

# Tris(triorganostannyltetrazoles): synthesis and supramolecular structures

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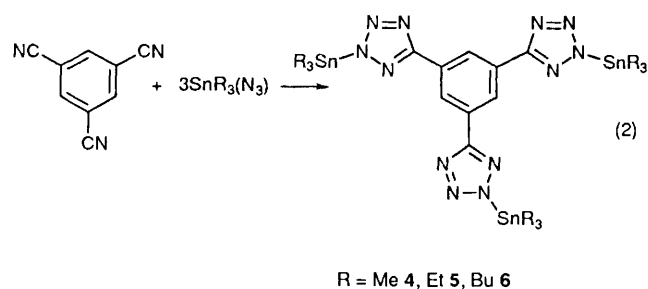
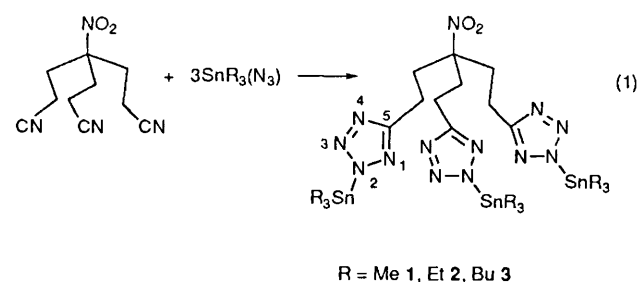
Six trifunctional triorganotin tetrazoles,  $(R_3SnN_4CCH_2CH_2)_3C(NO_2)$  and 1,3,5- $(R_3SnN_4C)_3C_6H_3$  ( $R = Me, Et$  or  $Bu$ ), have been synthesised by a cycloaddition route from  $SnR_3(N_3)$  and either  $(NCCH_2CH_2)_3C(NO_2)$  or 1,3,5- $(NC)_3C_6H_3$  as dipolarophile. The compounds have been characterised by  $^1H$ ,  $^{13}C$ ,  $^{119}Sn$  NMR and  $^{119}M\ddot{o}ssbauer$  spectroscopies, while the crystal structures of the tributyltin examples of each series reveal they adopt layered supramolecular arrays.

We have been investigating the structural chemistry of polyfunctional triorganotin tetrazoles primarily because of the diverse supramolecular chemistry these species exhibit.<sup>1,2</sup> The co-ordination sphere about the metal is invariably *trans*- $N_2SnR_3$ , such that tetrazole units bridge organotin fragments to propagate two- or three-dimensional arrays. The nature of the lattice is dependent on the hydrocarbon groups bonded to tin, which are packed into any cavities generated by the co-ordination polymer. Thus, 1,2- $(Et_3SnN_4C)_2C_6H_4$  adopts a non-planar layer structure while its butyl analogue, 1,2- $(Bu_3SnN_4C)_2C_6H_4$ , prefers a porous three-dimensional architecture.<sup>1</sup> In contrast, when a flexible alkyl chain is used to link two organotin tetrazoles as in 1,6- $(Bu_3SnN_4C)_2(CH_2)_6$ , a bilayer structure is observed which incorporates channels running in all three directions.<sup>2</sup> We now report the synthesis of trifunctional organotin tetrazoles based upon both rigid and flexible cores, and their supramolecular structures.

## Results and Discussion

### Synthesis and spectroscopy

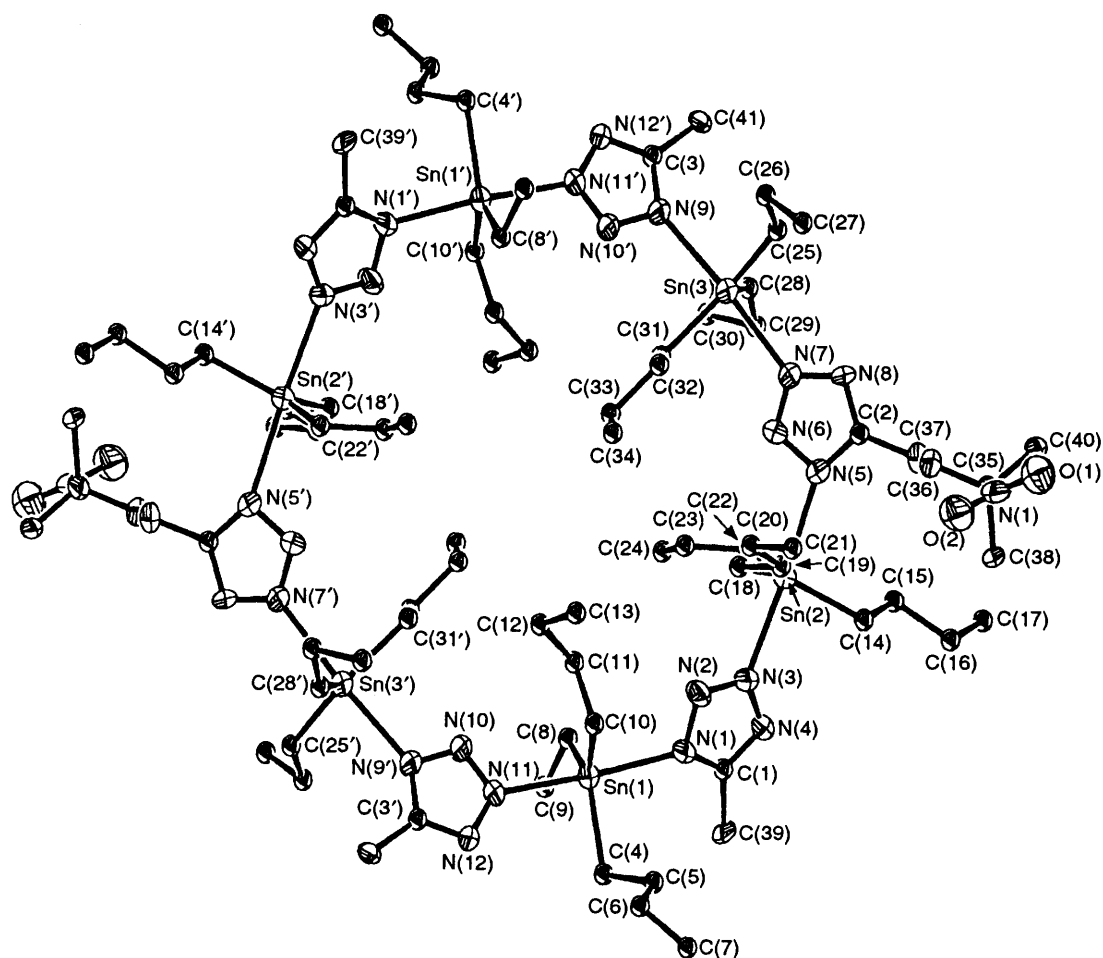
Six triorganotin-substituted tris(tetrazoles) have been synthesised employing either tris(2-cyanoethyl)nitromethane [equation (1)] or 1,3,5-tricyanobenzene [equation (2)] as



dipolarophiles in cycloaddition reactions with 3 equivalents of triorganotin azide. Compounds 1–3 and 6 were synthesised by direct reaction of the relevant nitrile and azide, while 4 and 5 were prepared under reflux in the inert, high-boiling solvents *p*-xylene and mesitylene respectively.

The course of reaction was followed by the disappearance of the IR bands due to  $\nu(CN)$  at *ca.* 2250 and  $\nu(N_3)$  at 2060  $cm^{-1}$ . In the case of 4 and 5 the course is also evident from the formation of a white precipitate in the initially clear solution. The crude products were purified where possible by recrystallisation from methanol or ethanol, though 1 was always obtained as a sticky glass; 2–6 are crystalline solids. The trimethyltin derivative 4 was isolated as a hexahydrate, as deduced from both microanalysis and infrared spectroscopic data, where broad bands at 3638 and 1638  $cm^{-1}$  clearly indicate the presence of water. The hydrated nature of 4 is also readily apparent from the broad singlet observed at  $\delta$  3.60 in the  $^1H$  NMR spectrum. A recent study has shown that isomorphous two-dimensional structures are adopted by cobalt, zinc and cadmium bis(tetrazolyl)borate complexes,<sup>3</sup> in each case stabilised by guest solvate ( $H_2O$ ) molecules. Only the N atom adjacent to the tetrazole ring CH functions as a donor atom to the metal, the other two available nitrogens forming hydrogen bonds to the embedded water of crystallisation. The rhombohedral openings do not, however, extend through the lattice as open channels, the adjacent layers being offset by half a unit cell so that the layers interlock with the formation of solvent-containing cavities.

