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FULL PAPER

Synthesis, characterisation and reaction chemistry of organotin-substituted bis(thiotetrazoles): supramolecular metallotetrazole structures containing hard and soft donors

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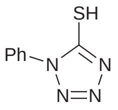
Four new organotin thiotetrazoles 1,4-$(R_3SnSCN_4)_2C_6H_4$ (R = Me, Et, Bu or Ph), along with their triphenyllead, diphenylthallium and phenylmercury analogues, have been synthesized. The supramolecular structure of 1,4-$(Bu_3SnSCN_4)_2C_6H_4$ has been found to consist of a 2-D sheet arrangement containing 32-membered $(C_4NCSSnN_2CSSnN_3)_2$ rings. In contrast, 1,4-$(Me_3SnSCN_4)_2C_6H_4$ crystallises as a bis(methanol) solvate in which 14-membered $(SnSCN_2HO)_2$ rings are linked through hydrogen bonds into a 1-D polymer.

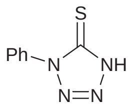
Introduction

We have been interested for some time in the supramolecular architectures created by organotin derivatives of polyfunctional tetrazoles.[1–3] The latter combine with various R_3Sn to yield products containing, without exception, the *trans*-N_2SnC_3 moiety, the linear N–Sn–N component of which acts as a rigid connector between azole units. The co-ordinatively versatile heterocycle, with four available donors all of which can be utilised in bonding in varying combinations, acts as a fulcrum about which lattice construction is orchestrated in two or more dimensions. Organotin tetrazoles thus represent an uncommon variant in supramolecular chemistry, where a combination of rigid ligands linking metals of various co-ordination numbers and stereochemistries *e.g.* $Cd(CN)_2$[4] is a more common approach to lattice construction.

In our previous work we have been able to use organotin tetrazoles to construct zigzag sheets [*e.g.* 1,2-$(Et_3SnN_4C)_2C_6H_4$],[1] planar sheets [*e.g.* 1,3,5-$(Bu_3SnN_4C)_3C_6H_3$],[3] bilayers [*e.g.* 1,6-$(Bu_3SnN_4C)_2(CH_2)_6$][2] and three-dimensional networks [*e.g.* 1,2-$(Bu_3SnN_4C)_2C_6H_4$].[1] In addition to ligand design, our experience suggests that the size of the hydrocarbon groups on tin also plays a crucial role in the way the lattice is constructed, by virtue of the fact that these groups need to be accommodated in any channels/cavities that are formed. The two variants of 1,2-$(R_3SnN_4C)_2C_6H_4$ cited above illustrate this point. Similar comments can be made about derivatives of the related ligand 1-phenyl-5-sulfanyl-1*H*-tetrazole (**I**), which we demonstrated some time ago preferentially co-ordinates through sulfur *via* its thiol (**Ia**), not thione (**Ib**), tautomer.[5]



Ia



Ib

Since we published the structure of $SnBu_2(SCN_4Ph)_2$, others have shown the ligand can act in a chelating [*e.g.* $SnPh_3(SCN_4Ph)$][6] or bridging manner, the latter generating both oligomers [*e.g.* $(Me_3SnSCN_4Ph)_3$][7] and polymers {*e.g.* $[(PhCH_2)_3SnSCN_4Ph]_\infty$}.[8] More recently, several neutral and anionic transition metal derivatives have also been structurally characterised[9] and we have discovered the first example of a potentially π-co-ordinated tetrazole in $PbPh_3SCN_4Ph$-1.[10] We now report our studies on the structural chemistry of 1,1′-*p*-phenylenebis[5(tributylstannylsulfanyl)tetrazole], 1,1′-*p*-phenylenebis[5-(trimethylstannylsulfanyl)tetrazole] (solvated with methanol) and related organometallic species, in which a polyfunctional tetrazole-based ligand containing both hard (N) and soft (S) donors is used as a component of supramolecular assemblies.

Results and discussion

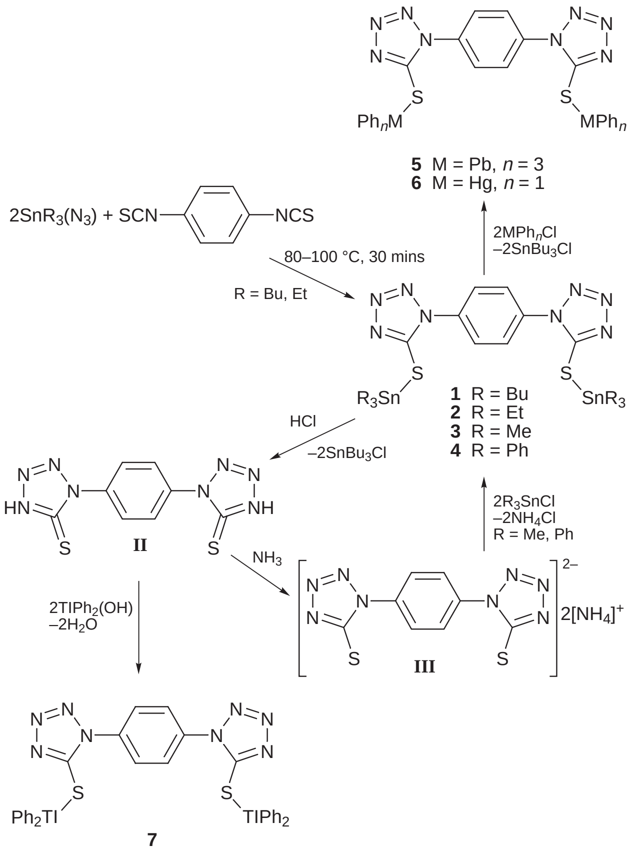
Synthesis

The cycloaddition of a triorganotin azide with 1,4-bis(isothiocyanato)benzene leads to the formation of **1** and **2** in yields in excess of 50% (Scheme 1). The course of the reactions was monitored by the disappearance of $\nu(N_3)$ and ν(NCS) in the IR spectra at *ca.* 2076 and 2112 cm^{-1}, respectively. Compound **1** was recrystallised from hot methanol but, surprisingly, **2** proved insoluble in alcohols.

