) V.T. Mazaev; O.V. Golovanov; A.S. Igumnov and V.H. Tsay, *Gig. Sanit.* 17, (1976)

(137) A.W. Sheldon, *J. Paint Technol.* **47**, 54, (1975).

(138) W.P. Ridley; L.J. Dizikes and J.M. Wood, *Science* **197**, 329, (1977).

(139) C. Huey; S. Brinkman and W.P. Iverson, *Proc. Internat. Conf. Transp. Persist. Chem. Aquat. Ecos.* ed. Q.N. Leham, N.R.C. Ottawa, 73, (1974).

(140) Y.K. Chau; P.T.S. Wong; O. Kramar and G.A. Bengert, Abstract of the International Conference on Heavy Metals in the Environment, Amsterdam, Sept. (1981)

(141) P.J. Craig and S. Rapsomanikis, *J. Chem. Soc.; Chem. Commun.* 114, (1982).

(142) N.I.O.S.H. Registry of Toxic Effects of Chemical Substances Washington (1979).

(143) The Merck Index ed. M. Windholz, Merck, Rahway 9th.. Ed. (1976).

(144) W.C. Bowan and M.J. Rand, "Textbook of Pharmacology", 2nd. Ed. Blackwall, (London) (1980).

(145) M.R. Boyd, *Nature* **269**, 713, (1977).

(146) E. MacDonald; E. Ihalainen and J.P. Pispa, *Acta. Pharmacol. Toxicol.* **48**, 418, (1981).

(147) T.D. Rogerson and C.F. Wilkinson; K. Hetarski, *Biochem. Pharmacol.* **26**, 1039, (1977).

(148) G.W. Ware, "Pesticides: Theory and Application", W.H. Freeman and Co. San Francisco (1978).

(149) B. Sugavanam, "Organotins in Agriculture", Int. Tin Res. Inst. Public. No. 607.

(150) A. Maric; S. Maserevic and Z. Jerkovic, *Zast. Bilja.* **35**, 207, (1984).

(151) A. Formigoni, *Fr. Pat. 2,443,203* (1980).

(152) P. Damotte and F. Colliot, *Fr. Pat. 2,507,861* (1982).

(153) Int. Tin. Res. Inst. Public. No. DS4.

(154) R.S. Tobias, *Organometal. Chem. Rev.* **1**, 93, (1966)

(155) A.G. Davies; J.P. Goddard; M.B. Hursthouse and P.C. Walker, *J. Chem. Soc.; Chem. Commun.* 597, (1983).

(156) P.G. Harrison, ed. "Organometallic Compounds of Ge, Sn and Pb." Chapman and Hall (London) (1985).

(157) K. Sisido; K. Nabika; T. Isida and S. Kozima, *J. Organometal. Chem.* **33**, 337, (1971).

(158) S. Kozima; T. Itano; N. Mihara; K. Sisido and T. Isida, *J. Organometal. Chem.* ***44**, 117, (1972).*

(159) Sumitomo Chemical Co. LTD. Jap. Pat. 82,72,905 (1982).

(160) Albright and Wilson LTD. *Can. Pat. 999,155* (1976).

(161) P. Jutzi and U. Gilge, *J. Heterocyclic. Chem.* **20**, 1011, (1983).

(162) P. Jutzi and U. Gilge, *J. Organometal. Chem.* **246**, 159, (1983).

(163) C. Parkanyi; N.S. Cho and G.S. Yoo, *J. Organometal. Chem.* **342**, 1, (1988)

(164) I. Fleming and M. Taddei, *Synthesis* 898, (1985)

(165) D.W. Allen; D.J. Derbyshire and I.W. Nowell, *J. Organometal. Chem.* **260**, 263, (1984).

(166) E.F. Godefroi and J.L. Schuermans, Ger Pat. 2063857 (1971) C.A. **75**, 118319, (1971).

(167) Comprehensive Heterocyclic Chemistry **VI**, 203.