As was the case for the trialkyltin-substituted tetrazoles which we have reported previously,<sup>1,2,4</sup> highly co-ordinating  $(CD_3)_2SO$  was required for the collection of NMR data for 1–6. The  $^1H$  and  $^{13}C$  NMR spectra of the new compounds are all consistent with the structures shown in equations (1) and (2). For each compound a single tertiary tetrazole ring carbon is discernible at *ca.*  $\delta$  161 in the  $^{13}C$  spectra, demonstrating the equivalence of all three  $CN_4$  rings on the NMR time-scale. The  $^{119}Sn$  NMR chemical shifts lie within the range  $\delta$  –36.0 to –50.1, similar to those reported for the analogous compounds containing only two organotin tetrazole units.<sup>1,2</sup> Collectively, the NMR data are wholly consistent with a *trans*-trigonal-bipyramidal geometry around tin. The  $^2J(^{119}Sn-^1H)$  values of 69.4 and 69.1 Hz for the trimethyltin derivatives 1 and 4 respectively are consistent with such a five-co-ordinate arrangement, and use of the empirical relationship put forward by Lockhart and Manders<sup>5</sup> relating these values with the Me–Sn–Me bond angle gives values of 119.3 and 119.1° for these two species, consistent with equatorial methyl groups in a trigonal-bipyramidal co-ordination sphere. For compounds where solubility allowed good-quality  $^{13}C$  NMR spectra to be recorded, the  $^1J(^{119}Sn-^{13}C)$  values of 529.4 (1), 496.4 (2) and



**Fig. 1** The asymmetric unit of compound **3** showing the atomic labelling. Selected geometric data: N(1)–Sn(1) 2.43(1), N(11)–Sn(1) 2.38(2), C(4)–Sn(1) 2.15(2), C(8)–Sn(1) 2.11(2), C(10)–Sn(1) 2.13(2), N(3)–Sn(2) 2.37(1), N(5)–Sn(2) 2.41(2), C(14)–Sn(2) 2.14(2), C(18)–Sn(2) 2.08(2), C(22)–Sn(2) 2.14(2), N(7)–Sn(3) 2.37(2), N(9)–Sn(3) 2.37(2), C(25)–Sn(3) 2.12(2), C(28)–Sn(3) 2.14(2) and C(31)–Sn(3) 2.12(2) Å; N(11)–Sn(1)–N(1) 175.6(5), N(5)–Sn(2)–N(3) 175.9(5) and N(9)–Sn(3)–N(7) 176.0(5)°

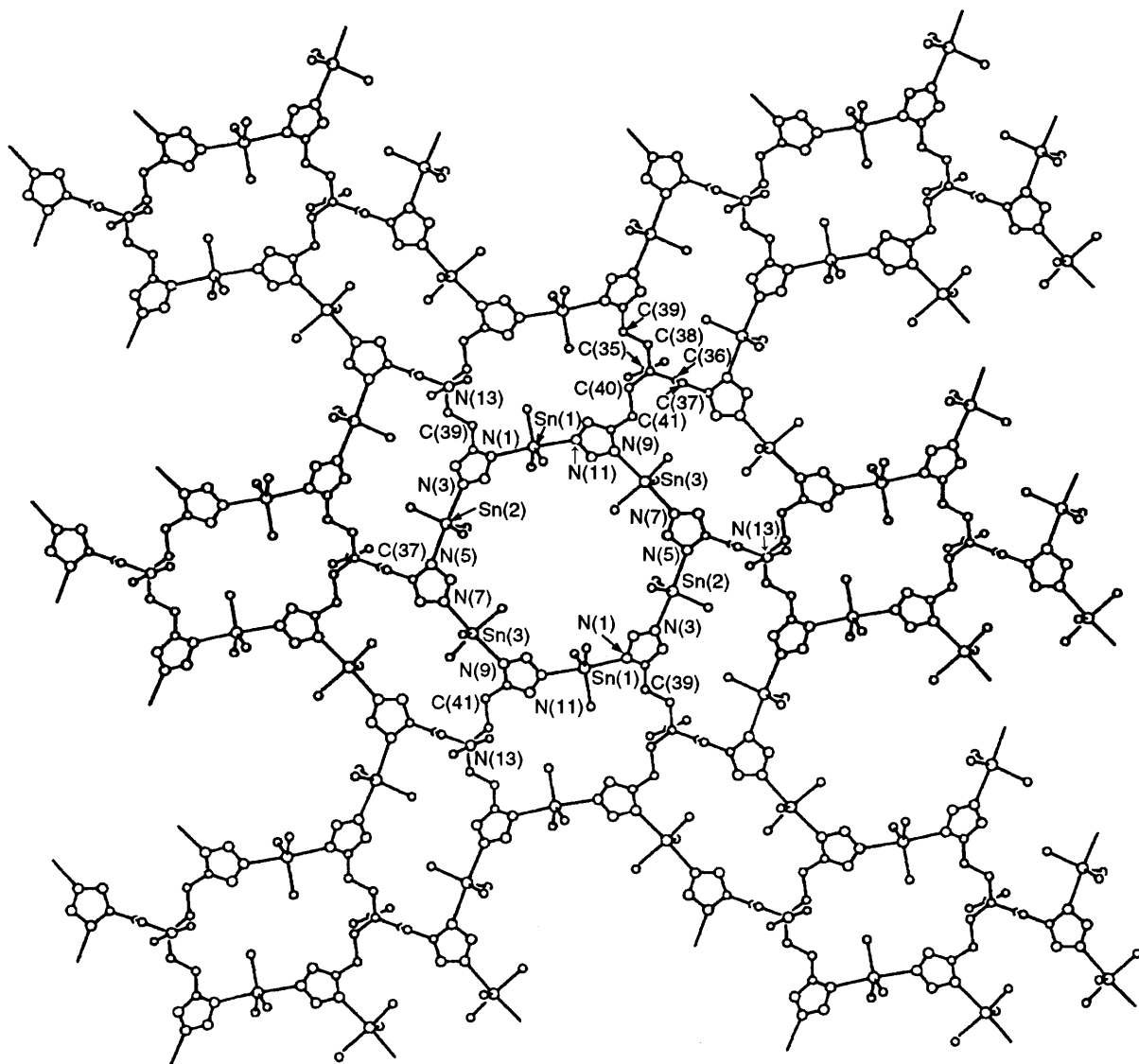
461.5 Hz (**6**) are again within the range expected for *trans*-trigonal-bipyramidal co-ordination at tin. The latter value can be used to estimate the mean C–Sn–C bond angle in solution using the relationship derived by Holecek and Lycka<sup>6</sup> for butyltin compounds and correlates with a C–Sn–C angle of 121.9°, also indicative of *trans*-trigonal-bipyramidal geometry at tin. Although no  $^1J(^{119}\text{Sn}-^{13}\text{C})$  coupling was observable for the tributyltin-substituted nitromethane derivative **3**, the  $^2J(^{119}\text{Sn}-^{13}\text{C})$  and  $^3J(^{119}\text{Sn}-^{13}\text{C})$  values of 31.0 and 77.5 Hz respectively are internally consistent with the analogous data recorded for **6** (29.4 and 75.3 Hz, respectively). The use of  $(\text{CD}_3)_2\text{SO}$  as solvent for these measurements creates some ambiguity as to the nature of the five-co-ordinate species present in solution as both solvated and oligomeric species would generate similar data. In addition, the data for the hexahydrated **4** could result from co-ordination of water in one of the axial sites around the metal, a situation we have found in both 1,4-( $\text{Bu}_3\text{SnN}_4\text{C}$ )<sub>2</sub> $\text{C}_6\text{H}_4\cdot\text{H}_2\text{O}$ <sup>7</sup> and ( $\text{Me}_3\text{SnN}_4\text{C}$ )<sub>2</sub> $\text{N}_2\cdot\text{H}_2\text{O}$ ,<sup>8</sup> and analogous to other solvated species such as 1,3-( $\text{R}_3\text{MN}_4\text{C}$ )<sub>2</sub>- $\text{C}_6\text{H}_4\cdot 2\text{MeOH}$  (R = Bu, M = Sn;<sup>1</sup> R = Ph, M = Pb<sup>9</sup>).

The Mössbauer spectra for the triorganotin-substituted tris(tetrazoles) have quadrupole splittings (q.s. = 3.42–3.93 mm s<sup>-1</sup>) indicative of *trans*-trigonal-bipyramidal co-ordination around tin.<sup>10</sup> In the solid state this geometry must occur through tetrazole N–Sn–N bridging interactions of a type similar to those observed in the structures of organotin tetrazoles which we have previously published.<sup>1,2,4</sup> The only possible exception to this general picture of the local bonding around tin is the hexahydrated **4** where both *trans*- $\text{N}_2\text{SnC}_3$  and

*trans*- $\text{NOSnC}_3$  co-ordination spheres are consistent with the Mössbauer data. The quadrupole splittings of these two possibilities ( $\text{N}_2\text{SnMe}_3$  vs.  $\text{NOSnMe}_3$ ) are expected to be of the same order [e.g. for  $\text{SnMe}_3(\text{NCO})$ , q.s. = 3.31 mm s<sup>-1</sup>]<sup>11</sup> and thus it is not possible to say which gives rise to the observed spectrum. Indeed, both environments may be present, and a precedent exists for the simultaneous observation of such tin sites in the trimethyltin-substituted tetrazole compound bis(trimethylstannyl)-5,5'-azotetrazole hydrate for which similar Mössbauer data have been recorded (q.s. = 3.90 mm s<sup>-1</sup>).<sup>8</sup> A mixture of tin sites such as this would also explain the observed line broadening in the spectrum of compound **4** ( $\Gamma = 1.07, 1.14$  mm s<sup>-1</sup>), although equally broad lines are evident in the spectra of the other phenylene-centred tris(tetrazoles) **5** and **6** ( $\Gamma = 1.15$ – $1.29$  mm s<sup>-1</sup>) which suggests that this may be an inherent feature of these compounds due to a multiplicity of slightly differing tin sites.

