Reactions of organotin tetrazoles: synthesis of functionalised poly-tetrazoles

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Reaction of 1,2-bis[2-(tributylstannyl)tetrazol-5-yl]benzene with 1,2-dibromoethane (1 : 10) yields the 1-*N*,1-*N*′-ethylene bridged cyclophane (**1**) while similar reactions with larger excesses (1 : 25) of 1,*n*-dibromoalkanes yield 1,2-bis[2-(bromoalkyl)tetrazol-5-yl]benzenes along with the unsymmetrical 1-*N*,2-*N*-substituted tetrazole isomers. Analogous products from 1,3-$(Bu_3SnN_4C)_2C_6H_4$ are also reported. Similar reactions occur between the two organotin compounds and 1-bromo-*n*-cyanoalkanes to give 1,*m*-bis[(cyanoalkyl)tetrazol-5-yl]benzenes (*m* = 2, 3) as both symmetric and unsymmetrically substituted tetrazole isomers, and which can be further developed to convert the pendant nitriles into tetrazoles by cycloaddition reactions with Bu_3SnN_3. The Bu_3Sn group is easily cleaved by H^+ to generate the related *N*-unsubstituted tetrazoles.

Introduction

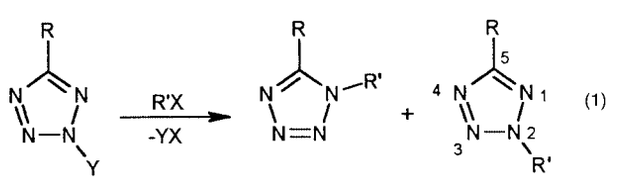
The synthesis of tetrazoles from the cycloaddition reaction between an azide and a nitrile is well established.[1,2] We have been investigating the use of organotin azides in this respect as such species react readily with nitriles considered to be poor dipolarophiles *e.g.* alkyl nitriles. Moreover, the resultant metallated heterocycles adopt a range of complex supramolecular structures in which five coordinate R_3SnN_2 units link the tetrazoles into layers,[3] two-dimensional networks of hexamers [1,3,5-$(Bu_3SnN_4C)_3C_6H_3$, 1,3,5-$(Bu_3SnN_4CCH_2CH_2)_3CNO_2$],[4] bilayers [1,6-$(Bu_3SnN_4C)_2(CH_2)_6$][5] and interpenetrating 3-D networks *e.g.* 1,2,4,5-$(Et_3SnN_4C)_4C_6H_2\cdot 2H_2O$.[6]

As part of our interest in tetrazoles in general we have looked at the use of organotin tetrazoles as precursors to new, functionalised poly-tetrazoles which can be used in other areas of synthesis. For example, protonated poly-tetrazoles could be used as acidic ligands toward other metals which themselves form unstable azides and are hence unsuited to direct synthesis *via* cycloaddition reactions. Macrocyclic poly-tetrazoles have also been reported by Butler *et al*. whose synthetic strategy also involved the stepwise elaboration of simpler functionalised tetrazole starting materials.[7] To this end, we now report on various aspects of the reaction of 1,2- and 1,3-$(Bu_3SnN_4C)_2C_6H_4$ with H^+, α,ω-dibromoalkanes and α-bromo-ω-cyanoalkanes.

Results and discussion

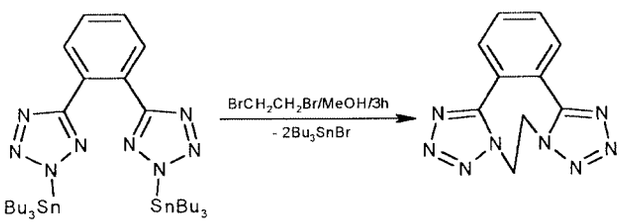
Reactions with α,ω-dibromoalkanes

Alkylation of 5-substituted mono-tetrazole derivatives is known to lead to mixtures of 1-*N*- and 2-*N*-substituted products,[8] the regiospecificity being dependent on the reaction conditions and the nature of the *C*- and *N*-substituents. Alkylation of *N*-metallated tetrazoles (Au,[9] Co,[10] SnR_3 [11]) with MeI or Me_2SO_4 has been found to yield predominantly (90%) 1,5-disubstituted tetrazoles [reaction (1)].



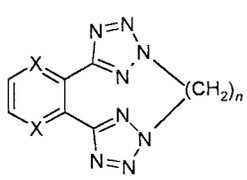
(1)

Reaction of 1,2-$(Bu_3SnN_4C)_2C_6H_4$ with a ten-fold excess of 1,2-dibromoethane in methanol leads to the formation of **1** in 37% yield (Scheme 1). The ^1H and ^{13}C NMR spectra of **1** each

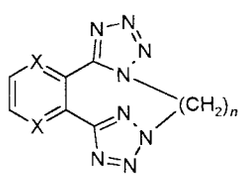


Scheme 1

show a single methylene resonance at 5.08 and 45.9 ppm, respectively. These values are characteristic of substitution at N^1 of the tetrazole ring,[8] as is the single resonance of the quaternary tetrazole-C^5 at 153.2 ppm. The overall simplicity of the aromatic regions of the spectra confirm this symmetrical pattern of substitution. The identity of **1** as a 1-*N*,1-*N*′-intramolecularly-bridged tetracyclic species rather than a larger macrocycle involving intermolecular bridges has been confirmed crystallographically, though the crystal chosen proved to be anhydrous rather than the monohydrate suggested by the microanalysis. The structure of the cyclophane **1** is shown in Fig. 1 and can be compared with three related structures (**Ia**–**c**).[12,13] In all four structures the two tetrazoles are twisted in



Ia: X = CH, *n* = 7
Ic: X = N, *n* = 7



Ib: X = CH, *n* = 7, dihydrate

relation to the central ring (**1**: 45.5°, 50.7°; **Ia**: 58.5°, 38.3°; **Ib**: 7.7°, 85.6°; **Ic**: 51.1°, 47.8°). The dihydrate **Ib** is most unsymmetrical due to the involvement of only one tetrazole in a network of hydrogen bonds, while **1** appears most symmetrical, presumably due the lack of rotational freedom which comes

with the shorter trans-tetrazole bridge. The ethylene bridge in **1** is the shortest yet incorporated into this family of heterocyclic cyclophanes and includes the first example of 1-*N*,1-*N*′-bridging. Cyclophanes **Ia**, **Ib** are examples of the more common 2-*N*,2-*N*′- and 1-*N*,2-*N*′-substitution patterns.