Compound **1** was converted into the metal-free tetrazole **II** by refluxing with aqueous HCl, and the absence of an IR band at *ca.* 2550 cm^{-1} corresponding to ν(SH) suggests **II** probably exists in the thione form. Indeed, a band assignable to ν(C=S) was observed at 1049 cm^{-1}. The ammonium salt **III** was generated by bubbling ammonia through a solution of **II** for 30 min; **III** then enabled the synthesis of both trimethyl- and triphenyltin derivatives (**3**, **4**) by a salt elimination process, the former crystallising from methanol as a bis-solvate while the latter was unsolvated. Reaction of **1** with 2 equivalents of $PbPh_3Cl$ resulted in elimination of $SnBu_3Cl$ and formation of a bis(organolead) derivative **5**. The bis(phenylmercury) analogue **6** was prepared similarly but proved difficult to characterise structurally due to its insolubility. A condensation reaction involving **II** and $TlPh_2(OH)$ led to the diorganothallium analogue **7**, which crystallised as a dihydrate.

Spectroscopy

Table 1 gives the Mössbauer and NMR data for the triorganotin-substituted thiotetrazoles **1**–**4**. The quadrupole splittings (q.s.) for the three alkyltin species are in the range 3.32–3.39 mm s^{-1} which are consistent with a polymeric, five-co-ordinate *trans*-$XYSnC_3$ trigonal bipyramidal geometry in the solid state.[11] The arrangement (X = N, Y = S) has been confirmed in



Scheme 1

Table 1 The NMR [a] and Mössbauer data [b]

Compound	$\delta(^{119}Sn)$	$^1J(Sn–^{13}C)$ [c]	i.s.	q.s.	Ref.
$SnBu_3SCN_4Ph$	112.5	328	1.48	3.32	5
$SnPh_3SCN_4Ph$	−69.4		1.33	2.38	6
1	122.8	327	1.50	3.32	This work
2	−10.3	474	1.52	3.39	This work
3·2MeOH	−23.7	491, 515 [d]	1.38	3.35	This work
4	−65.0	—	1.22	2.29	This work
5	−235.5 [e]				This work

[a] For $(CD_3)_2SO$ solutions at 25 °C except for compound **4** which was heated to 100 °C; δ in ppm relative to $SnMe_4$, J in Hz. [b] Recorded at 78 K and data given as mm s^{-1}. [c] For unresolved $^{117,119}Sn$ couplings. [d] $^2J(^{117,119}Sn–^1H)$ (unresolved): 68.5 Hz. [e] $\delta(^{207}Pb)$.

$(Me_3SnSCN_4Ph)_3$ (q.s. 3.15 mm s^{-1})[7] while $SnBu_3(SCN_4Ph)$, which has not been crystallographically characterised, has a q.s. of 3.32 mm s^{-1}.[5] In **3**, which crystallises with two molecules of MeOH, both *trans*-$NSSnC_3$ and *trans*-$OSSnC_3$ arrangements are possible. A Me(H)O→Sn co-ordination has been observed previously in $1,3\text{-}(Bu_3SnN_4C)_2C_6H_4\cdot 2MeOH$,[1] but literature precedent for a *trans*-$SOSnC_3$ tin environment, as well as related Mössbauer data, is scarce. The compound $SnMe_3[O(S)P(OMe)_2]$ has a q.s. of 3.89 mm s^{-1}[12] and presumably adopts the same *trans*-$OSSnC_3$ structure as $SnMe_3[O(S)PMe_2]$[13] but there is no direct analogy for **3** where a co-ordinated solvent is incorporated, which, by its nature, is likely to be more weakly bound to tin and hence exhibit a lower q.s. Mössbauer spectroscopy is therefore not sufficient to distinguish unambiguously between the two possibilities but crystallography has confirmed a *trans*-$SOSnC_3$ centre (see below). The q.s. for **4** is 2.29 mm s^{-1} and is comparable with the value 2.38 mm s^{-1} for $SnPh_3(SCN_4Ph)$ which is essentially tetrahedral at tin with only a very weak chelating interaction with a ring nitrogen [3.275(3) Å].[6]

Table 2 Selected metric data (bond lengths in Å, angles in °) for compound **1***

Sn(1)–C(17)	2.09(1)	Sn(2)–C(29)	2.11(1)
Sn(1)–C(13)	2.10(1)	Sn(2)–C(21)	2.13(1)
Sn(1)–C(9)	2.11(2)	Sn(2)–C(25)	2.13(1)
Sn(1)–S(2)	2.574(2)	Sn(2)–S(1)	2.554(3)
Sn(1)–N(6′)	2.781(7)	Sn(2)–N(2″)	2.810(7)
S(1)–C(1)	1.716(9)	S(2)–C(8)	1.726(9)
C(17)–Sn(1)–C(13)	125.0(8)	C(29)–Sn(2)–C(21)	122.2(5)
C(17)–Sn(1)–C(9)	110.8(8)	C(29)–Sn(2)–C(25)	117.6(6)
C(13)–Sn(1)–C(9)	118.4(5)	C(21)–Sn(2)–C(25)	114.5(5)
C(17)–Sn(1)–S(2)	92.9(4)	C(29)–Sn(2)–S(1)	101.1(4)
C(13)–Sn(1)–S(2)	101.9(3)	C(21)–Sn(2)–S(1)	89.5(3)
C(9)–Sn(1)–S(2)	98.8(4)	C(25)–Sn(2)–S(1)	103.2(3)
C(17)–Sn(1)–N(6′)	79.7(4)	C(29)–Sn(2)–N(2″)	82.0(4)
C(13)–Sn(1)–N(6′)	82.6(4)	C(21)–Sn(2)–N(2″)	80.4(3)
C(9)–Sn(1)–N(6′)	83.9(4)	C(25)–Sn(2)–N(2″)	84.0(4)
S(2)–Sn(1)–N(6′)	172.6(2)	S(1)–Sn(2)–N(2″)	169.4(2)
C(1)–S(1)–Sn(2)	104.0(3)	C(8)–S(2)–Sn(1)	101.8(3)