#### Crystal structure of nitrotris[2-(2-tributylstannyltetrazol-5-yl)ethyl]methane **3**

The asymmetric unit of compound **3**, consisting of three molecular units, is shown in Fig. 1 with selected bond lengths and angles. As with the structures of several related organotin tetrazoles, that of **3** relies on packing of the butyl groups on tin into the cavities created within the lattice. As such, disorder of these alkyl groups is a constant problem and thus only the general outline of the structure is discussed. However, despite these crystallographic problems, both the tin–tetrazole

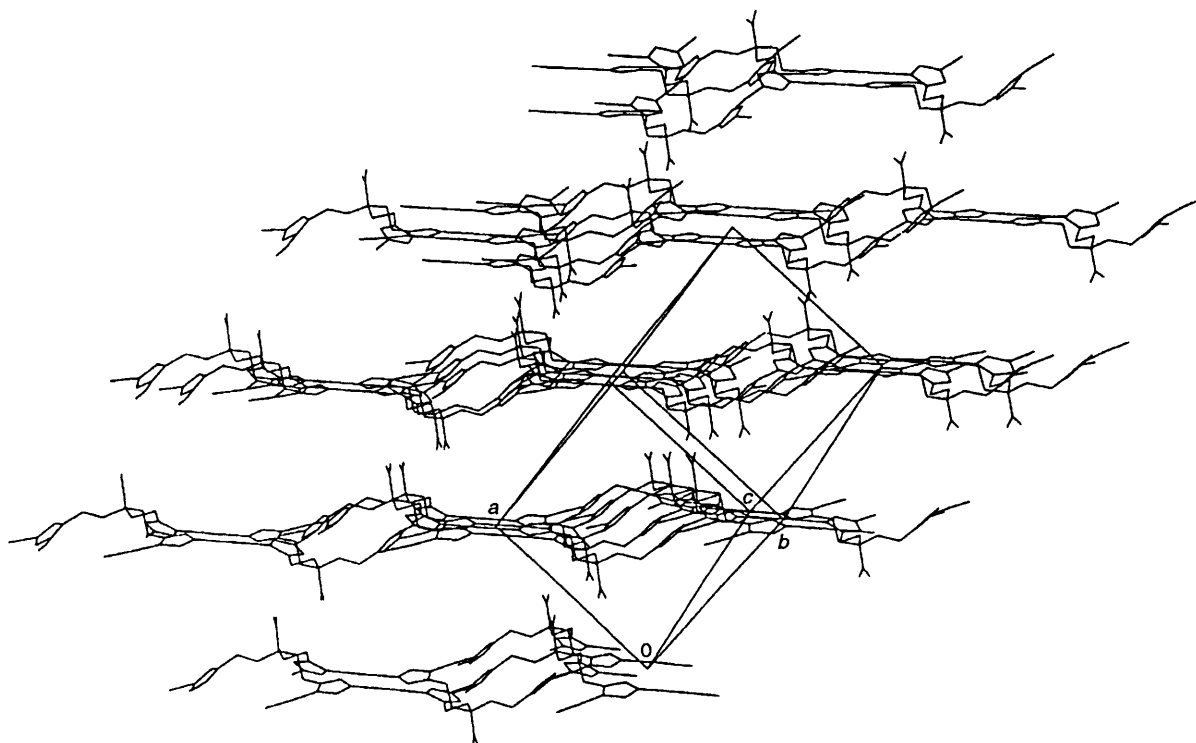


**Fig. 2** The layer structure of compound **3** highlighting the snow-flake nature of the lattice. Only the  $\alpha$ -carbons of the butyl groups attached to tin are shown for clarity

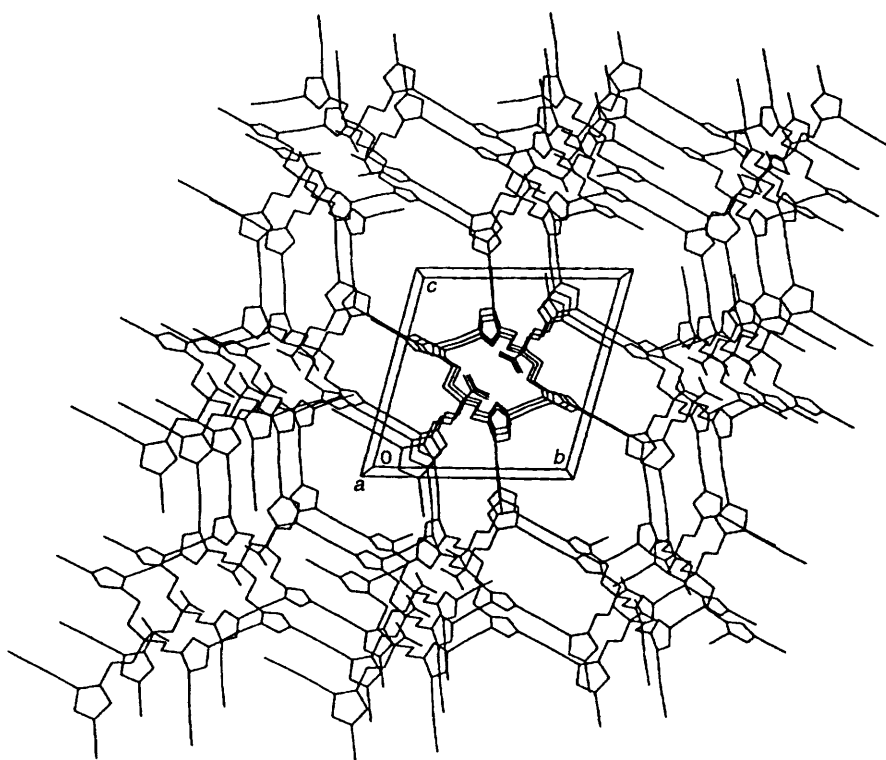
interactions and the overall lattice architecture have been unambiguously ascertained.

The local geometry about each of the three tin atoms in the asymmetric unit is *trans*- $N_2SnC_3$ , as suggested by the spectroscopic data and found in all previously examined tin tetrazoles.<sup>1,2</sup> The axial positions are occupied by tetrazole  $N^1$  and  $N^3$  atoms [see equation (1) for numbering scheme] and in each case the N–Sn–N bond angle is close to  $180^\circ$  [ $N(1)–Sn(1)–N(11)$   $175.6(5)$ ,  $N(3)–Sn(2)–N(5)$   $175.9(5)$  and  $N(7)–Sn(3)–N(9)$   $176.0(5)^\circ$ ] while the six individual N–Sn bond lengths are equivalent within experimental error (see Fig. 1). Such bond lengths are typical of other tin tetrazoles.<sup>1,2</sup> The  $N^1 + N^3$  co-ordination of the tetrazole is the one most commonly encountered, presumably as the sterically least-demanding combination of ligating atoms. The  $N^1 + N^4$  tetrazole co-ordination does, however, occur in the bicyclic species  $Ph_2Sn(CH_2)_3CN_4$ ,<sup>2</sup> while the less common  $N^2 + N^3$  co-ordination is typified by the tetrazoles of  $[Mn_2(CO)_6(N_4CCF_3)_3]^-$ .<sup>12</sup> With respect to tin, the metal has a choice of hindered ( $N^1$ ;  $N^4$  is equivalent in this respect) or more open nitrogens ( $N^2$ ;  $N^3$  is structurally equivalent), and in **3** each tin favours  $N^1 + N^2$  co-ordination. We have observed this mode previously in  $1,2-(Bu_3SnN_4C)_2C_6H_4$ , though both  $N^1 + N^1$  [ $1,2-(Et_3SnN_4C)_2C_6H_4$ ] and  $N^2 + N^2$  [ $1,2-(Et_3SnN_4C)_2C_6H_4$ ] bonding are also known.<sup>1</sup>