When a large excess (25:1) of α,ω-dibromoalkanes is employed however, bis(bromoalkytetrazolyl)benzenes **2a**,**b**–**11a**,**b** are produced (Scheme 2). Two major products, the 2-*N*, 2-*N*′- (**a**) and 1-*N*,2-*N*′-substituted (**b**) isomers, are formed in these reactions, though in some instances (**3**, **10**, **11**) the latter isomer, although suggested by TLC, was formed in too small a quantity to be isolated on a preparative scale. Typically, the 2-*N*,2-*N*′-isomer is seen to predominate in a ratio of *ca.* 3:1. More rigid substituents *e.g.* bromo-substituted *m*-xylyl (**12**) can be introduced in a similar manner. Compounds **10**–**12** have recently been prepared by Butler and Fleming from the *N*-unsubstituted tetrazoles and the appropriate dihaloalkane in the presence of Et_3N; yields of the minor 1-*N*,2-*N* isomer were of the order of 5%.[14]

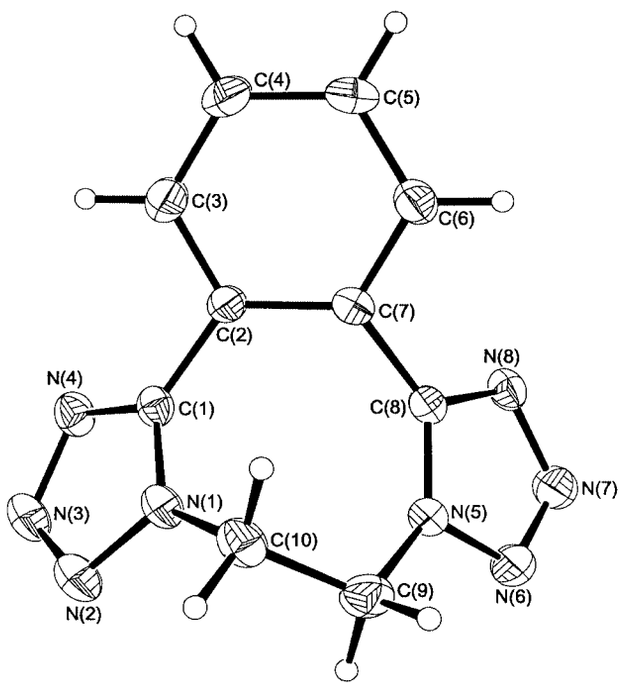


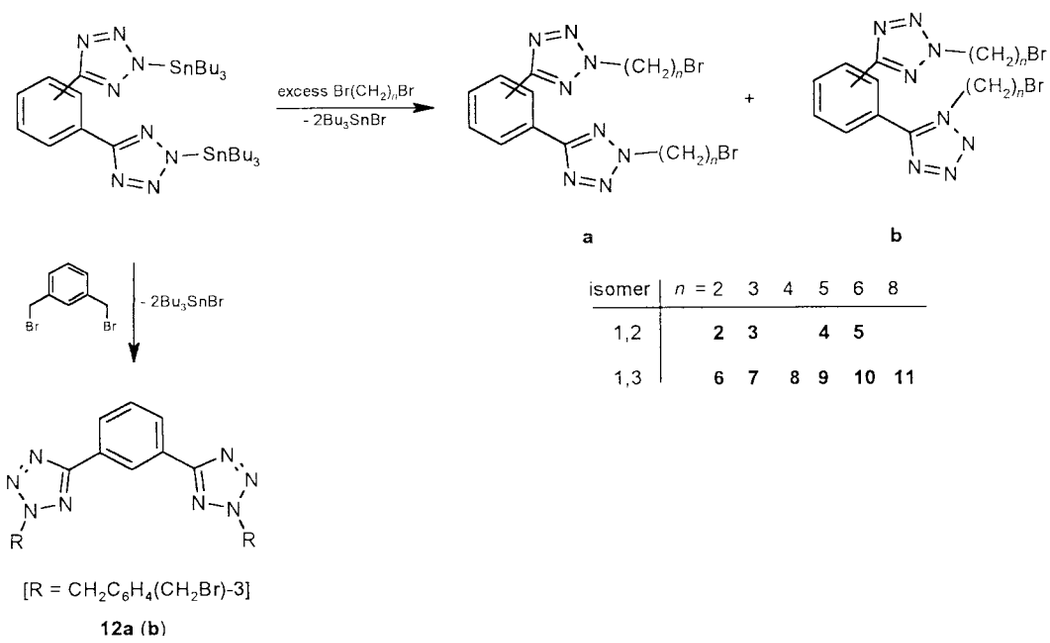
Fig. 1 The asymmetric unit of **1**. Thermal ellipsoids are at the 30% probability level.

The isomeric 2-*N*,2-*N*′ and 1-*N*,2-*N*′ derivatives **2**–**11** are readily distinguishable from their respective ^{1}H and ^{13}C NMR spectra. Methylene groups attached to N^1 are more shielded by *ca.* 0.15–0.35 ppm in the ^{1}H spectra and by 4–6 ppm in the ^{13}C spectra relative to their N^2-substituted counterparts.[8] Thus the symmetrical 2-*N*,2-*N*′-substituted compounds reported here show a single resonance at *ca.* 4.50 and 53.0 ppm in the ^{1}H and ^{13}C spectra respectively, attributable to the equivalent $-CH_2N^2$ and $-CH_2N^{2'}$ resonances. On the other hand the unsymmetrical derivatives show additional signals at *ca.* 4.10 and 47.0 ppm arising from the $-CH_2N^1$ grouping. Such differences in chemical environment are also transmitted down the length of the tetrazole-bonded alkyl chain, so that the spectra of the unsymmetrically-substituted compounds are more complex, with, in most cases, a separate signal resolvable for each individual methylene group of the two bromoalkyl substituents. In contrast, the symmetrically-disposed 2-*N*,2-*N*′-substituted derivatives show half the number of methylene resonances because of the chemical equivalence of the chains. The ^{13}C chemical shift of the tetrazole C^5 atom also differs significantly in 1,5- and 2,5-disubstituted tetrazoles, appearing at *ca.* 155.0 and 162.0 ppm respectively.[8] The symmetrical 2-*N*,2-*N*′-substituted compounds thus give rise to a single resonance corresponding to the second of these possibilities while both signals are apparent in the 1-*N*,2-*N*′-substituted compounds.

These structural assignments are unequivocally confirmed by the X-ray crystallographic study of the 2-*N*,2-*N*′-substituted **6a** (Fig. 2).