* Primed and double-primed atoms are related to their unprimed counterparts by $-x + 0.5, y + 0.5, -z$ and $-x + 1.5, y + 0.5, -z + 1$, respectively.

Table 3 Selected metric data (bond lengths in Å, angles in °) for compound **3**

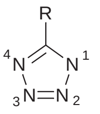
Sn(1)–C(2)	2.132(7)	Sn(1)–O(1)	2.464(5)
Sn(1)–C(1)	2.133(6)	Sn(1)–S(1)	2.607(2)
Sn(1)–C(3)	2.141(7)	S(1)–C(4)	1.723(7)
C(1)–Sn(1)–O(1)	82.2(2)	C(4)–S(1)–Sn(1)	101.1(2)
C(3)–Sn(1)–O(1)	85.0(2)	C(2)–Sn(1)–C(1)	115.2(3)
C(2)–Sn(1)–S(1)	91.1(2)	C(2)–Sn(1)–C(3)	120.9(3)
C(1)–Sn(1)–S(1)	99.3(2)	C(1)–Sn(1)–C(3)	120.3(3)
C(3)–Sn(1)–S(1)	98.5(2)	C(2)–Sn(1)–O(1)	83.7(2)
O(1)–Sn(1)–S(1)	174.7(1)		

The NMR data (Table 1), recorded in dmso, indicate that any intermolecular interactions in solid **1** are lost and that tin has a tetrahedral environment in solution. Similarly, a co-ordination number (c.n.) of 4 is maintained by compound **4** in solution. Both $\delta(^{119}Sn)$ and $^{1,2}J$ data are consistent with c.n. = 5 for both **2** and **3** in solution, but in both cases it is likely that this is achieved by dmso co-ordination to tin. Similarly, $\delta(^{207}Pb)$ for **5** (−235.5) is also indicative of a co-ordination number of 5 at the metal, and is comparable with data for other triphenyllead tetrazoles in dmso (−251 to −360),[14] where once again dmso, as solvent, is probably involved in complexation.

The ^1H and ^{13}C NMR data are unremarkable, save for the occurrence of the quaternary ring carbon at *ca.* δ 160 in the ^{13}C spectra which confirms the presence of the tetrazole ring.

Crystallography

Selected metric data for compounds **1** and **3** are given in Tables 2 and 3, respectively. For purposes of comparison, the Sn–S, Sn–N, C–S bond lengths and the C–Sn–C bond angle of previously known organotin-substituted thiotetrazoles are summarised in Table 4. For descriptive purposes, we number the tetrazole ring nitrogens as 1–4 for comparing the co-ordination mode of the tetrazole, while with respect to tin we group the nitrogens into either N^1 (*i.e.* N^1 or N^4) or N^2 (*i.e.* N^2 or N^3) categories, these representing the two differing degrees of hindrance for metal binding. The system can equally well be applied to the thiotetrazoles, though here N^1 is arylated and cannot co-ordinate further to a metal.



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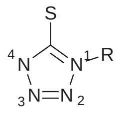

thiotetrazole

Table 4 Comparative geometric data for compounds **1** and **3** and related compounds

Compound	Sn–S/Å	Sn–N/Å	C–S/Å	C–Sn–C/°	Ref.
1	2.574(2), 2.554(3)	2.781(7),[a] 2.810(7)[a]	1.716(9), 1.726(9)	110.8(8)–125.0(8)	This work
3	2.607(2)	2.464(5)[b]	1.723(7)	115.2(3)–120.9(3)	This work
$SnBu_2(SCN_4Ph)_2$	2.477(4)	2.99[c]	1.76(2)	130.7(4)	5
$[(PhCH_2)_3SnSCN_4Ph]_\infty$	2.565(4), 2.614(5)	2.68(1),[a] 2.56(1)[a] 3.16,[c] 3.20[c]	1.72(1)	111.4(4)–126.1(5)	8
$SnPh_3(SCN_4Ph)$	2.482(1)	3.275(3)[c]	1.728(4)	113.6(1)–122.7(1)	6
$(Me_3SnSCN_4Ph)_3$	2.565(4)	2.75(1),[a] 3.29(1)[c]	1.73(2)	115.8(8)–120(1)	7

[a] Intermolecular. [b] Sn–O. [c] Intramolecular.