Each trimetallic asymmetric unit is centred around an inversion centre which thereby generates hexagonal rings (Fig. 1). Such rings are not common, but have previously been observed both by us [ $(Ph_3SnO_2PPh_2)_6$ ]<sup>13</sup> and others [ $Ph_3SnO_2P(OMe)Me$ ]<sub>6</sub>,<sup>14</sup>  $Ph_3SnO_2CCH_2NC(O)C_6H_4C(O)$ <sup>15</sup> and  $(Bu_2SnO_2CCH_2CH_2S)_6$ .<sup>16</sup> However, unlike the examples quoted, the hexameric rings of **3**, which embody a  $N_{18}Sn_6$  heterocycle, are not isolated but form part of a highly polymeric lattice propagated in two dimensions *via trans*-trigonal-bipyramidal  $N_2SnBu_3$  bridging interactions (Fig. 2). The hexagonal constructions are interlinked into the overall snow-flake-like appearance *via* the ethyl chains of the substituted nitromethane units. In this manner the hexagonal rings are bounded by six approximately rhombohedral openings each incorporating two tin centres and of empirical formula  $C_{14}N_8Sn_2$ . These latter openings are, in turn, constructed from the adjacent sides of two hexagonal rings, linked at each end by the five-carbon chain provided by two ethyl groups and the nitro-bonded methane carbon. Each substituted nitromethane thus provides the bridgehead for three six-sided rings, with facile hexamer packing assisted by the inherent three-fold symmetry of the tris(tetrazole) ligand. The cavities provided by the hexagonal rings are of the order of 12 Å in diameter and are completely filled by the butyl groups on tin which protrude into each interior.



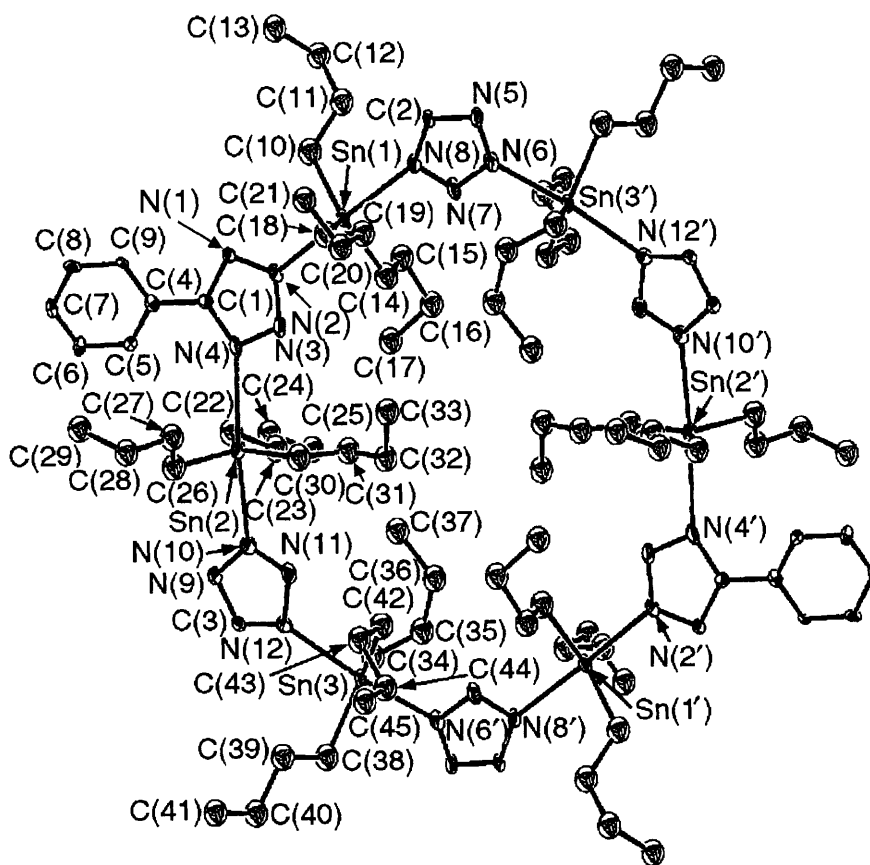
**Fig. 3** View of compound 3 parallel to the layers, showing their inherent non-planarity. The butyl groups attached to tin have been omitted for clarity



**Fig. 4** The microchannel structure of compound 3 generated by stacking of the layers. The butyl groups attached to tin have been omitted for clarity

As can be seen from Fig. 3, the individual polymeric sheets of compound 3 lie approximately parallel to one another. The interlamellar region is populated by the tin-bonded butyl groups and the tripodal nitromethane units which alternately project above and below the plane of polymer propagation. This latter feature ensures that the individual sheets are not planar, but are puckered and stacked rather like the layers of an egg box. This provides for a mean interlayer separation

of 10.1 Å, measured orthogonally between the approximately linear N–Sn–N vectors of the individual sheets. Although the individual cavities of each sheet are not positioned directly above each other, Fig. 4 reveals that when the array of stacked layers is viewed obliquely the structure is observed to consist of linear microchannels. Two types of channels can be discerned, constructed respectively from the arrays of large hexagonal and rhombohedral cavities described above.



**Fig. 5** The asymmetric unit of compound **6** showing the atomic labelling. Selected geometric data: N(2)–Sn(1) 2.36(1), N(8)–Sn(1) 2.45(1), C(10)–Sn(1) 2.09(2), C(14)–Sn(1) 2.14(2), C(18)–Sn(1) 2.11(2), N(4)–Sn(2) 2.47(1), N(10)–Sn(2) 2.35(1), C(22)–Sn(2) 2.13(2), C(26)–Sn(2) 2.14(1), C(30)–Sn(2) 2.15(3), N(12)–Sn(3) 2.48(1), Sn(3)–N(6) 2.35(1), C(34)–Sn(3) 2.15(2), C(38)–Sn(3) 2.13(1) and C(42)–Sn(3) 2.15(2) Å; N(8)–Sn(1)–N(2) 178.3(4), N(10)–Sn(2)–N(4) 174.8(3) and N(6)–Sn(3)–Sn(12) 174.0(4)°

#### Crystal structure of 1,3,5-tris-(2-tributylstannyltetrazol-5-yl)-benzene **6**

The asymmetric unit of compound **6** is illustrated in Fig. 5 along with the labelling scheme used in the text and selected bond lengths and angles. It contains three tin centres which all have *trans*-N<sub>2</sub>SnC<sub>3</sub> stereochemistry. The Sn–N bonds lie in the region of those observed for **3**, and both short [Sn(1)–N(2) 2.36(1), Sn(2)–N(10) 2.35(1) and Sn(3)–N(6) 2.35(1) Å] and long [Sn(1)–N(8) 2.45(1), Sn(2)–N(4) 2.47(1) and Sn(3)–N(12) 2.48(1) Å] bonds are discernible for each tin, presumably corresponding to intra- and inter-molecular interactions, respectively. The regularity of the bipyramidal geometry about tin is evidenced by the linearity of the three N–Sn–N moieties [N(2)–Sn(1)–N(8) 178.3(4), N(4)–Sn(2)–N(10) 174.8(3) and N(6)–Sn(3)–N(12) 174.0(4)°]. In addition, the N<sup>1</sup> + N<sup>3</sup> co-ordination of each tetrazole (N<sup>1</sup> + N<sup>2</sup> with respect to tin) is identical to that of **3**. Compound **6** also adopts an equivalent two-dimensional structural motif to that of the substituted nitromethane derivative **3** (Fig. 6) to form a two-dimensional infinitely polymeric network of tetrazole hexamers (internal diameter *ca.* 12 Å). Facile hexamer packing is again assisted by the inherent three-fold character of the tris(tetrazole) ligand which serves an identical role in lattice construction to that of the ethyl-substituted nitromethane unit of **3**. The supramolecular structures of **3** and **6** do, however, differ as a result of the inherent planarity of the bridging C<sub>6</sub>H<sub>3</sub> unit (in contrast to the tripodal nature of the nitromethane group in **3**) which enforces a greater degree of planarity on the individual sheets (Fig. 7). Any deviation from planarity in **6** is controlled by the angle of twist between the central C<sub>6</sub> plane and those of the respective tetrazoles attached to the 1, 3 and 5 positions. The C(2)-containing tetrazole is virtually coplanar with the phenyl ring [N(8)–C(2)–C(8)–C(7) 1.6°] whereas the remaining tetrazoles

are somewhat skewed [C(5)–C(4)–C(1)–N(1) 21.8, C(5)–C(6)–C(3)–N(12) 21.1°]. The individual layers of **6** are separated by a mean interplanar distance of *ca.* 11.3 Å, while viewing these layers obliquely reveals the same open channels running through the structure as occurs in **3** (Fig. 8). Again it should be emphasised that the apparently open structure is in fact filled by the pendant butyl groups on tin.

#### Conclusion

Trifunctional organotin tetrazoles centred on planar C<sub>6</sub>H<sub>3</sub> or tripodal nitromethane frameworks generate similar sheet-like structures, which differ only in the planarity of the layer structures which are inherently related to the nature of the ligands. These sheet architectures are a new structural type for organotin tetrazoles, and contrast the supramolecular arrays (zigzag sheet, bilayer) previously observed for difunctional systems.