(168) "Antimicrobial Drug Action" , D.I. Edwards (1980), Macmillan, p.317

(169) "Principles of Fungicidal Action", J.G. Horsefall PhD (1956), Chronica Botanica Co., p.67

(170) I.R. Rowland; B.G. Lake; J.C. Phillips and S.D. Gangolli, *Mutat. Res.*, **72**, 63, (1980)

(171) E. Marchetti; G. Mattalia and V. Rosnat, *J. Med. Chem.* **11**, 1092, (1968)

(172) I.J. Turchi and M.J.S. Dewar, *Chem. Rev.*, **75**, 432, (1975) and references therin.

(173) N.N. Ragsdale in "Antifungal Compounds" ed. M.R. Siegel; H.D. Sisler, Dekker, New York, **2**, 333, (1977)

(174) B. Iddon and B.L. Lim., *J. Chem. Soc.; Perkin Trans. I*,. 272, (1983)

(175) Y. Watanabe; Y. Ueno; T. Araki; T. Endo and M. Okawara, *Tetrahedron Letts.* **27**, 215, (1986)

(176) Comprehensive Heterocyclic Chemistry, **VI**, 357.

(177) R. Hodges and M. Grimmett, *Aust. J. Chem.*, **21**, 1085, (1968)

(178) B.J. Millard and A.F. Temple; *Org. Mass Spec.*, **1**, 285, (1968)

(179) Comprehensive Organometallic Chemistry, **11**, 530

(180) J. Holecek and A. Lycka; *Inorganica Chemica Acta*, **118**, L15-16, (1986)

(181) J.E. Phillips and R.H. Herber, *J. Organometal. Chem.* **268**, 39, (1984)

(182) H. Chikashita; S. Ikegami; T. Okumura and K. Itoh, *Synthesis*, 375, (1986)

(183) R.K. Ingham; S.D. Rosenberg and H. Gilman, *Chem. Rev.*, **60**, 459, (1960)

(184) H. Gilman and J.A. Beel, *J. Am. Chem. Soc.*, **71**, 2328, (1949)

(185) C. Rai and J.B. Braunworth, *J. Org. Chem.*, **26**, 3434, (1961)

(186) G.J.M. Van der Kerk; J.G. Noltes and J.G.A Luijten, *J. Appl. Chem.* **7**, 366, (1957)

(187) E.J. Corey and D.L. Boger, *Tetrahedron Letts.* **1**, 5, (1978)

(188) C.L. Foy in "Herbicides: Chemistry, Degradation and Modes of Action" eds. P.C. Kearney; D.D. Kaufman, Dekker, New York, 2nd edn. **2**, 777, (1976).

(189) J.P. Phillips, *Chem. Rev.*, **56**, 217, (1956)

(190) S.J. Blunden; B.N. Patel; P.J. Smith and B. Sugavanam, *Appl. Organometal. Chem.*, **1**, 241, (1987)

(191) A.O. Wolfe in "Antibiotics", Springer-Verlag, New York,. **3**, 623, (1975)

(192) A. Kleeman, *Chem.-Ztg.*, **101**, 389, (1977)

(193) H. Beschke; A. Kleeman; W. Clauss; W. Kurze; K. Mathes and S. Habersang, "Ullmans Encyclopaedie der Technischen Chemie", **19**, 591, (1980)

(194) K.C. Molloy; S.J. Blunden and R. Hill, *J. Chem. Soc.; Dalton Trans.* 1259, (1988)

(195) E.M. Holt; F.A.K. Nasser; A. Wilson, Jr. and J.J. Zuckerman, *Organometallics*, **4**, 2073, (1985)

(196) L. Verdonck and C.P. Van der Kelen, *J. Organometal. Chem.*, **11**, 491, (1968)

(197) M. Gielen, *Bull. Soc. Chim. Belge.*, **92**, 409, (1983)

(198) S.Z. Abbas and R.C. Poller, *J. Chem. Soc.; Dalton Trans.*, 1769, (1974)

(199) H.C. Clark and R.C. Poller, *Can. J. Chem.*, **48**, 928, (1970)