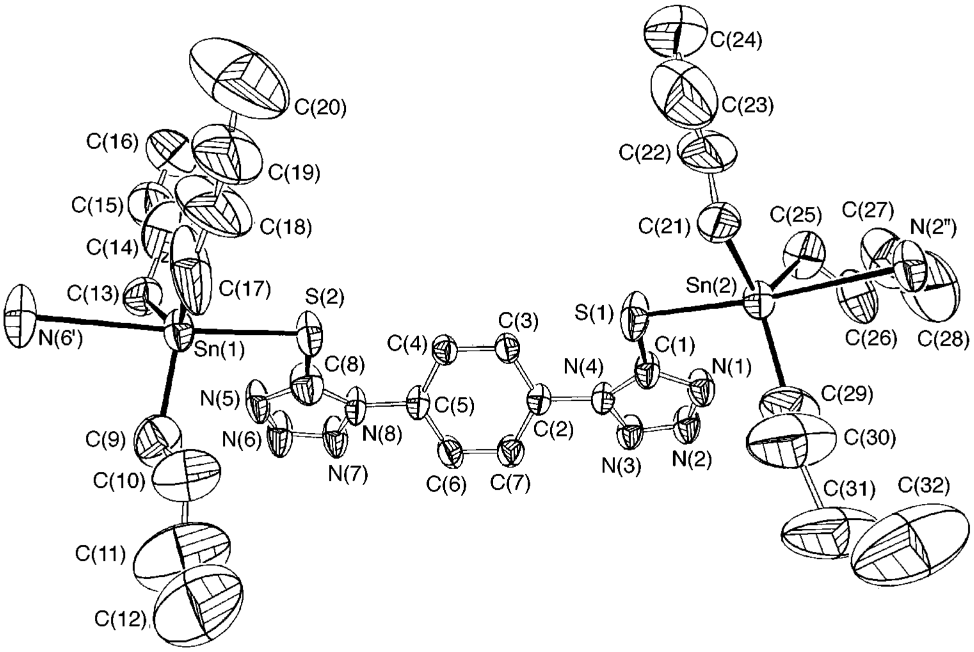

Fig. 1 The asymmetric unit of compound **1** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% level.

Compound 1. The asymmetric unit of compound **1** contains two trigonal bipyramidal *trans*-$NSSnC_3$ centres (Fig. 1) consistent with the Mössbauer q.s. data (see above). Each tin is directly bonded to the sulfur of the attached ligand and is further co-ordinated intermolecularly by a nitrogen [either N(2′) or N(6′)] from the tetrazole of a neighbouring molecule. Both nitrogen and sulfur attached to a given tin form part of the same ligand group, *i.e.* the structure can be viewed as parallel chains, one based on Sn(1) and the ligand containing S(2), N(6) the other based on Sn(2), S(1), N(2) groupings. The arrangement can be seen as identical to that of $Sn(CH_2Ph)_3(SCN_4Ph)$[8] but with the phenyl group attached to the tetrazole common to a pair of parallel strands (Fig. 2). The two Sn–S distances [Sn(1)–S(2) 2.574(2); Sn(2)–S(1) 2.554(3) Å] are comparable with the Sn–S bond lengths of previously known organotin thiotetrazoles (Table 4) although they are at the longer end of the range. The intermolecular Sn–N bonds [Sn(1)–N(6′) 2.781(7); Sn(2)–N(2″) 2.810(7) Å] are similar to the intermolecular Sn–N bond lengths of $[(PhCH_2)_3SnSCN_4Ph]_\infty$ and $(Me_3SnSCN_4Ph)_3$ (Table 4) but longer than the intermolecular Sn–N bond length of hydrated 2,2′-*p*-phenylenebis(tributylstannyltetrazole) [Sn(1)–N(6′) 2.573(6) Å],[14] presumably as a result of the lower Lewis acidity of tin arising from S, rather than N, primary bonding. Metal–ligand bonding thus takes place primarily through the sulfur exocyclic to the tetrazole rather than the nitrogen. The N–Sn–S bond angles approach 180° [N(6′)–Sn(1)–S(2) 172.6(2); S(1)–Sn(2)–N(2″) 169.4(2)°].

The N^3 co-ordination of the tetrazole with respect to the tin is that of lowest steric hindrance and is the mode adopted in both $[(PhCH_2)_3SnSCN_4Ph]_\infty$[8] and $(Me_3SnSCN_4Ph)_3$.[7] For comparison with known organotin tetrazoles, each tetrazole can be described as bidentate and exhibiting $N^1 + N^3$ co-ordination, the N^1 site in the thiotetrazoles being occupied by the phenyl ring. The $N^1 + N^3$ mode of co-ordination is the most common for organotin tetrazole and organtin thiotetrazoles.[15]

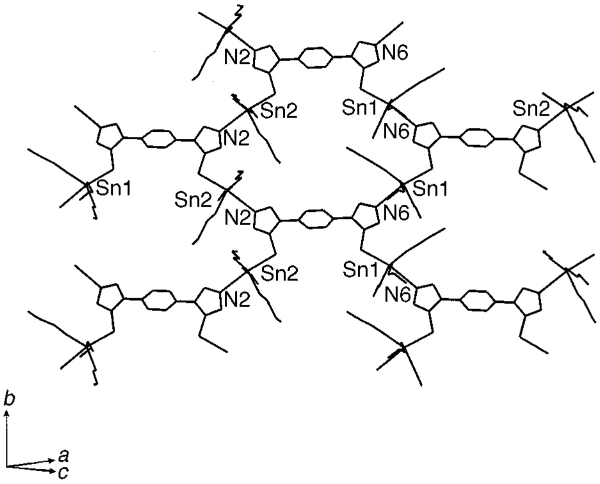

Fig. 2 The sheet structure of compound **1** viewed along the −1, 0, 1 direction.