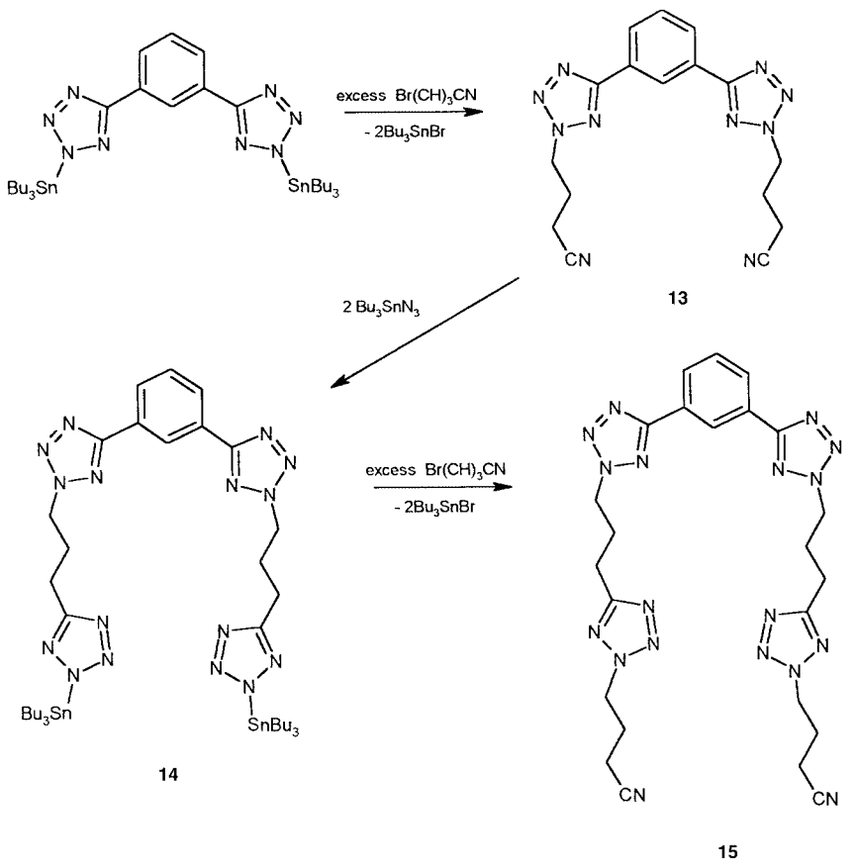
Reactions with α-bromo-ω-cyanoalkanes

Similar methodology to that described above can be employed to introduce nitrile-terminated substituents, which can in turn be elaborated into additional tetrazole functionalities. Thus, excess 1-bromo-3-cyanopropane reacts with 1,3-bis[2-(tributylstannyl)tetrazol-5-yl]benzene[3] to yield **13**, which can subsequently be converted to **14** by a cycloaddition reaction with Bu_3SnN_3. The Mössbauer spectrum of **14** has a quadrupole splitting (qs) of 3.70 mm s^{-1}, typical of *trans*-N_2SnR_3; recrystallisation of **14** from methanol afforded **14**·2MeOH whose qs is



isomer	*n* = 2	3	4	5	6	8
1,2	**2**	**3**		**4**	**5**	
1,3	**6**	**7**	**8**	**9**	**10**	**11**

Scheme 2



Scheme 3

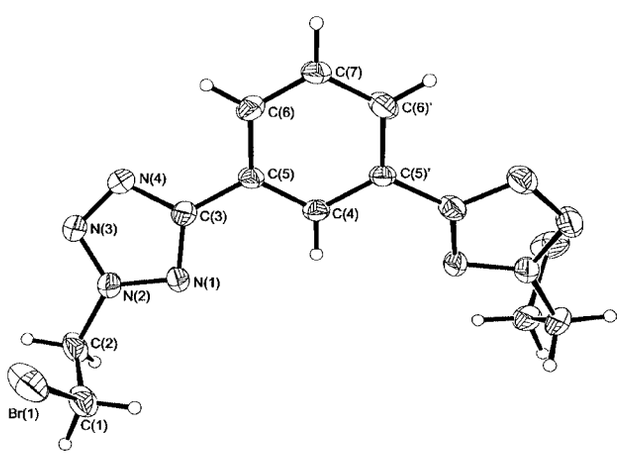
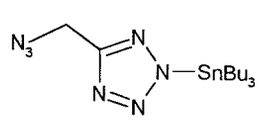


Fig. 2 The asymmetric unit of **6a**. Thermal ellipsoids are at the 30% probability level. The planes of the tetrazole rings are each twisted 13.2° with respect to the plane of the phenyl ring. Primed atoms are related to their unprimed analogues by the two-fold axis along the C(4)–C(7) vector.

somewhat reduced (3.50 mm s^{-1}) and thus suggests that methanol coordinates tin in one of its axial sites, in preference to intermolecular coordination from a tetrazole nitrogen. We have previously determined the structure of the related bis-methanol solvate 1,3-$(Bu_3SnN_4C)_2C_6H_4$·2MeOH which incorporates the suggested tin–solvent coordination.[3]

Compound **14** reacts further with $Br(CH_2)_3CN$ to give **15**, an orange oil, in 8% yield after purification by column chromatography (Scheme 3). The 2-*N*,2-*N*′-substitution pattern was difficult to verify by ^1H NMR due to the two different, but closely related NCH_2-environments. In the ^{13}C NMR, however, only two NCH_2 signals are seen (51.2, 52.3 ppm) indicative of two pairs of 2-*N*,2-*N*′-substituted tetrazoles. Further confirmation comes from the appearance of two signals due to C^5 of the tetrazole at positions (164.6, 165.4 ppm) more typical of 2-*N*, 5-*C* than 1-*N*,5-*C* substitution (see above). Nitrile carbons were seen at 118.0 ppm, and the nitrile group confirmed from the ν(CN) at 2249 cm^{-1} in the infrared spectrum.

The build-up of multi-functional tetrazoles by the sequential introduction of pendant nitriles onto preformed tetrazoles is apparently more facile than the alternative of introducing pendant azide groups. Thus, **16**, synthesised from Bu_3SnN_3 and



16

$NCCH_2N_3$,[15] failed to react with malononitrile at 180 °C over an hour. Clearly, the organotin-activated azides are more reactive in the cycloaddition reaction than alkyl azides.