(200) A.G. Maddock and R.H. Platt, *J. Chem. Soc. (A)*, 1191, (1971)

(201) R. Barbieri; F. DI Bianca; E. Rivarola and F. Huber, *Inorganica Chemica Acta*, **108**, 141, (1985)

(202) K. Kim; J.A. Ibers; O.S. Jung and Y.S. Sohn, *Acta Cryst.*, **C43**, 2319, (1987)

(203) J. Potenza; R.J. Johnson and D. Mastropaolo, *Acta. Cryst.*, **B32**, 941, (1976)

(204) V.G. Kumar Das; C. Wei and E. Sinn, *J. Organometal. Chem.* in press.

(205) V.G. Kumar Das; C. Wei and E. Sinn, *Inorg. Chim. Acta.* in press

(206) K. Furue; T. Kimura; N. Yasuoka; N. Kasai and M. Kakudo, *Bull. Chem. Soc. Jap.*, **43**, 1661, (1970)

(207) P.F. Lindley and P. Carr, *J. Cryst. Molec. Struct.*, **4**, 173, (1974)

(208) G. Van Koten; J.T.B.H. Jastrzebski; J.G. Noltes; W.M.G.F. Potenagel; J. Kroon and A.L. Spek, *J. Am. Chem. Soc.*, **100**, 5021, (1978)

(209) G. Van Koten; J.T.B.H. Jastrzebski; J.G. Noltes; G.J. Verhoeck ; J. Kroon and A.L. Spek, *J. Chem. Soc.; Dalton Trans.*, 1352, (1980)

(210) N.G. Bokii; Yu. T. Struchkov; D.N. Kravstov and E.M. Rokhlina, *J. Struct. Chem.*, **14**, 458, (1973)

(211) G.J.M. Van der Kerk; J.G. Noltes and J.G.A. Luijten, *J. Appl. Chem.* **7**, 356, (1957)

(212) G.J.M. Van der Kerk and J.G. Noltes, *J. Appl. Chem.* **9**, 106, (1959)

(213) E. Czerwinska; Z. Eckstein; Z. Ejmocki and R. Kowalik, *Bull. Acad. Pol. Sci. Ser. Sci. Chim.*, **15**, 335, (1967)

(214) K.C. Molloy; T.G. Purcell; D. Cunningham; P. McCardle and T. Higgins, *Appl. Organometal. Chem.*, **1**, 119, (1987)

(215) R.D. Brasington and R.C. Poller, *J. Organometal. Chem.*, **40**, 115, (1972)

(216) R.D. Taylor and J.L. Wardell, *J. Organometal. Chem.*, **77**, 311, (1974)

(217) J.H. Nelson; V. Cooper and R.W. Rudolph, *Inorg. Nucl. Chem. Lett.*, **16**, 263, (1980)

(218) P.F. Juby; T.W. Hudyma and M. Brown, *J. Med. Chem, 11, 111, (1968)*

(219) R.L. Buchanan; V. Sprancmanis and R.A. Partyka, J. Med. Chem., **12**, 1001, (1969)

(220) J.M. Essery, *J. Med. Chem.*, 12, 703, (1969)

(221) G.P. Ellis and D. Shaw, *J. Med. Chem.*, **15**, 865, (1972)

(222) R.M. Herbst in "Essays in Biochemistry", (S. Groff, ed.), p 141 Wiley, New York, (1956)

(223) D.W. Esplin and D.M. Woodbury, *J. Pharmacol. Exp. Therap.*, **118**, 129, (1956)

(224) B.A. Dreikorn, *Ger. Offen.* 2,134,146 (1972) [CA **76** 99676 (1972)

(225) E.F George and V.D. Ridell, *Ger. Offen*, 2,310,049 (1973) [CA **80** 23539 (1974)]

(226) T. Kamatani; S. Tsubouchi and N. Yamamoto, *Jap. Pat.*, 71 35742 (1971) [CA **76** 14550 (1972)]