#### Experimental

Spectra were recorded on the following instruments: JEOL GX270 (<sup>1</sup>H, <sup>13</sup>C NMR), GX60Q and EX400 (<sup>119</sup>Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.<sup>17</sup>

Tris(2-cyanoethyl)nitromethane was obtained from Aldrich and used without further purification, while 1,3,5-tricyanobenzene was synthesised from the corresponding amide using thionyl chloride and dimethylformamide.<sup>18,19</sup> Triorganotin azides SnR<sub>3</sub>(N<sub>3</sub>) were prepared by literature methods (R = Me,<sup>20</sup> Et<sup>1</sup> or Bu<sup>21</sup>) and employed without further purification.

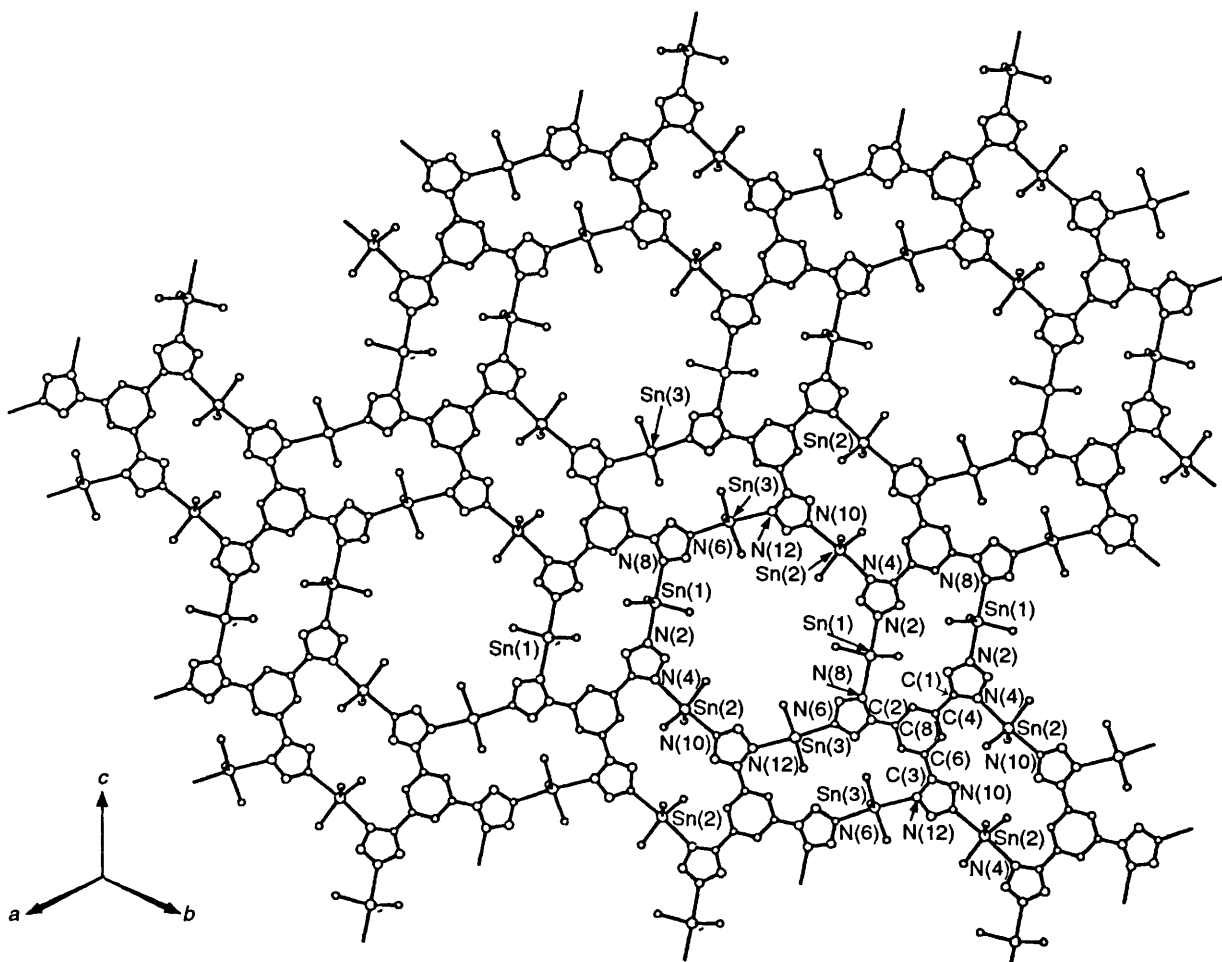


Fig. 6 The layer structure of compound 6 showing the hexagonal motif. Only the  $\alpha$ -carbons of the butyl groups attached to tin are shown for clarity

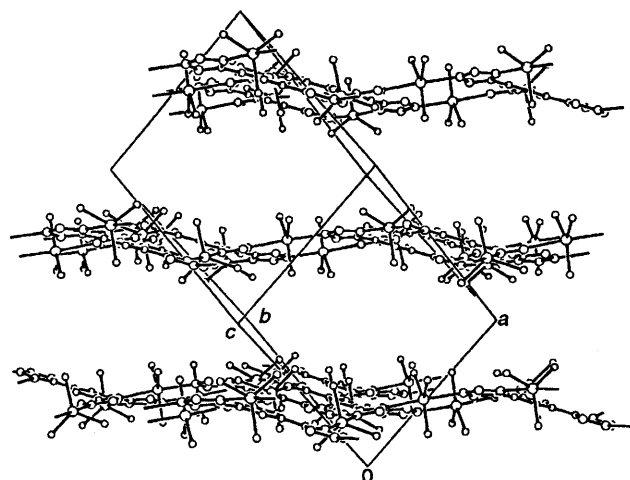


Fig. 7 View of compound 6 parallel to the layers, showing their relative planarity compared to that of 3 (see Fig. 3). Only the  $\alpha$ -carbons of the butyl groups attached to tin are shown for clarity

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

### Syntheses

**1,3,5-Tricarbamoylbenzene.** Benzene-1,3,5-tricarbonyl trichloride (8.0 g, 30 mmol) was stirred cautiously with aqueous concentrated ammonia solution (75 cm<sup>3</sup>). Once the vigorous exothermic reaction had subsided, the resulting dense white

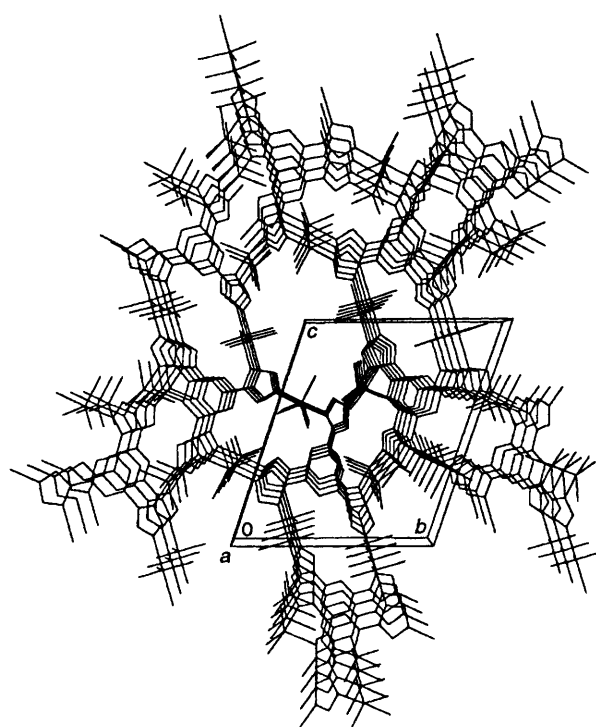


Fig. 8 The microchannel structure of compound 6 generated by stacking of the layers. Only the  $\alpha$ -carbons of the butyl groups attached to tin are shown for clarity

precipitate was stirred at room temperature for 2 h. The solid was then filtered off, washed successively with ethanol and