Cleavage reactions

The cycloaddition between Bu_3SnN_3 and RCN affords a facile route to novel tetrazoles, which can be isolated in their non-metallated (N–H) form by reaction with HCl. Three phenylene- and one methylene-bridged bis(*N*-unsubstituted tetrazoles) (**17**–**20**), which have previously been cited with respect to polymerisation reactions,[16] have been prepared this way (Scheme 4). For comparison, **14** was cleaved to give **21**, characterised as the 2-*N*,2-*N*′ isomer by the ^{13}C shifts of the NCH_2 (54.2 ppm) and C^5 (166.6 ppm) groups. The ^1H NMR has a single resonance due to the two equivalent NCH_2 groups at 4.89 ppm.

These *N*-unsubstituted tetrazoles are often solvated, either from the crystallisation solvent (MeOH) or from atmospheric moisture, and slow crystallisation of **17** yielded crystals of a tetrahydrate (Fig. 3). The two tetrazole units are each twisted

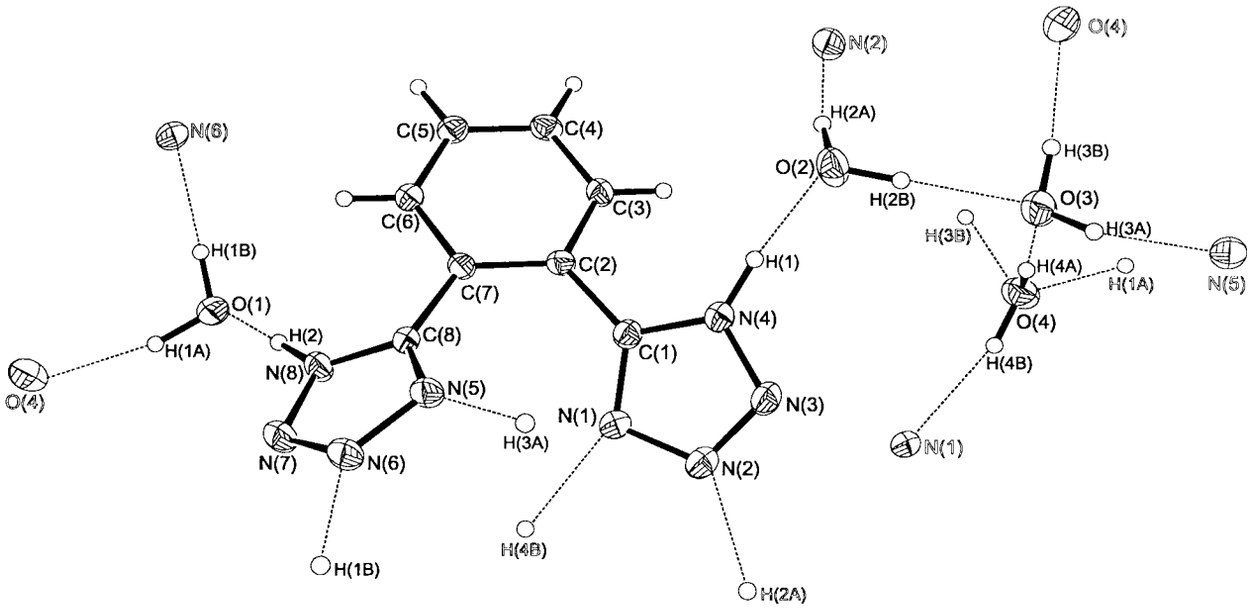
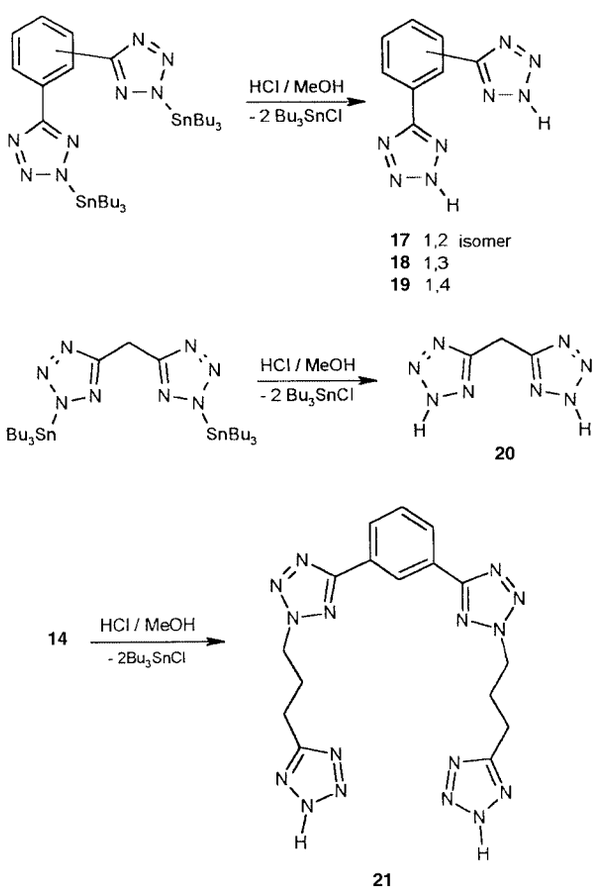


Fig. 3 The asymmetric unit of **17**. Thermal ellipsoids are at the 30% probability level.



Scheme 4

with respect to the central C_6H_4 ring (34.1°, 34.8°) to allow both heterocycles to engage in extensive hydrogen bonding. The NH groups form the strongest H-bonds [H(1)–O(2) 1.71(2), H(2)–O(1) 1.69(2)Å], with weaker H-bonds forming from nitrogens in the N^3 and N^4 positions of each ring [N(1)–H(4B) 2.03(2), N(2)–H(2A) 1.90(2), N(5)–H(3A) 2.00(2), N(6)–H(1B) 1.93(2) Å]. The incorporation of two additional water molecules into the lattice generates a network of H-bonds (Fig. 4). There is π-stacking of the benzenoid units of adjacent molecules with tetrazoles arranged on alternating sides of the stack. The two water molecules directly H-bonded to the N–H groups [based on O(1) and O(2)] are each three-coordinated, the available hydrogens bonding either to a ring nitrogen [H(1B)–N(6), H(2A)–N2] or one of the "guest" waters [H(1A)–O(4) 1.86(2), H(2B)–O(3) 1.90(2) Å]. Each of the "guest" waters is four-coordinated, in which the hydrogen atoms H-bond to either nitrogen [H(3A)–N(5), H(4B)–N(1)] or another water [H(3B)–O(4) 1.86(3), H(4A)–O(3) 1.86(3) Å]. The lone pairs on these four-coordinated oxygens form further H-bonds to other water molecules [O(3)–H(2B), O(3)–H(4A); O(4)–H(1A), O(4)–H(3B)].