(227) H.D. Torre, *Ger. Offen*, 1, 914, 553. [CA **72** 12736]

(228) E.F.V. Scriven and K. Turnbull, *Chem. Rev.*, **88**, 351, (1988)

(229) M. Pereyre; J-P. Quintard and A. Rahm, in "Tin in Organic Synthesis", Butterworths, London, p.308. (1987)

(230) K. Sisido; K. Nabika; T. Isida and S. Kozma, *J. Organometal. Chem.*, **33**, 337, (1971)

(231) A.G. Davies and J.D. Kennedy; *J. Chem. Soc.*, **(C)**, 759, (1970)

(232) A.R. Katritsky and C.W. Rees, Comprehensive Heterocyclic Chemistry, **V**, p.797, (1984)

(233) G.B. Ansell, *J. Chem. Soc.; Perkin Trans. II*, 2036, (1973)

(234) N.C. Baenziger; A.D. Nelson; A. Tulinsky; J.H. Bloor and A.I. Popov, *J. Am. Chem. Soc.*, **89**, 6463, (1967)

(235) N.C. Baenziger and R. Schultz, *Inorg. Chem.*, **10**, 661, (1971)

(236) R.L. Bodner and A.I. Popov, *Inorg. Chem.*, **11**, 1410, (1972)

(237) R.H. Erlich and A.I. Popov, *J. Phys. Chem.*, **74**, 338, (1970)

(238) H.W. Roesky; M. Witt; M. Diehl; I.W. Bats and H. Fuess, *Chem. Ber.* **112**, 1372, (1979)

(239) R. Allman; R. Hohlfeld; A. Waskowska and J. Lorberth, *J. Organometal. Chem.*, **192**, 353, (1980)

(240) M. Birkhahn; R. Hohlfeld; W. Massa; R. Schmidt and J. Lorberth, *J. Organometal. Chem.*, **192**, 47, (1980)

(241) R.A. Forder and G.M. Sheldrick, *J. Organometal. Chem.*, **21**, 115, (1970)

(242) Y.M. Chow, *Inorg. Chem.*, **10**, 1938, (1971)

(243) R.A. Forder and G.M. Sheldrick, *J. Chem. Soc.*, **A**, 1107, (1971)

(244) I. Hammann; K.H. Buchel; K. Bungarz and L. Born, *Pflanzen-Nachrichten Bayer*, **31**, 61, (1978)

(245) J.S. Thayer and R. West, *Inorg. Chem.*, **3**, 889, (1964)

(246) W.T. Reichle, *Inorg. Chem.*, **3**, 402, (1964)

(247) L. Birkofer and P. Wegner, *Chem. Ber.*, **99**, 2512, (1966)

(248) R.A. Henry, W.G. Finnegan and E. Lieber, *J. Amer. Chem. Soc.*, **76**, 88, (1954)

(249) W.L. Garbrecht and R.M. Herbst, *J. Org. Chem.*, **18**, 1269, (1953)

(250) J.C. Krauer and W.A. Sheppard, *J. Org. Chem.*, **32**, 3580, (1967)

(251) E.B. Baker and A.I. Popov, *J. Phys. Chem.*, **76**, 2403, (1972)

(252) L. Guibe and E.A.C. Lucken, *Molec. Phys.*, **14**, 73, (1968)

(253) A. Alvanipour, N.H. Buttrus, C. Eaborn, P.B. Hitchcock, A.I. Mansour and A.K. Saxena, *J. Organometal. Chem.*, **349**, 29, (1988)

(254) G.J.M. Van der Kerk; J.G. Noltes; J.G.A. Luijten, *J. Appl. Chem.*, **7**, 366, (1957)

(255) D. Seyferth; S.B. Andrews, *J. Organometal. Chem.*, **30**, 151, (1971)

(256) G.M. Sheldrick, SHELX86, A computer program for crystal structure determination, University of Goetingen 1986.