The supramolecular structure of compound **1** is dominated by two-dimensional sheets as shown in Fig. 2. Atoms Sn(1) and Sn(2) in the asymmetric unit interact with N(6) and N(2) of the lattice neighbours generated *via* the symmetry operators $0.5 - x$, $0.5 + y$, $-z$ and $1.5 - x$, $0.5 + y$, $1 - z$, respectively. The axial nitrogens co-ordinated to the tin lie in the plane of the polymer sheets. These sheets are dominated by 32-membered rings containing four tins, four sulfurs, twelve tetrazole nitrogens, four tetrazole carbons and eight phenyl carbons. The interlayer region is filled by the equatorial *n*-butyl groups as shown Fig. 3. The supramolecular arrays of other organotin tetrazoles also include planar and puckered two-dimensional arrays. The closest analogies for **1** can be drawn with nitrotris[2-(2-tributylstannyltetrazol-5-yl)ethyl]methane and 1,3,5-tris(tributylstannyltetrazol-5-yl)benzene which are also two-dimensional sheet structures,[3] though these are built to include only 24-atom (Sn_6N_{18}) rings. Indeed, the size of the rings in **1**, enlarged as they are by the phenylene groups inherent in the ligand, is surprisingly large for accommodating only four of the butyl groups of the associated tin atoms. In contrast, both planar tris-substituted tetrazoles pack ten butyl groups from six tins into the cavity of the 24-atom ring. This suggests that with suitable ligand design far more porous structures than previously identified are achievable.

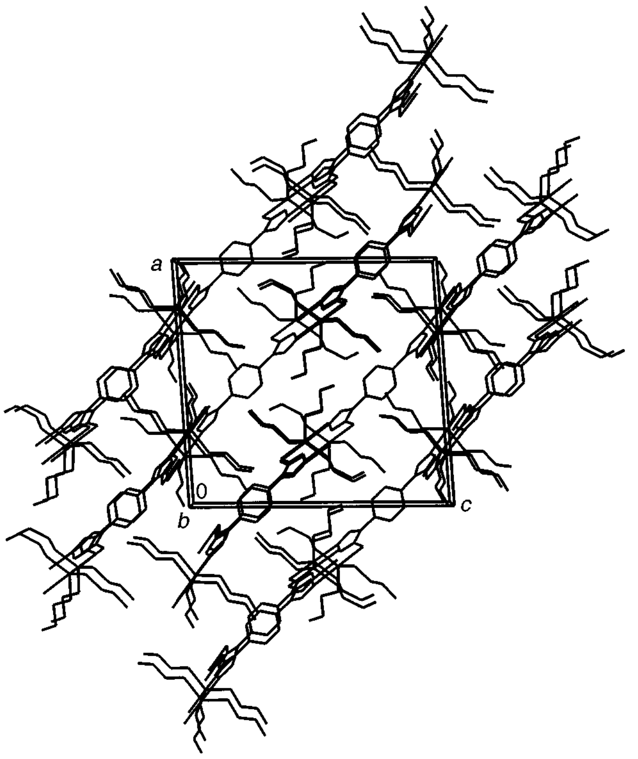

Fig. 3 The sheet structure of compound **1** viewed along *b* to illustrate the filling of the interlayer region by the butyl groups on tin.

Compound 3·2MeOH. X-Ray quality crystals of compound **3** were obtained by slow evaporation of a methanolic solution at room temperature; data were collected at low temperature as the crystals desolvated at ambient temperatures in the absence of mother-liquor. The asymmetric unit (Fig. 4) was found to consist of one half of the molecule, the remainder being generated by an inversion centre at the midpoint of the C_6 ring. Each tin is trigonal bipyramidal *trans*-SOSnC$_3$ with the axial positions occupied by O(1) of the co-ordinated methanol molecule and S(1) of the thiotetrazole. The O–Sn–S bond angle is close to 180° [O(1)–Sn(1)–S(1) 174.7(1)°]. The Sn(1)–S(1) bond length [2.607(2) Å] is the longest such distance observed when compared with those of **1** and with other known organotin-substituted thiotetrazoles (Table 4). No other data for solvated organotin thiotetrazoles exist for comparison of the Sn(1)–O(1) bond length [2.464(5) Å], although it is longer than the analogous bond in related 1,3-$(Bu_3SnN_4C)_2C_6H_4$·2MeOH [2.398(9) Å].[1] In addition, comparison can be made with data for $(Me_3SnOSPMe_2)_\infty$ which also has a *trans*-SOSnC$_3$ centre where the Sn–O bond is, as expected, stronger [2.267(6) Å].[13] The tetrazole adopts the common $N^1 + N^3$ co-ordination mode (N^1 bonded to the phenyl ring) seen in **1**.

The salient feature of the supramolecular structure of compound **3** is that of a one-dimensional hydrogen-bonded polymer, as shown in Fig. 5, in which the co-ordinated methanol hydrogen bonds to N(2) of a neighbouring tetrazole [O(1)···N(2) 2.801(8); H(1)···N(2) 1.84(3) Å; O(1)–H(1)–N(2) 173(5)°]. The polymers are, in effect, fourteen-membered $(SnSCN_2HO)_2$ rings linked by phenylene bridges. We have observed similar twelve-membered rings in the structure of 1-phenyl 5-diphenylthallium tetrazole which simply lacks the sulfurs of the thiotetrazole in **3**.[14]

Conclusion

Four organotin thiotetrazoles 1,4-$(R_3SnSCN_4)_2C_6H_4$ (R = Me, Et, Bu or Ph) along with the triphenyllead, diphenylthallium and phenylmercury analogues have been synthesized. The

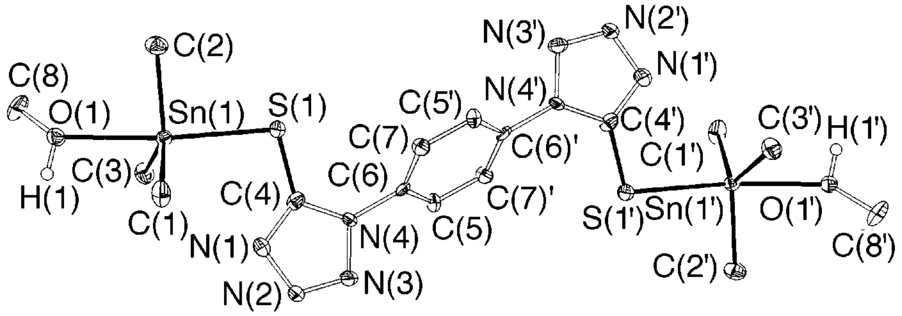

Fig. 4 The symmetric unit of compound **3** showing the labelling scheme used in the text and tables. Thermal ellipsoids are at the 30% level.