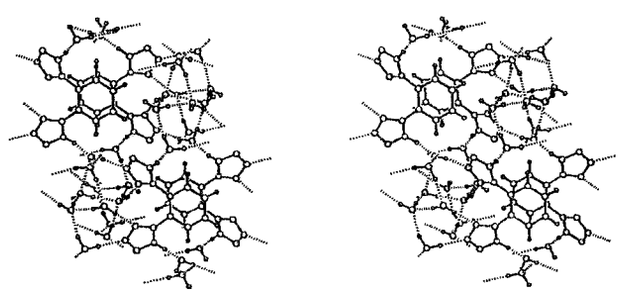


Fig. 4 A stereoscopic view of the unit cell contents of **17** showing the network of hydrogen bonds. Angles between the tetrazole rings and the central C_6H_4 unit are 34.1 and 34.8° for rings based on N(1) and N(5), respectively.

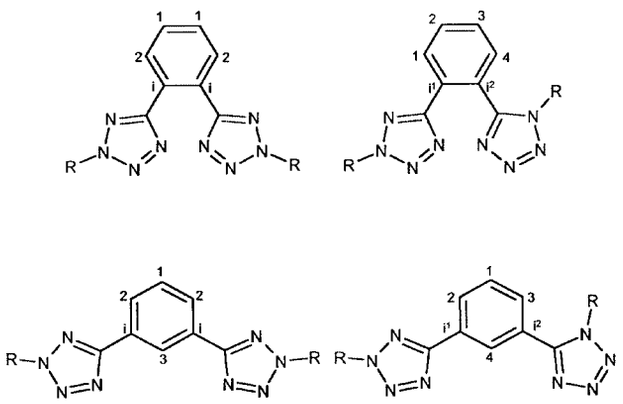
The structure emphasises the versatile nature of tetrazoles in crystal engineering. Our earlier work on metallo-tetrazoles has unearthed one compound, 1,4-$(Ph_2TlN_4C)(CH_2)_4$,[17] in which all four ring nitrogens of each tetrazole are involved in bonding, though the N^1,N^3,N^4 combination inherent in **17** appears one of the most common.

Conclusions

Cleavage of the organotin groups from 1,*n*-$(Bu_3SnN_4C)_2C_6H_4$ ($n = 2,3$) with α,ω-dihaloalkanes can yield 1-*N*,1-*N*′-bridged cyclophanes (1,2-$Br_2C_2H_4$) or, when the dihalide is in large excess, mixtures of 1-*N*,2-*N*′- and 2-*N*,2-*N*′-substituted ω-haloalkyltetrazoles. The use of α-halo-ω-cyanoalkanes can generate mixtures of 1-*N*,2-*N*′- and 2-*N*,2-*N*′-substituted ω-cyanoalkyltetrazoles from which further tetrazoles can be generated by reaction with Bu_3SnN_3. All the organotin-substituted tetrazoles are easily converted to their *N*-unsubstituted analogues by reaction with HCl.

Experimental

Spectra were recorded on the following instruments: JEOL GX270 (^{1}H, ^{13}C NMR), GX400 (^{119}Sn NMR), Perkin-Elmer 599B (IR). Details of our Mössbauer spectrometer and related procedures are given elsewhere.[18] 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 were recorded on saturated solutions. The numbering scheme used in the assignment of NMR data is shown below.



Syntheses

1,2-($Bu_3SnN_4C)_2C_6H_4$ (**22**), 1,3-($Bu_3SnN_4C)_2C_6H_4$ (**23**), 1,4-($Bu_3SnN_4C)_2C_6H_4$ (**24**) and ($Bu_3SnN_4C)_2CH_2$ (**25**) were prepared as described previously.[3,5] All other reagents were of commercial origin (*e.g.* Aldrich) and used without further purification.

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.

9,10-Dihydroditetrazolo[5,1-*a*:1′,5′-*e*][2,5]benzodiazocine (1). Compound **22** (1.75 g, 2.2 mmol) was refluxed with 1,2-dibromoethane (4.1 g, 22.0 mmol) in methanol (50 ml) for three hours. *In vacuo* removal of solvent from the colourless solution yielded a glass which was triturated with hexane to afford a colourless powder which was collected by filtration. Compound **1** was isolated as colourless needles by fractional crystallisation from methanol solution (0.20 g, 37%). Analysis: Found(Calc. for $C_{10}H_8N_8\cdot H_2O$): C 46.7(46.5); H 3.20(3.87); N 43.3(43.4)%. ^{1}H NMR [δ (ppm), MeOH-d_4]: 5.08 [s, 4H, 2 CH_2], 7.91 [m, 4H, H^1, H^2-C$_6H_4$]. ^{13}C NMR [δ (ppm), MeOH-d_4]: 45.9 [2 *C*H$_2$], 123.5 [2 i-*C*$_6$H$_4$], 131.9 [2 C^1-*C*$_6$H$_4$], 132.1 [2 C^2-*C*$_6$H$_4$], 153.2 [2 *C*N$_4$].

1,2-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:2a) and 1,2-bis[(2-bromoethyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:2b). Compound **22** (2.0 g, 2.5 mmol) was heated to 110 °C as a neat suspension in 1,2-dibromoethane (7 ml) for three hours. This resulted in a viscous amber solution which, on cooling, was chromatographed on silica gel employing a gradient of petroleum ether (bp 40–60 °C) to CH_2Cl_2. Compounds **2a** and **2b** were isolated as crystalline solids after recrystallisation from CH_2Cl_2. **2a**: Analysis: Found(Calc. for $C_{12}H_{12}Br_2N_8$): C 34.1(33.7); H 2.84(2.81); N 25.9(26.1)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 3.73 [t, 4H, 2 CH_2Br], 4.89 [t, 4H, CH_2N^2, CH_2N$^{2\prime}$], 7.54 [dd, 2H, H^1-C$_6H_4$], 7.85 [dd, 2H, H^2-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.0 [2 *C*H$_2$Br], 53.9 [*C*H$_2$N^2, *C*H$_2$N$^{2\prime}$], 127.3 [2 i-*C*$_6$H$_4$], 130.3 [2 C^1-*C*$_6$H$_4$], 130.6 [2 C^2-*C*$_6$H$_4$], 164.7 [2 *C*N$_4$]. **2b**: Analysis: Found(Calc. for $C_{12}H_{12}Br_2N_8$): C 33.5(33.7); H 3.20(2.81); N 25.6(26.1)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 3.65 [m, 4H, 2 CH_2Br], 4.36 [t, 2H, CH_2N^1], 4.84 [t, 2H, CH_2N$^{2\prime}$], 7.50–7.75 [m, 3H, H^{1}H^{2}H^3-C$_6H_4$], 8.28 [d, 1H, H^4-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.3 [*C*H$_2$Br], 27.8 [*C*H$_2$Br], 48.5 [*C*H$_2$N^1], 54.0 [*C*H$_2$N$^{2\prime}$], 122 2 [i^1-*C*$_6$H$_4$], 126.9 [i^2-*C*$_6$H$_4$], 29.3 [C^1-*C*$_6$H$_4$], 130.6 [C^2-*C*$_6$H$_4$], 131.8 [C^3-*C*$_6$H$_4$], 131.9 [C^4-*C*$_6$H$_4$], 154.3 [*C*N$_4$ (N^{1}CH$_2$)], 163.0 [*C*N$_4$ (N$^{2\prime}$CH$_2$)].