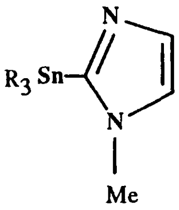
(257) G.M. Sheldrick, SHELX76, A computer program for crystal structure determination, University of Cambridge 1976.

(258) D.T. Cromer and J.B. Mann, *Acta. Crystallogr., Sect. A.* ***A24***, *321, (1968)*

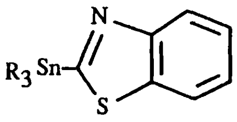
(259) R.F. Stewart, E.R. Davidson and W.T. Simpson, J. Chem. Phys. **42**, 3175, (1965)

(260) D.T. Cromer and D.J. Liberman, *J. Chem. Phys.*, **53**, 1891. (1970)

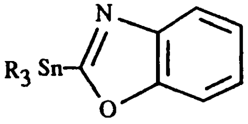
(261) C.K. Johnson, ORTEP, Oak Ridge Natl. Lab. (Rep.) ORNL. (US) 1965-3794 revised (1971).



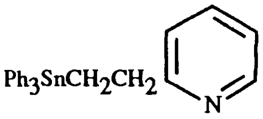
R = Me , Bu , Ph ;
(1) (2) (3)



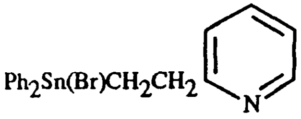
R = Me , Bu , Ph ;
(4) (5) (6)



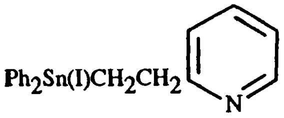
R = Ph
(7)



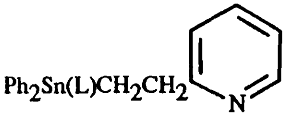
(8)



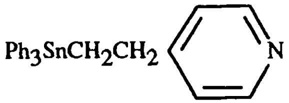
(11)



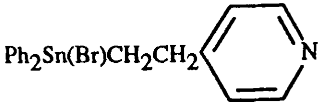
(13)



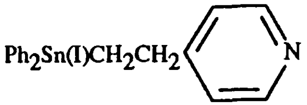
L = SC(S)NMe$_2$ **(16)**
L = SC(S)NEt$_2$ **(19)**
L = OAc **(20)**
L = OCOPh **(21)**



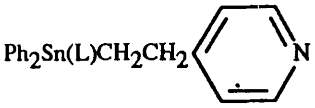
(9)



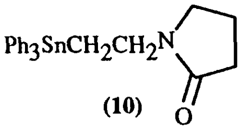
(12)



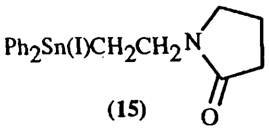
(14)



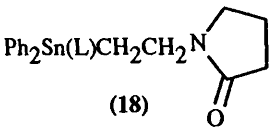
L = SC(S)NMe$_2$ **(17)**



(10)

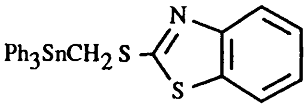


(15)

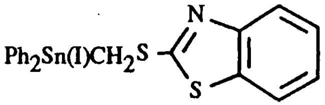


(18)

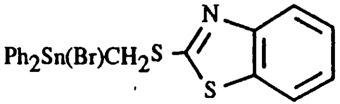
L = SC(S)NEt$_2$



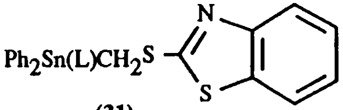
(22)



(26)

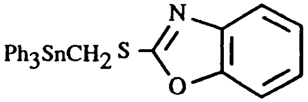


(27)

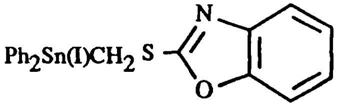


(31)

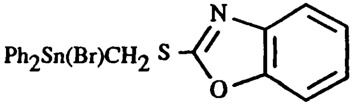
$L = SC(S)NEt_2$



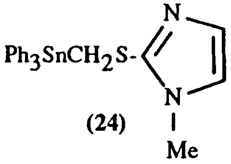
(23)