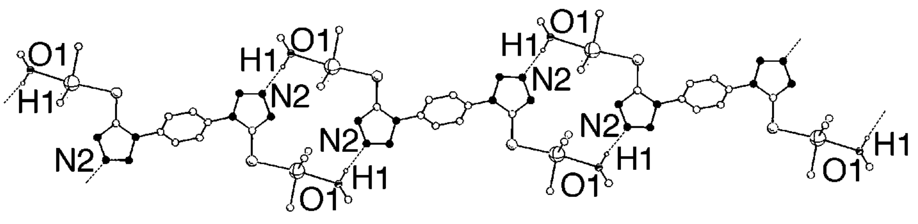

Fig. 5 The polymeric structure of compound **3** showing the intermolecular hydrogen bonds.

supramolecular structure of 1,4-$(Bu_3SnSCN_4)_2C_6H_4$ has been found to consist of a 2-D sheet arrangement containing 32-membered $(C_4NCSSnN_2CSSnN_3)_2$ rings. In contrast, 1,4-$(Me_3SnSCN_4)_2C_6H_4$ crystallises as a bis(methanol) solvate in which 14-membered $(SnSCN_2HO)_2$ rings are linked through hydrogen bonds into a 1-D polymer.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^1H, ^{13}C NMR), GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[16] Isomer shift data are relative to $CaSnO_3$. For all compounds, infrared spectra were recorded as Nujol mulls on KBr plates and all NMR data on saturated solutions in $(CD_3)_2SO$ unless indicated otherwise.

Organotin azides $SnR_3(N_3)$ (R = Bu[17] or Et[1]) and $TlPh_2(OH)$[18] were prepared by literature methods. Other reagents were obtained commercially and used without further purification.

CAUTION: Owing to their potentially explosive nature, all preparations and subsequent reactions with organotin azides were conducted under an inert atmosphere behind a rigid safety screen.

Syntheses

1,1′-*p*-Phenylenebis[(5-tributylstannylsulfanyl)tetrazole] 1. A mixture of tributyltin azide (6.96 g, 21.0 mmol) and 1,4-diisothiocyanatobenzene (2.04 g, 10.6 mmol) were heated while stirring under N_2 at 100 °C for half an hour. The resultant yellow-white solid was recrystallised from hexanes yielding compound **1** as a white microcrystalline solid (5.02 g, 55%), m.p. 122 °C [Found (Calc. for $C_{16}H_{29}N_4SSn$): C, 44.6 (44.9); H, 6.81 (6.83); N, 13.0 (13.1)%]. ^1H NMR: δ 8.01 (s, 4 H, C_6H_4), 1.62 [m, 12 H, $SnCH_2CH_2CH_2CH_3$]; 1.54 (m, 12 H, $SnCH_2CH_2CH_2CH_3$), 1.48 (m, 12 H, $SnCH_2CH_2CH_2CH_3$) and 0.91 [t, 18 H, $(CH_2)_3CH_3$]. ^{13}C NMR: δ 155.7 (CN_4), 135.1 ($C^{1,4}$ of C_6H_4), 124.6 ($C^{2,3,5,6}$ of C_6H_4), 28.5 ($SnCH_2CH_2CH_2CH_3$), 27.0 [$Sn(CH_2)_2CH_2CH_3$], 16.6 [$SnCH_2(CH_2)_2CH_3$] and 13.6 [$(CH_2)_3CH_3$]; $^1J[^{13}C–^{117,119}Sn]$ 327 (unresolved), $^3J[^{13}C–^{117,119}Sn]$ 66 Hz (unresolved). ^{119}Sn NMR: δ 122.8. IR (cm^{-1}, Nujol): 3457, 2924, 2855, 2363, 2340, 2168, 1653, 1601, 1509, 1464, 1418, 1375, 1300, 1277, 1219, 1080, 1039, 1011 and 837. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.50; q.s. = 3.32.

1,1′-*p*-Phenylenebis[(5-triethylstannylsulfanyl)tetrazole] 2. A mixture of triethyltin azide (2.91 g, 11.73 mmol) and 1,4-diisothiocyanatobenene (1.13 g, 5.87 mmol) was heated while stirring under N_2 at 88 °C for half an hour. The resultant yellow-white solid was washed with hexanes leaving the product as an analytically pure white powder (2.12 g, 53%); mp 184 °C (decomp.) [Found (Calc. for $C_{10}H_{17}N_4SSn$): C, 34.9 (34.9); H, 4.80 (4.94); N, 16.7 (16.3)%]. ^1H NMR: δ 8.06 (s, 4 H, C_6H_4) and 1.20–1.30 (m, 30 H, CH_2CH_3); $^2J[^1H–^{117,119}Sn]$ 90 Hz (unresolved). ^{13}C NMR: δ 163.0 (CN_4), 135.1 ($C^{1,4}$ of C_6H_4), 124.7 ($C^{2,3,5,6}$ of C_6H_4), 11.5 (CH_2CH_3) and 10.5 (CH_2CH_3); $^1J[^{13}C–^{117,119}Sn]$ 237 Hz (unresolved). ^{119}Sn NMR: δ −10.3. IR (cm^{-1}, KBr): 2947, 1606, 1518, 1446, 1371, 1300, 1277, 1218, 1120, 1082, 1039, 1010, 952, 839, 715 and 677. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.52; q.s. = 3.39.