1,2-Bis[(3-bromopropyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:3a). This compound was prepared by the same general method from **22** and 1,3-dibromopropane as a waxy solid. Analysis: Found(Calc. for $C_{14}H_{16}Br_2N_8$): C 36.7(36.8); H 3.46(3.51); N 24.1(24.5)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 2.51 [m, 4H, CH_2], 3.40 [t, 4H, 2 CH_2Br], 4.77 [t, 4H, CH_2N^2, CH_2N$^{2\prime}$], 7.60 [dd, 2H, H^1-C$_6H_4$], 7.89 [dd, 2H, H^2-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 29.3 [*C*H$_2$], 32.2 [2 *C*H$_2$Br], 51.3 [*C*H$_2$N^2, *C*H$_2$N$^{2\prime}$], 127.3 [2 i-*C*$_6$H$_4$], 130.6 [2 C^1-*C*$_6$H$_4$], 130.8 [2 C^2-*C*$_6$H$_4$], 164.7 [2 *C*N$_4$].

1,2-Bis[(5-bromopentyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:4a) and 1,2-bis[(5-bromopentyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:4b). These compounds were prepared by the same general method from **22** and 1,5-dibromopentane as waxy solids. **4a**: Analysis: Found(Calc. for $C_{18}H_{24}Br_2N_8$): C 42.9(42.2); H 5.12(4.69); N 21.6(21.8)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.39 [m, 4H, 2 CH_2], 1.76–1.82 [m, 4H, 2 CH_2], 1.88–1.94 [m, 4H, 2 CH_2], 3.31 [t, 4H, 2 CH_2Br], 4.50 [t, 4H, CH_2N^2, CH_2N$^{2\prime}$], 7.52 [dd, 2H, H^1-C$_6H_4$], 7.80 [dd, 2H, H^2-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 24.6 [2 *C*H$_2$], 28.2 [2 *C*H$_2$], 31.6 [2 *C*H$_2$], 33.0 [2 *C*H$_2$Br], 52.5 [*C*H$_2$N^2, *C*H$_2$N$^{2\prime}$], 127.1 [2 i-*C*$_6$H$_4$], 129.9 [2 C^1-*C*$_6$H$_4$], 130.3 [2 C^2-*C*$_6$H$_4$], 164.1 [2 *C*N$_4$]. **4b**: Analysis: Found(Calc. for $C_{18}H_{24}Br_2N_8$): C 42.6(42.2); H 4.86(4.69); N 21.5(21.8)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.23–1.35 [m, 4H, 2 CH_2], 1.62–1.86 [m, 8H, 4 CH_2], 3.23 [t, 2H, CH_2Br], 3.33 [t, 2H, CH_2Br], 3.99 [t, 2H, CH_2N^1], 4.42 [2, 2H-CH_2N$^{2\prime}$], 7.42 [d, 1H, H^1-C$_6H_4$], 7.57–7.71 [m, 2H, H^2, H^3-C$_6H_4$], 8.25 [d, 1H, H^4-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 24.5 [*C*H$_2$], 24.6 [*C*H$_2$], 27.8 [*C*H$_2$], 27.9 [*C*H$_2$], 31.4 [*C*H$_2$], 31.5 [*C*H$_2$], 32.9 [*C*H$_2$Br], 33.0 [*C*H$_2$Br], 47.0 [*C*H$_2$N^1], 52.7 [*C*H$_2$N$^{2\prime}$], 122.7 [i^1-*C*$_6$H$_4$], 127.3 [i^2-*C*$_6$H$_4$], 129.2 [C^1-*C*$_6$H$_4$], 130.2 [C^2-*C*$_6$H$_4$], 130.9 [C^3-*C*$_6$H$_4$], 131.4 [C^4-*C*$_6$H$_4$], 153.8 [*C*N$_4$ (N^{1}CH$_2$)], 162.7 [*C*N$_4$ (N$^{2\prime}$CH$_2$)].

1,2-Bis[(6-bromohexyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:5a) and 1,2-bis[(6-bromohexyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:5b). These compounds were prepared by the same general method from **22** and 1,6-dibromohexane as viscous oils. **5a**: Analysis: Found(Calc. for $C_{20}H_{28}Br_2N_8$): C 45.3(44.5); H 5.30(5.19); N 20.6(20.7)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.15–1.26 [m, 4H, 2 CH_2], 1.31–1.36 [m, 4H, 2 CH_2], 1.73 [m, 4H, 2 CH_2], 1.88 [m, 4H, 2 CH$_2$], 3.29 [t, 4H, 2 CH_2Br], 4.48 [t, 4H, CH_2N^2, CH_2N$^{2\prime}$], 7.51 [dd, 2H, H^1-C$_6H_4$], 7.79 [dd, 2H, H^2-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 24.96 [2 *C*H$_2$], 27.0 [2 *C*H$_2$], 28.7 [2 *C*H$_2$], 32.0 [2 *C*H$_2$], 33.3 [2 *C*H$_2$Br], 52.5 [*C*H$_2$N^2, *C*H$_2$-N$^{2\prime}$], 127.0 [2 i-*C*$_6$H$_4$], 129.8 [2 C^1-*C*$_6$H$_4$], 130.1 [2 C^2-*C*$_6$H$_4$], 163.8 [2 *C*N$_4$]. **5b**: Analysis: Found(Calc. for $C_{20}H_{28}Br_2N_8$): C 44.7(44.5); H 5.40(5.19); N 19.3(20.7)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.18–1.45 [m, 8H, 4 CH_2], 1.64–1.86 [m, 8H, 4 CH_2], 3.26 [t, 2H, CH_2Br], 3.34 [t, 2H, CH_2Br], 3.97 [t, 2H, CH_2N^1], 4.41 [t, 2H, CH_2N$^{2\prime}$], 7.41 [d, 1H, H^1-C$_6H_4$], 7.59 [t, 1H, H^2-C$_6H_4$], 7.69 [t, 1H, H^3-C$_6H_4$], 8.28 [d, 1H, H^4-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 25.4 [*C*H$_2$], 25.4 [*C*H$_2$], 27.3 [*C*H$_2$], 27.3 [*C*H$_2$], 28.8 [*C*H$_2$], 29.1 [*C*H$_2$], 32.2 [*C*H$_2$], 32.3 [*C*H$_2$], 33.3 [*C*H$_2$Br], 33.5 [*C*H$_2$Br], 47.3 [*C*H$_2$N^1], 53.0 [*C*H$_2$N$^{2\prime}$], 127.7 [i^1-*C*$_6$H$_4$], 129.51 [i^2-*C*$_6$H$_4$], 130.7 [C^1-*C*$_6$H$_4$], 130.5 [C^2-*C*$_6$H$_4$], 131.1 [C^3-*C*$_6$H$_4$], 131.2 [C^4-*C*$_6$H$_4$], 154.0 [*C*N$_4$ (N^{1}CH$_2$)], 162.9 [*C*N$_4$ (N$^{2\prime}$CH$_2$)].