**Table 1** Fractional atomic coordinates ( $\times 10^4$ ) for compound 3

Atom	x	y	z	Atom	x	y	z
Sn(1)	3 426(1)	9 407(1)	7 180(1)	C(13)	3 314(45)	10 425(37)	9 881(34)
Sn(2)	2 623(1)	6 267(1)	10 649(1)	C(14)	3 602(16)	5 097(11)	10 684(16)
Sn(3)	-690(1)	6 985(1)	13 495(1)	C(15)	2 985(20)	4 277(17)	10 726(22)
N(1)	3 623(12)	7 846(9)	7 976(8)	C(16)	3 811(27)	3 478(17)	10 695(32)
N(2)	3 360(14)	7 718(8)	8 852(9)	C(17)	3 242(45)	2 647(22)	10 759(58)
N(3)	3 306(12)	6 851(9)	9 181(9)	C(18)	3 028(22)	7 417(14)	10 943(18)
N(4)	3 520(13)	6 413(8)	8 530(9)	C(19)	3 885(31)	7 102(22)	11 572(28)
N(5)	1 905(13)	5 780(10)	12 153(9)	C(20)	4 085(33)	7 895(27)	11 971(30)
N(6)	1 105(13)	6 347(10)	12 250(9)	C(21)	4 986(42)	7 601(39)	12 566(40)
N(7)	793(11)	6 189(10)	13 083(10)	C(22)	1 156(21)	6 283(34)	10 161(30)
N(8)	1 358(12)	5 495(10)	13 560(9)	C(23)	660(56)	7 221(31)	9 779(49)
N(9)	-2 167(12)	7 850(9)	13 809(10)	C(24)	-149(67)	7 170(54)	9 138(64)
N(10)	-2 216(14)	8 705(9)	13 389(12)	C(25)	-405(24)	6 507(20)	14 855(12)
N(11)	3 098(13)	10 933(9)	6 442(10)	C(26)	-195(56)	7 017(54)	15 533(52)
N(12)	3 689(12)	11 521(9)	5 948(10)	C(27)	912(66)	6 791(76)	15 808(69)
N(13)	5 350(15)	4 267(14)	14 303(11)	C(28)	-1 571(29)	6 089(23)	13 080(29)
O(1)	5 742(13)	3 782(12)	14 938(12)	C(29)	-1 748(73)	5 650(60)	12 333(53)
O(2)	5 603(13)	5 031(10)	13 976(11)	C(30)	-2 699(83)	6 102(86)	11 858(68)
C(1)	3 703(12)	7 049(10)	7 812(10)	C(31)	-565(35)	7 967(25)	12 271(19)
C(2)	2 017(13)	5 257(11)	12 979(11)	C(32)	259	8 424	12 611
C(3)	-3 135(14)	7 723(11)	14 180(11)	C(33)	550(57)	9 247(40)	11 819(33)
C(4)	4 767(17)	9 371(19)	6 314(17)	C(34)	1 532(80)	9 590(79)	12 026(77)
C(5)	5 658(28)	8 891(24)	6 833(28)	C(35)	4 531(17)	3 949(10)	13 848(10)
C(6)	6 495(39)	9 497(35)	6 849(64)	C(36)	3 718(15)	4 726(10)	13 655(12)
C(7)	7 531(29)	8 964(57)	6 864(69)	C(37)	2 814(18)	4 490(10)	13 186(12)
C(8)	1 945(19)	9 171(31)	6 935(34)	C(38)	5 022(13)	3 781(9)	12 960(9)
C(9)	1 828(72)	9 260(57)	5 943(37)	C(39)	4 025(14)	6 890(10)	6 913(9)
C(10)	3 805(38)	9 788(33)	8 325(23)	C(40)	4 126(13)	3 051(9)	14 448(9)
C(11)	2 697(38)	9 847(33)	8 672(31)	C(41)	-3 475(15)	6 801(9)	14 695(10)
C(12)	2 552(50)	10 612(48)	9 156(45)				

diethyl ether before drying for 16 h at 110 °C. This yielded the product (5.46 g, 88%) as an amorphous white solid, insoluble in all common solvents [Found (Calc. for  $C_9H_9N_3O_3$ ): C, 50.2 (52.2); H, 4.20 (4.35); N, 18.6 (20.2)%]. IR ( $cm^{-1}$ , Nujol mull): 3391, 3198, 1698, 1655, 1632, 1590, 1111 and 633.

**1,3,5-Tricyanobenzene.** 1,3,5-Tricarbamoylbenzene (4.6 g, 22.2 mmol) was stirred in dimethylformamide (35  $cm^3$ ) and thionyl chloride (6  $cm^3$ ) added to the suspension over 1 h maintaining the temperature at 60 °C. Stirring at this temperature was maintained for 6 h during which time complete dissolution occurred. The resulting solution was poured into dilute HCl (100  $cm^3$ ) to decompose unreacted  $SOCl_2$ , giving a dense white precipitate. This solid was filtered off, washed with water until neutral to litmus and dried at 120 °C for 14 h. Crystallisation from ethanol and acetone yielded the product as colourless needles (1.50 g, 45%) [Found (Calc. for  $C_6H_3N_3$ ): C, 70.4 (70.6); H, 1.90 (1.95); N, 27.4 (27.5)%]. NMR [ $(CD_3)_2SO$ ]:  $^1H$ ,  $\delta$  8.80 (s, 3 H, *o*- $C_6H_3$ );  $^{13}C$ , 114.1 (CN); 115.9 (*ipso*-C of  $C_6H_3$ ) and 140.4 (*o*-C of  $C_6H_3$ ). IR ( $cm^{-1}$ , Nujol mull): 3083 [ $\nu_{asym}(CH)$ ], 2249 [ $\nu(CN)$ ], 1377, 911 and 675.

**Nitrotris[2-(2-trimethylstannyltetrazol-5-yl)ethyl]methane 1.** Trimethyltin azide (1.65 g, 8.0 mmol) was heated under nitrogen with tris(2-cyanoethyl)nitromethane (0.60 g, 2.7 mmol) to 190 °C for 1 h resulting in a viscous brown oil which solidified on cooling. This was dissolved in methanol and filtered through activated charcoal to give a colourless solution. Removal of the solvent *in vacuo* yielded compound 1 as a sticky colourless glass which was dried under vacuum (1.42 g, 63%) [Found (Calc. for  $C_{19}H_{39}N_{13}O_2Sn_3$ ): C, 27.7 (27.2); H, 4.80 (4.60); N, 20.5 (21.7)%]. NMR [ $(CD_3)_2SO$ ]:  $^1H$ ,  $\delta$  -0.17 (s, 27 H,  $CH_3$ ); 1.70 (m, 6 H,  $CH_2CN_4$ ) and 2.05 [m, 6 H,  $NO_2C(CH_2)_3$ ];  $^2J[C^1H_3-^{117,119}Sn]$  66.5, 69.4;  $^{13}C$ ,  $\delta$  -0.3 ( $CH_3$ ), 19.6 ( $CH_2CN_4$ ), 33.7 [ $NO_2C(CH_2)_3$ ], 93.8 ( $NO_2C$ ) and 160.6 ( $CN_4$ );  $^1J[^{13}CH_3-^{117,119}Sn]$  507.4, 529.4 Hz;  $^{119}Sn$ ,  $\delta$

-49.0.  $^{119m}Sn$  Mössbauer ( $mm\ s^{-1}$ ): isomer shift (i.s.) = 1.27, quadrupole splitting (q.s.) = 3.42.

**Nitrotris[2-(2-triethylstannyltetrazol-5-yl)ethyl]methane 2.** Triethyltin azide (6.0 g, 24.2 mmol) and tris(2-cyanoethyl)nitromethane (1.78 g, 8.08 mmol) were heated neat under nitrogen to 170 °C for 1 h. The reactants set to a solid mass during this period and were extracted with methanol in a Soxhlet apparatus. Decolourisation with activated charcoal, followed by crystallisation at -20 °C, yielded compound 2 as colourless needles (3.2 g, 42%), m.p. 235 °C (decomp.) [Found (Calc. for  $C_{28}H_{57}N_{13}O_2Sn_3$ ): C, 34.8 (34.9); H, 5.85 (5.90); N, 18.8 (18.9)%]. NMR [ $(CD_3)_2SO$ ]:  $^1H$ ,  $\delta$  1.16 (t, 27 H,  $CH_3$ ), 1.25 (m, 18 H,  $CH_2CH_3$ ), 2.50 (m, 6 H,  $CH_2CN_4$ ) and 2.74 [m, 6 H,  $NO_2C(CH_2)_3$ ];  $^{13}C$ ,  $\delta$  10.1 ( $CH_2CH_3$ ), 10.2 ( $CH_2CH_3$ ), 19.6 ( $CH_2CN_4$ ), 33.6 [ $NO_2C(CH_2)_3$ ], 93.7 ( $NO_2C$ ) and 161.1 ( $CN_4$ );  $^1J[^{13}CH_2CH_3-^{117,119}Sn]$  474.3, 496.4 Hz;  $^{119}Sn$ ,  $\delta$  -50.1.  $^{119m}Sn$  Mössbauer ( $mm\ s^{-1}$ ): i.s. = 1.50, q.s. = 3.80. IR ( $cm^{-1}$ , KBr disc): 2969, 2946, 2870, 1541, 1482, 1451, 1383 and 684.