1,1′-*p*-Phenylenebis(5-thioxotetrazole)–methanol (1/1) II. Concentrated hydrochloric acid (1.50 mL, 18 mmol) was added dropwise to a well stirred solution of compound **1** (3.0 g, 3.5 mmol) in hot methanol (300 mL). The resultant colourless solution was refluxed for an hour. After cooling, methanol was removed *in vacuo* and the remaining white solid washed with hexanes to remove $SnBu_3Cl$ and recrystallised from methanol to give the product as a white solid (0.96 g, 99%); mp 200 °C (decomp.) [Found (Calc. for $C_8H_6N_8S_2 \cdot CH_3OH$): C, 34.9 (34.7); H, 2.05 (2.74); N, 38.5 (38.1)%]. ^1H NMR: δ 8.17 (s, 4 H, C_6H_4) and 3.18 (s, 3 H, CH_3OH). ^{13}C NMR: δ 162.5 (CN_4), 134.5 ($C^{1,4}$ of C_6H_4) and 125.4 ($C^{2,3,5,6}$ of C_6H_4). IR (cm^{-1}, KBr disc): 3553, 3414, 3069, 2937, 2750, 1637, 1616, 1522, 1477, 1385, 1350, 1296, 1275, 1217, 1049, 989, 851, 767, 657 and 590.

Diammonium 1,1′-*p*-phenylenebis(tetrazole-5-thiolate) III. Ammonia gas was bubbled through a solution of compound **II** in methanol (350 mL) for 30 min. The methanol was removed *in vacuo* to yield **III** in quantitative yield, mp 190 °C (decomp.) [Found (Calc. for $C_4H_6N_5S$): C, 31.4 (30.8); H, 3.90 (3.85); N, 44.2 (44.9)%]. ^1H NMR: δ 8.16 (s, 4 H, C_6H_4) and 7.30 (s, 8 H, NH_4^+). ^{13}C NMR: δ 167.5 (CN_4), 135.5 ($C^{1,4}$ of C_6H_4) and 123.5 ($C^{2,3,5,6}$ of C_6H_4). IR (cm^{-1}, Nujol): 3443, 2955, 2924, 2855, 2363, 2342, 1734, 1653, 1559, 1516, 1458, 1420, 1375, 1358, 1292, 1283, 1219, 1089, 1040 and 1013.

1,1′-*p*-Phenylenebis[(5-trimethylstannylsulfanyl)tetrazole]–methanol (1/2) 3. A solution of trimethyltin chloride (0.62 g, 3.12 mmol) in methanol (100 mL) was added dropwise to a well stirred solution of compound **III** (0.50 g, 1.56 mmol) in methanol (200 mL) and the reaction mixture refluxed for 3 h. Subsequently, the methanol was removed *in vacuo* and the white solid refluxed in acetone (300 mL) for 30 min. Hot filtration resulted in a yellow solution. The acetone was removed *in vacuo* and the resulting yellow-white solid recrystallised from methanol to yield **3** as a yellow crystalline product (0.73 g, 77%), mp 175 °C (decomp.) [Found (Calc. for $C_7H_{11}N_4SSn \cdot CH_3OH$): C, 28.5 (28.7); H, 4.32 (4.49); N, 17.0 (16.8)%]. ^1H NMR: δ 8.06 (s, 4 H, C_6H_4), 3.16 (s, 6 H, CH_3OH), 0.64 (s, 12 H, $SnCH_3$); $^2J[^1H–^{117,119}Sn]$ 68.5 Hz (unresolved). ^{13}C NMR: δ 164.7 (CN_4), 135.1 ($C^{1,4}$ of C_6H_4), 124.5 ($C^{2,3,5,6}$ of C_6H_4), 48.7 (CH_3OH) and 0.9 (CH_3); $^1J[^{13}C–^{117,119}$ Sn] 491, 515 Hz. ^{119}Sn NMR: δ −23.7. IR (cm^{-1}, KBr disc): 3245, 2924, 2855, 2363, 2342, 1520, 1512, 1464, 1368, 1352, 1298, 1277, 1219, 1117, 1098, 1082, 1020, 1010, 837 and 789. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.38; q.s. = 3.35.

1,1′-*p*-Phenylenebis[(5-triphenylstannylsulfanyl)tetrazole] 4. A solution of triphenyltin chloride (0.76 g, 1.97 mmol) in methanol (10 mL) was added dropwise to a well stirred solution of compound **III** (0.31 g, 0.99 mmol) in methanol (250 mL) and the reaction refluxed for 3 h. The reaction was worked up in the same way as for **3** to yield **4** as a white powder (0.42 g, 40%), mp 160–162 °C [Found (Calc. for $C_{22}H_{17}N_4SSn$): C, 53.2 (54.1); H, 3.46 (3.48); N, 11.5 (11.5)%]. ^1H NMR (100 °C): δ 7.89–7.42 (m, 34 H, phenyl). ^{13}C NMR (100 °C): δ 141.7, 135.7, 134.9, 129.0, 128.3, 125.2, 124.0 and 118.0 (phenyl). ^{119}Sn NMR (100 °C): δ −65.0. IR (cm^{-1}, KBr disc): 3414, 3067, 1637, 1618, 1522, 1479, 1429, 1379, 1238, 1226, 1091, 1074, 1016, 997, 837, 731, 696, 619, 574 and 453. ^{119m}Sn Mössbauer (mm s^{-1}): i.s. = 1.22; q.s. = 2.29.