1,3-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:6a) and 1,3-bis[(2-bromoethyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:6b). These compounds were prepared by the same general method from **23** and 1,2-dibromoethane and were isolated, after

recrystallisation from CH_2Cl_2, as colourless crystalline solids. **6a**: Analysis: Found(Calc. for $C_{12}H_{12}Br_2N_8$): C 34.1(33.7); H 2.91(2.81); N 25.4(26.1)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 3.86 [t, 4H, 2 CH_2Br], 5.01 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.57 [t, 1H, H^1-C_6H_4], 8.20 [dd, 2H, 2 H^2-C_6H_4], 8.86 [s, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.1 [2 CH_2Br], 54.0 [CH_2N^2, $CH_2N^{2\prime}$], 125.3 [C^1-C_6H_4], 127.9 [2 C^2-C_6H_4], 128.7 [C^3-C_6H_4], 129.6 [2 i-C_6H_4], 164.8 [2 CN_4]. **6b**: Analysis: Found(Calc. for $C_{12}H_{12}Br_2N_8$): C 33.0(33.7); H 2.89(2.81); N 25.5(26.2)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 3.81 [t, 2H, CH_2Br], 3.86 [t, 2H, CH_2Br], 4.80 [t, 2H, CH_2N^1], 5.02 [t, 2H, $CH_2N^{2\prime}$], 7.66 [m, 1H, H^1-C_6H_4], 7.76 [m, 1H, H^2-C_6H_4], 8.33 [m, 1H, H^3-C_6H_4], 8.42 [m, 1H, H^4-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.1 [CH_2Br], 28.0 [CH_2Br], 49.0 [CH_2N^1], 54.2 [$CH_2N^{2\prime}$], 124.5 [i^1-C_6H_4], 127.2 [C^1-C_6H_4], 128.5 [i^2-C_6H_4], 129.6 [C^2-C_6H_4], 130.2 [C^3-C_6H_4], 130.9 [C^4-C_6H_4], 154.5 [CN_4 (N$^1CH_2$)], 164.1 [CN_4 (N$^{2\prime}CH_2$)].

1,3-Bis[(3-bromopropyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:7a) and 1,3-bis[(3-bromopropyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:7b). These compounds were prepared by the same general method from **23** and 1,3-dibromopropane and were isolated as waxy solids. **7a**: Analysis: Found(Calc. for $C_{14}H_{16}Br_2N_8$): C 36.5(36.8); H 3.40(3.51); N 23.7(24.5)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 2.56 [m, 4H, 2 CH_2], 3.41 [t, 4H, 2 CH_2Br], 4.80 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.54 [t, 2H, H^1-C_6H_4], 8.17 [dd, 2H, 2 H^2-C_6H_4], 8.81 [dd, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 28.9 [2 CH_2], 31.9 [2 CH_2Br], 51.3 [CH_2N^2, $CH_2N^{2\prime}$], 125.1 [C^1-C_6H_4], 128.1 [2 C^2-C_6H_4], 128.5 [2 i-C_6H_4], 129.5 [C^3-C_6H_4], 164.6 [2 CN_4]. **7b**: Analysis: Found(Calc. for $C_{14}H_{16}Br_2N_8$): C 36.8(36.8); H 3.63(3.51); N 23.8(24.5)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 2.51 [m, 4H, 2 CH_2], 3.36 [t, 2H, CH_2Br], 3.41 [t, 2H, CH_2Br], 4.60 [t, 2H, CH_2N^1], 4.80 [t, 2H, $CH_2N^{2\prime}$], 7.63 [t, 1H, H^1-C_6H_4], 7.74 [d, 1H, H^2-C_6H_4], 8.27 [d, 1H, H^3-C_6H_4], 8.37 [s, 1H, H^4-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 28.8 [CH_2], 28.9 [CH_2], 31.7 [CH_2Br], 31.8 [CH_2Br], 46.3 [CH_2N^1], 51.3 [$CH_2N^{2\prime}$], 124.4 [i^1-C_6H_4], 126.8 [C^1-C_6H_4], 128.5 [i^2-C_6H_4], 129.3 [C^2-C_6H_4], 130.0 [C^3-C_6H_4], 130.4 [C^4-C_6H_4], 153.9 [CN_4 (N$^1CH_2$)], 163.8 [CN_4 (N$^{2\prime}CH_2$)].