**Nitrotris[2-(2-tributylstannyltetrazol-5-yl)ethyl]methane 3.** A suspension of tris(2-cyanoethyl)nitromethane (4.35 g, 19.8 mmol) in tributyltin azide (20.14 g, 60.9 mmol) was heated to 200 °C under nitrogen for 2 h. This resulted in a solid off-white mass. Extended extraction with methanol in a Soxhlet apparatus gave compound 3 as a microcrystalline solid (11.04 g, 46%), m.p. 216 °C (decomp.) [Found (Calc. for  $C_{46}H_{93}N_{13}O_2Sn_3$ ): C, 45.3 (45.4); H, 7.85 (7.65); N, 15.0 (15.0)%]. NMR [ $(CD_3)_2SO$ ]:  $^1H$ ,  $\delta$  0.80 (t, 27 H,  $CH_3$ ), 1.19-1.32 (m, 36 H,  $CH_2CH_2CH_2CH_3$ ), 1.50 (m, 18 H,  $CH_2CH_2CH_2CH_3$ ), 2.50 (m, 6 H,  $CH_2CN_4$ ) and 2.75 [m, 6 H,  $NO_2C(CH_2)_3$ ];  $^{13}C$ ,  $\delta$  13.6 ( $CH_3$ ), 18.2 [ $CH_2(CH_2)_2CH_3$ ], 19.8 ( $CH_2CN_4$ ), 26.4 [ $(CH_2)_2CH_2CH_3$ ], 27.7 ( $CH_2CH_2CH_2CH_3$ ), 33.7 [ $NO_2C(CH_2)_3$ ], 92.7 ( $NO_2C$ ) and 160.6 ( $CN_4$ );  $^2J[CH_2-^{13}CH_2CH_2CH_3-^{117,119}Sn]$  31.0 (unresolved),  $^3J[(C-H_2)^{13}CH_2CH_3-^{117,119}Sn]$  77.5 Hz (unresolved);  $^{119}Sn$ ,  $\delta$

**Table 2** Fractional atomic coordinates ( $\times 10^4$ ) for compound **6**

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Atom	<i>x</i>	<i>y</i>	<i>z</i>
Sn(1)	9 121(1)	-2 720(1)	-659(1)	C(16)	8 195(21)	148(19)	57(15)
Sn(2)	5 518(1)	-3 909(1)	3 002(1)	C(17)	7 760(22)	-382(19)	1 032(15)
Sn(3)	1 280(1)	-1 166(1)	3 697(1)	C(18)	8 311(16)	-3 773(14)	-990(10)
N(1)	8 855(9)	-4 564(8)	1 212(6)	C(19)	7 938(20)	-3 497(16)	-1 822(12)
N(2)	8 397(9)	-3 716(8)	790(6)	C(20)	7 361(23)	-4 409(18)	-1 893(20)
N(3)	7 475(9)	-3 502(7)	1 269(6)	C(21)	8 243(33)	-5 219(29)	-1 951(29)
N(4)	7 285(9)	-4 202(7)	2 047(6)	C(22)	6 417(11)	-3 281(10)	3 634(8)
N(5)	10 295(8)	-859(7)	-3 568(6)	C(23)	6 254(13)	-2 140(11)	3 534(10)
N(6)	9 670(9)	-277(7)	-3 132(6)	C(24)	6 941(15)	-1 729(13)	3 980(11)
N(7)	9 382(9)	-756(7)	-2 289(6)	C(25)	6 788(19)	-612(16)	3 886(14)
N(8)	9 816(9)	-1 676(7)	-2 166(6)	C(26)	5 025(11)	-5 486(9)	3 530(8)
N(9)	3 573(8)	-3 792(7)	4 713(6)	C(27)	5 209(13)	-6 044(12)	2 854(10)
N(10)	3 862(9)	-3 473(8)	3 837(6)	C(28)	4 806(14)	-7 161(12)	3 244(10)
N(11)	3 225(8)	-2 760(7)	3 525(6)	C(29)	5 505(16)	-7 816(15)	3 796(12)
N(12)	2 460(8)	-2 593(7)	4 197(6)	C(30)	4 880(18)	-3 285(14)	1 901(9)
C(1)	8 144(10)	-4 831(9)	1 983(7)	C(31)	5 078(23)	-2 125(14)	1 484(16)
C(2)	10 386(10)	-1 723(9)	-2 964(7)	C(32)	4 548(26)	-1 841(26)	728(16)
C(3)	2 719(10)	-3 229(8)	4 911(7)	C(33)	5 117(27)	-2 236(27)	-28(19)
C(4)	8 274(10)	-5 743(9)	2 692(7)	C(34)	2 206(11)	-200(10)	4 062(8)
C(5)	7 795(10)	-5 803(9)	3 547(7)	C(35)	2 673(13)	820(12)	3 383(10)
C(6)	7 887(10)	-6 690(9)	4 201(7)	C(36)	3 396(13)	729(12)	2 550(10)
C(7)	8 464(10)	-7 485(9)	3 987(7)	C(37)	4 388(15)	55(14)	2 655(12)
C(8)	8 982(9)	-7 411(9)	3 142(7)	C(38)	-202(10)	-1 867(9)	4 637(8)
C(9)	8 918(9)	-6 523(9)	2 503(7)	C(39)	-369(12)	-3 034(11)	4 836(9)
C(10)	10 702(10)	-3 006(10)	-468(8)	C(40)	-1 356(14)	-3 498(13)	5 591(11)
C(11)	11 668(10)	-2 273(11)	-1 089(9)	C(41)	-1 538(15)	-4 623(13)	5 720(12)
C(12)	12 808(13)	-2 408(16)	-897(15)	C(42)	1 759(13)	-1 423(11)	2 473(9)
C(13)	13 204(26)	-3 495(17)	-833(21)	C(43)	1 188(18)	-2 309(16)	2 410(14)
C(14)	8 246(12)	-1 471(11)	-327(9)	C(44)	113(18)	-1 974(16)	2 339(14)
C(15)	8 893(20)	-738(18)	-246(16)	C(45)	-463(26)	-2 835(23)	2 246(20)

-36.0.  $^{119\text{m}}\text{Sn}$  Mössbauer ( $\text{mm s}^{-1}$ ): i.s. = 1.42, q.s. = 3.61. IR ( $\text{cm}^{-1}$ , KBr disc): 2959, 2924, 2872, 2855, 1549, 1477, 1464, 1402, 1377, 1358, 1225, 1140, 1080, 879, 700 and 680.

**1,3,5-Tris(2-trimethylstannyltetrazol-5-yl)benzene 4.** 1,3,5-Tricyanobenzene (0.58 g, 3.8 mmol) and trimethyltin azide (2.34 g, 11.4 mmol) were refluxed under nitrogen in *p*-xylene (50  $\text{cm}^3$ ) for 1 h. The initial colourless solution became a suspension as the reaction progressed. This was then cooled, filtered and washed with diethyl ether. Crystallisation from methanol gave compound **4** (2.21 g, 70%) as a hexahydrate, m.p. > 240 °C [Found (Calc. for  $\text{C}_{18}\text{H}_{42}\text{N}_{12}\text{O}_6\text{Sn}_3$ ): C, 24.7 (24.6); H, 4.45 (4.70); N, 19.1 (19.1)%]. NMR [ $(\text{CD}_3)_2\text{SO}$ ]:  $^1\text{H}$ ,  $\delta$  0.70 (s, 27 H,  $\text{CH}_3$ ), 3.60 (br s, 12 H,  $\text{H}_2\text{O}$ ) and 8.73 (s, 3 H, *o*-H of  $\text{C}_6\text{H}_3$ );  $^2\text{J}[\text{C}^1\text{H}_3-^{117,119}\text{Sn}]$  69.1 Hz (unresolved);  $^{13}\text{C}$ ,  $\delta$  -0.2 ( $\text{CH}_3$ ), 124.3 (*o*-C of  $\text{C}_6\text{H}_3$ ), 131.0 (*ipso*-C of  $\text{C}_6\text{H}_3$ ) and 162.0 ( $\text{CN}_4$ );  $^{119}\text{Sn}$ ,  $\delta$  -37.3.  $^{119\text{m}}\text{Sn}$  Mössbauer ( $\text{mm s}^{-1}$ ): i.s. = 1.34, q.s. = 3.70. IR ( $\text{cm}^{-1}$ , KBr disc): 3638, 2999, 2918, 2791, 1638, 1418, 1217, 1163, 1010, 785, 750, 551 and 461.