1,1′-*p*-Phenylenebis[(5-triphenylplumbylsulfanyl)tetrazole]-toluene (2/1) 5. A solution of triphenyllead chloride (0.56 g, 1.18 mmol) in methanol (200 mL) was added dropwise to a well stirred solution of compound **1** (0.50 g, 0.58 mmol) also in hot methanol (150 mL). The resultant clear solution was refluxed for 10 h. Subsequently, methanol was removed *in vacuo* and the resulting white product washed with hexanes and recrystallised from toluene to give **5** as a white crystalline product (0.22 g, 33%), mp 218–220 °C (decomp.) [Found (Calc. for $C_{44}H_{34}N_8Pb_2S_2 \cdot 0.5CH_3C_6H_5$): C, 47.7 (47.5); H, 3.32 (3.17); N, 9.48 (9.35)%]. ^1H NMR: δ 7.84, 7.74, 7.60–7.32 (phenyl) and 3.07 (s, $CH_3C_6H_5$). ^{13}C NMR: δ 160.0 (CN_4), 135.8, 134.5, 129.4, 128.7 and 124.3 (phenyl). ^{207}Pb NMR: δ −235.5 (100 °C). IR (cm^{-1}, Nujol): 2926, 2855, 1933, 1836, 1715, 1633, 1603, 1568, 1435, 1377, 1335, 1298, 1233, 1098, 1026, 1011, 997, 857, 760, 741 and 696.

Table 5 Crystallographic data for compounds **1** and **3***

	1	**3**
Empirical formula	$C_{32}H_{58}N_8S_2Sn_2$	$C_8H_{15}N_4OSSn$
M	856.36	333.99
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/a$	$P\bar{1}$
T/K	293(2)	170(2)
a/Å	17.602(2)	6.755(2)
b/Å	12.639(2)	10.253(4)
c/Å	18.733(6)	10.452(4)
α/°	—	70.44(4)
β/°	93.79(1)	83.67(4)
γ/°	—	70.84(3)
U/Å^3	4158(2)	644.3(4)
Z	4	2
μ(Mo-Kα)/mm^{-1}	1.332	2.128
Reflections collected	6015	2790
Goodness of fit on F^2	1.003	1.165
$R1$, $wR2$ $[I > 2\sigma(I)]$	0.0496, 0.1059	0.0347, 0.0978
(all data)	0.1341, 0.1524	0.0512, 0.1051

* Details in common; λ(Mo-Kα) 0.70930 Å; full-matrix least-squares refinement on F^2.

1,1′-*p*-Phenylenebis[(5-phenylmercuriosulfanyl)tetrazole] 6. This was prepared in a similar manner to compound **5** from a methanolic solution (100 mL) of **1** (0.53 g, 0.61 mmol) and a solution of phenylmercury(II) chloride (0.38 g, 1.27 mmol) in methanol (130 mL). A white precipitate formed instantaneously, which was collected by washing with hexanes and filtering. The product was found to be insoluble in most commonly available solvents (0.40 g, 80%), mp 190–192 °C (decomp.) [Found (Calc. for $C_{10}H_7HgN_4S$): C, 28.2 (28.9); H, 1.74 (1.68); N, 13.0 (13.5)%], IR (cm^{-1}, Nujol): 3441, 2955, 2924, 2855, 1624, 1524, 1464, 1431, 1372, 1294, 1271, 1235, 1094, 1041, 1020, 997, 982, 843, 723 and 629.

1,1′-*p*-Phenylenebis[(5-diphenylthalliosulfanyl)tetrazole] dihydrate 7. A solution of diphenylthallium hydroxide (0.100 g, 0.267 mmol) in methanol (200 mL) was added dropwise to a well stirred solution of compound **II** (0.04 g, 0.134 mmol) in hot methanol (60 mL). After refluxing for 3 h the cloudy solution was cooled to room temperature and the volume of solvent decreased under reduced pressure, resulting in the precipitation of a white solid which was collected by filtration and dried *in vacuo* (0.06 g, 43%), mp 202 °C (decomp.) [Found (Calc. for $C_{11}H_{12}N_4STl\cdot H_2O$): C, 38.7 (37.3); H, 2.42 (2.72); N, 11.3 (10.9%)]. ^{1}H NMR δ 8.28–7.29 (m, 24 H, phenyl). ^{13}C NMR δ 164.0 (CN$_4$), 137.3, 136.9, 135.6, 130.9, 128.8, 126.5 and 123.9 (phenyl). IR (cm^{-1}, KBr): 3414, 3044, 2924, 1616, 1510, 1475, 1431, 1363, 1340, 1296, 1280, 1215, 1093, 1078, 1006, 997, 841, 723, 688 and 451.

X-Ray crystallography

Crystal data are summarised in Table 5.

Compound 1. A crystal of approximate dimensions 0.4 × 0.4 × 0.4 mm was used for data collection. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant. The C–C bond lengths in the butyl group containing carbons C(17)–C(20) were constrained to an ideal distance of 1.54 Å, as early refinement cycles indicated some instability in this region of the electron density map. This action was reflected in an improvement of residuals. The asymmetric unit is shown in Fig. 1.

Compound 3. A crystal of approximate dimensions 0.5 × 0.4 × 0.25 mm was used for data collection. In the final least squares cycles all atoms were allowed to vibrate anisotropically. Hydrogen atoms were included at calculated positions where relevant, except for the methanolic proton [H(1)] which was located and refined at a distance of 0.98 Å from O(1). The asymmetric unit is shown in Fig. 4 (unprimed labels).

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