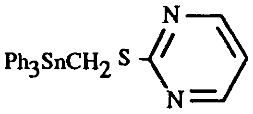
(28)



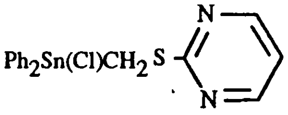
(29)



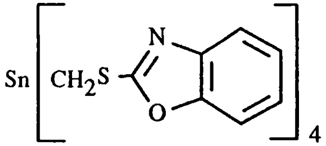
(24)



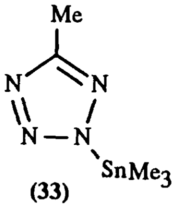
(25)

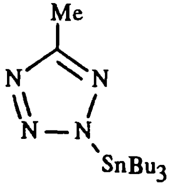


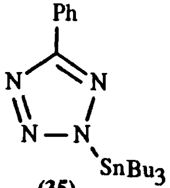
(30)

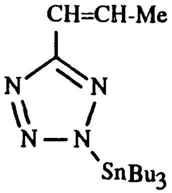


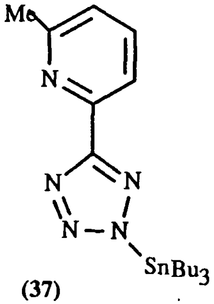
(32)

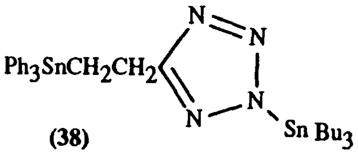

(33)

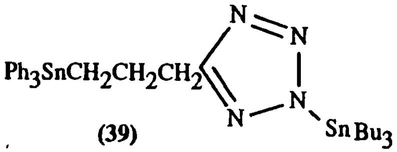

(34)

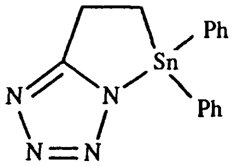

(35)

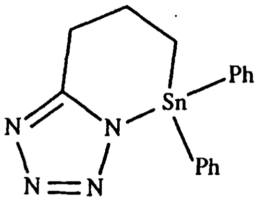

(36)

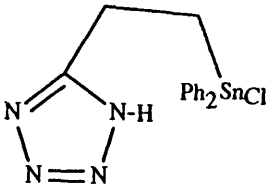

(37)

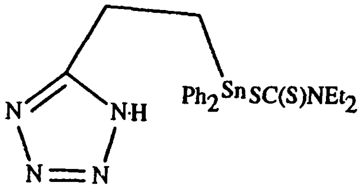

(38)

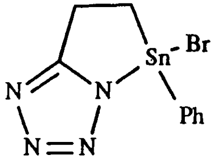

(39)


(40)


(41)


(42)


(43)


Sn
Br
Ph
N
N
N
N

(44)

Ph_2SnBu_2

(45)

$Ph(Br)SnBu_2$

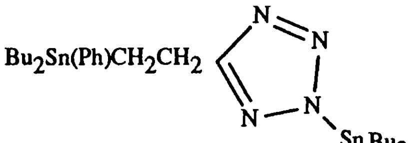
(46)

$Ph(H)SnBu_2$

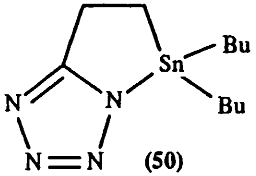
(47)

$Bu_2Sn(Ph)CH_2CH_2CN$

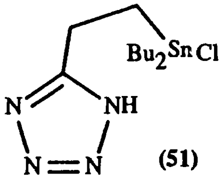
(48)


Bu2Sn(Ph)CH2CH2
N
N
N
N
SnBu3

(49)


Sn
Bu
Bu
N
N
N
N

(50)


Bu2SnCl
N
NH
N
N

(51)

Ph_2SnMe_2

(52)

$Ph(Br)SnMe_2$

(53)

$Ph(H)SnMe_2$

(54)