**1,3,5-Tris(2-triethylstannyltetrazol-5-yl)benzene 5.** 1,3,5-Tricyanobenzene (2.0 g, 8.07 mmol) and triethyltin azide (0.41 g, 2.68 mmol) were refluxed in mesitylene (50  $\text{cm}^3$ ) under nitrogen for 2 h. The resulting colourless suspension was filtered and washed with diethyl ether. Successive crystallisation from methanol and ethanol yielded compound **5** (1.24 g, 52%) as colourless needles, m.p. > 240 °C [Found (Calc. for  $\text{C}_{27}\text{H}_{48}\text{N}_{12}\text{Sn}_3$ ): C, 35.9 (36.1); H, 5.30 (5.35); N, 18.1 (18.7)%]. NMR [ $(\text{CD}_3)_2\text{SO}$ ]:  $^1\text{H}$ ,  $\delta$  1.26 (t, 27 H,  $\text{CH}_2\text{CH}_3$ ), 1.37 (m, 18 H,  $\text{CH}_2\text{CH}_3$ ) and 8.76 [s, 3 H, *o*-H of  $\text{C}_6\text{H}_3$ ];  $^{13}\text{C}$ ,  $\delta$  7.8 ( $\text{CH}_2\text{CH}_3$ ), 10.3 ( $\text{CH}_2\text{CH}_3$ ), 124.1 (*o*-C of  $\text{C}_6\text{H}_3$ ), 131.0 (*ipso*-C of  $\text{C}_6\text{H}_3$ ) and 162.0 ( $\text{CN}_4$ );  $^{119}\text{Sn}$ ,  $\delta$  -45.3.  $^{119\text{m}}\text{Sn}$  Mössbauer ( $\text{mm s}^{-1}$ ): i.s. = 1.52, q.s. = 3.93. IR ( $\text{cm}^{-1}$ , KBr disc): 2975, 2950, 2923, 2870, 1456, 1412, 1325, 1217, 1024, 791, 749, 683, 526 and 454.

**1,3,5-Tris(2-tributylstannyltetrazol-5-yl)benzene 6.** 1,3,5-Tricyanobenzene (1.0 g, 6.54 mmol) was heated under nitrogen

as a suspension in tributyltin azide (6.50 g, 19.6 mmol). Although the reaction mixture set to a white solid at 110 °C heating was continued to 160 °C at which point it was allowed to cool. The resulting white solid was extracted by methanol in a Soxhlet apparatus and the resulting solution cooled to yield compound **6** as a colourless microcrystalline solid (4.8 g, 65%), m.p. > 240 °C [Found (Calc. for  $\text{C}_{45}\text{H}_{84}\text{N}_{12}\text{Sn}_3$ ): C, 47.1 (47.0); H, 7.50 (7.30); N, 14.7 (14.6)%]. NMR [ $(\text{CD}_3)_2\text{SO}$ ]:  $^1\text{H}$ ,  $\delta$  0.83 (t, 27 H,  $\text{CH}_3$ ); 1.26-1.47 (m, 36 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 1.54-1.62 (m, 18 H,  $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ) and 8.73 (s, 3 H, *o*-H of  $\text{C}_6\text{H}_3$ );  $^{13}\text{C}$ ,  $\delta$  13.5 ( $\text{CH}_3$ ), 18.3 [ $\text{CH}_2(\text{CH}_2)_2\text{CH}_3$ ], 26.3 [ $(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ], 27.7 ( $\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 124.0 (*o*-C of  $\text{C}_6\text{H}_3$ ), 131.0 (*ipso*-C of  $\text{C}_6\text{H}_3$ ) and 162.0 ( $\text{CN}_4$ );  $^1\text{J}[\text{C}^1\text{H}_2(\text{C}-\text{H}_2)_2\text{CH}_3-^{117,119}\text{Sn}]$  461.5 (unresolved),  $^2\text{J}[\text{CH}_2^{13}\text{CH}_2\text{CH}_2-\text{CH}_3-^{117,119}\text{Sn}]$  29.4 (unresolved),  $^3\text{J}[(\text{CH}_2)_2^{13}\text{CH}_2\text{CH}_3-^{117,119}\text{Sn}]$  75.3 Hz (unresolved);  $^{119}\text{Sn}$ ,  $\delta$  -49.9.  $^{119\text{m}}\text{Sn}$  Mössbauer ( $\text{mm s}^{-1}$ ): i.s. = 1.50, q.s. = 3.83. IR ( $\text{cm}^{-1}$ , KBr disc): 2957, 2925, 2870, 2856, 1464, 1412, 1377, 1321, 1219, 1080, 880, 789, 748, 679 and 455.

#### X-Ray crystallography

**Compound 3.** Suitable crystals were grown by very slow evaporation of a methanol solution. A crystal of approximate dimensions 0.3  $\times$  0.3  $\times$  0.2 mm was used for data collection.

**Crystal data.**  $\text{C}_{46}\text{H}_{93}\text{N}_{13}\text{O}_2\text{Sn}_3$ ,  $M = 1214.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 13.241(4)$ ,  $b = 15.567(5)$ ,  $c = 15.621(12)$  Å,  $\alpha = 75.01(3)$ ,  $\beta = 85.27(5)$ ,  $\gamma = 85.36(3)^\circ$ ,  $U = 3093.7$  Å $^3$ ,  $Z = 2$ ,  $D_c = 1.30$  g  $\text{cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 12.40$   $\text{cm}^{-1}$ ,  $F(000) = 1252$ .

Data were measured at room temperature on a CAD4 automatic four-circle diffractometer in the range  $2 \leq \theta \leq 24^\circ$ . 10 118 Reflections were collected of which 3379 were unique with  $I \geq 3\sigma(I)$ . Data were corrected for Lorentz and polarisation effects and also for linear crystal decay of approximately 37% in the X-ray beam. No absorption correction was applied. The structure was solved by direct methods and refined using the SHELX<sup>22,23</sup> suite of programs. In the final least-squares cycles all atoms except for the butyl



carbons [C(4)–C(34)] were allowed to vibrate anisotropically. Unfortunately, not all of the butyl carbons could be located [ $\gamma$ -,  $\delta$ -C on Sn(1);  $\delta$ -C on Sn(2); two  $\delta$ -C on Sn(3)], primarily as a consequence of crystal decay but also as a result of thermal motion in the solid state. This is clearly evidenced by the relatively large isotropic thermal parameters associated with certain carbon atoms, and to assist convergence during the latter stages of refinement, the C–C bond lengths associated with sections of the butyl chains were refined at a fixed distance of 1.54 Å (see Supplementary data). For similar reasons, the coordinates of C(32) were fixed during the refinement cycles. In addition, the distance between pairs of carbons ( $n, n + 2$ ;  $n = 1$  was restricted to a value of 2.52 Å. Hydrogen atoms were not included.

Final residuals after 10 cycles of least squares were  $R = 0.0629$ ,  $R' = 0.0710$ , for a weighting scheme of  $w = 0.3137/[\sigma^2(F) + 0.020194F^2]$ , based on  $F$ . Maximum final shift/e.s.d. was 0.022. The maximum and minimum residual densities were 0.33 and  $-0.18 \text{ e \AA}^{-3}$  respectively. Final fractional atomic coordinates are given in Table 1.

**Compound 6.** Suitable crystals were grown by very slow evaporation of a methanol solution. A crystal of approximate dimensions  $0.3 \times 0.2 \times 0.15 \text{ mm}$  was used.

*Crystal data.*  $\text{C}_{45}\text{H}_{84}\text{N}_{12}\text{Sn}_3$ ,  $M = 1149.3$ , triclinic, space group  $P\bar{1}$ ,  $a = 12.544(4)$ ,  $b = 13.846(5)$ ,  $c = 17.035(7) \text{ \AA}$ ,  $\alpha = 71.54(3)$ ,  $\beta = 74.28(4)$ ,  $\gamma = 86.97(5)^\circ$ ,  $U = 2699.7 \text{ \AA}^3$ ,  $Z = 2$ ,  $D_c = 1.41 \text{ g cm}^{-3}$ ,  $\mu(\text{Mo-K}\alpha) = 14.2 \text{ cm}^{-1}$ ,  $F(000) = 1176$ .

Data were measured at 170 K as for compound 3. 9248 Reflections were collected of which 3379 were unique with  $I \geq 3\sigma(I)$ . Data were corrected as for 3. The structure was solved by Patterson methods and refined using the SHELX<sup>22,23</sup> suite of programs. In the final least-squares cycles all atoms except the butyl carbons [C(10)–C(45)] were allowed to vibrate anisotropically. In addition, three butyl groups [C(10)–C(13), C(18)–C(21), C(30)–C(33)] were restricted to maintain C–C bond lengths of 1.54 Å during the latter stages of refinement, which helped to reduce the final shift/e.s.d. maxima, and afforded a small reduction in the residual values. Hydrogen atoms were included at calculated positions.

Final residuals after 12 cycles of least squares were  $R = 0.0700$ ,  $R' = 0.0721$ , for a weighting scheme  $w = 2.4176/[\sigma^2(F) + 0.001679F^2]$ , based on  $F$ . Maximum final shift/e.s.d. was 0.001. The maximum and minimum residual densities were 1.18 and  $-0.56 \text{ e \AA}^{-3}$  respectively. An empirical absorption did not significantly reduce this maximum [which is primarily a result of some disorder in the C(33) region] and hence was not applied. Final fractional atomic coordinates are given in Table 2.

Complete atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1.

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