1,3-Bis[(4-bromobutyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:8a) and 1,3-bis[(4-bromobutyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:8b). These compounds were prepared by the same general method from **23** and 1,4-dibromobutane as a crystalline solid and a viscous oil respectively. **8a**: Analysis: Found(Calc. for $C_{16}H_{20}Br_2N_8$): C 39.2(39.7); H 4.18(4.13); N 22.6(23.1)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.89–1.99 [m, 4H, 2 CH_2], 3.46 [t, 4H, 2 CH_2Br], 4.72 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.62 [t, 1H, H^1-C_6H_4], 8.24 [dd, 2H, 2 H^2-C_6H_4], 8.90 [t, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.8 [2 CH_2], 29.2 [2 CH_2], 32.1 [2 CH_2Br], 52.2 [CH_2N^2, $CH_2N^{2\prime}$], 125.2 [C^1-C_6H_4], 128.2 [2 i-C_6H_4], 128.5 [2 C^2-C_6H_4], 129.5 [C^3-C_6H_4], 164.6 [2 CN_4]. **8b**: Analysis: Found(Calc. for $C_{16}H_{20}Br_2N_8$): C 40.4(39.7); H 4.26(4.13); N 22.7(23.1)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.87–1.98 [m, 4H, 2 CH_2], 2.11–2.18 [m, 2H, CH_2], 2.19–2.32 [m, 2H, CH_2], 3.41 [t, 2H, CH_2Br], 3.47 [t, 2H, CH_2Br], 4.55 [t, 2H, CH_2N^1], 4.74 [t, 2H, $CH_2N^{2\prime}$], 7.73 [t, 1H, H^1-C_6H_4], 7.88 [d, 1H, H^2-C_6H_4], 8.37 [d, 1H, H^3-C_6H_4], 8.45 [s, 1H, H^4-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 27.8 [CH_2], 28.2 [CH_2], 29.1 [CH_2], 29.2 [CH_2], 32.0 [CH_2Br], 32.1 [CH_2Br], 47.3 [CH_2N^1], 52.4 [$CH_2N^{2\prime}$], 124.8 [i^1-C_6H_4], 126.7 [C^1-C_6H_4], 128.7 [i^2-C_6H_4], 129.4 [C^2-C_6H_4], 130.1 [C^3-C_6H_4], 130.5 [C^4-C_6H_4], 153.8 [CN_4 (N$^1CH_2$)], 163.9 [CN_4 (N$^{2\prime}CH_2$)].

1,3-Bis[(5-bromopentyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:9a) and 1,3-bis[(5-bromopentyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′:9b). These compounds were prepared by the same general method from **23** and 1,5-dibromopentane as viscous oils. **9a**: Analysis: Found(Calc. for $C_{18}H_{24}Br_2N_8$): C 43.3(42.2); H 4.76(4.69); N 20.9(21.8)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.51 [m, 4H, 2 CH_2], 1.90 [m, 4H, 2 CH_2], 2.08 [m, 4H, 2 CH_2], 3.38 [t, 4H, 2 CH_2Br], 4.66 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.59 [t, 1H, H^1-C_6H_4], 8.21 [dd, 2H, 2 H^2-C_6H_4], 8.88 [t, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 24.9 [2 CH_2], 28.4 [2 CH_2], 31.8 [2 CH_2], 33.0 [2 CH_2Br], 52.9 [CH_2N^2, $CH_2N^{2\prime}$], 125.1 [C^1-C_6H_4], 128.2 [2 i-C_6H_4], 128.4 [2 C^2-C_6H_4], 129.5 [C^3-C_6H_4], 164.5 [2 CN_4]. **9b**: Analysis: Found(Calc. for $C_{18}H_{24}Br_2N_8$): C 42.0(42.2); H 4.80(4.69); N 20.8(21.8)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.37–1.53 [m, 4H, 2 CH_2], 1.74–2.07 [m, 8H, 4 CH_2], 3.27–3.56 [m, 4H, 2 CH_2Br], 4.43 [t, 2H, CH_2N^1], 4.63 [t, 2H, $CH_2N^{2\prime}$], 7.62–7.76 [m, 2H, H^{1}H^2-C_6H_4], 8.29–8.36 [m, 2H, H^{3}H^4-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 24.9 [2 CH_2], 28.4 [CH_2], 28.8 [CH_2]: 31.7 [CH_2], 31.8 [CH_2], 32.9 [CH_2Br], 33.0 [CH_2Br], 47.9 [CH_2N^1], 53.0 [$CH_2N^{2\prime}$], 124.8 [i^1-C_6H_4], 126.7 [C^1-C_6H_4], 128.8 [i^2-C_6H_4], 129.4 [C^2-C_6H_4], 130.1 [C^3-C_6H_4], 130.4 [C^4-C_6H_4], 153.7 [CN_4 (N$^1CH_2$)], 163.8 [CN_4 (N$^{2\prime}CH_2$)].

1,3-Bis[2-(6-bromohexyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:10a). This compound was prepared by the same general method from **23** and 1,6-dibromohexane as a waxy solid. Analysis: Found(Calc. for $C_{20}H_{28}Br_2N_8$): C 44.6(44.5); H 5.29(5.19); N 20.5(20.7)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.21–1.32 [m, 4H, 2 CH_2], 1.35–1.45 [m, 4H, 2 CH_2], 1.63–1.82 [m, 4H, 2 CH_2], 1.85–1.96 [m, 4H, 2 CH_2], 3.31 [t, 4H, 2 CH_2Br], 4.50 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.53 [t, 1H, H^1-C_6H_4], 7.81 [dd, 2H, 2 H^2-C_6H_4], 8.41 [t, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 25.2 [2 CH_2], 27.2 [2 CH_2], 28.9 [2 CH_2], 32.2 [2 CH_2], 33.4 [2 CH_2Br], 52.7 [CH_2N^2, $CH_2N^{2\prime}$], 127.2 [2 i-C_6H_4], 129.3 [C^1-C_6H_4], 129.9 [2 C^2-C_6H_4], 130.3 [C^3-C_6H_4], 164.1 [2 CN_4].

1,3-Bis[2-(8-bromooctyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′:11a). This compound was prepared by the same general method from **23** and 1,8-dibromooctane as a colourless oil whch solidified to a waxy solid on standing. Analysis: Found (Calc. for $C_{24}H_{36}Br_2N_8$): C 48.8(48.4); H 6.23(6.04); N 18.9(18.8)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 1.25–1.47 [m, 16H, 8 CH_2], 1.81–1.88 [m, 4H, 2 CH_2], 2.06–2.10 [m, 4H, 2 CH_2], 3.40 [t, 4H, 2 CH_2Br], 4.68 [t, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.63 [t, 1H, H^1-C_6H_4], 8.26 [dd, 2H, 2 H^2-C_6H_4], 8.90 [t, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 26.2 [2 CH_2], 27.9 [2 CH_2], 28.4 [2 CH_2], 28.7 [2 CH_2], 29.3 (2 CH_2); 32.6 (2 CH_2); 33.8 [2 CH_2Br], 53.2 [CH_2N^2, $CH_2N^{2\prime}$], 125.2 [C^1-C_6H_4], 128.3 [2 i-C_6H_4], 128.4 [2 C^2-C_6H_4], 129.5 [C^3-C_6H_4], 164.5 [2 CN_4].

1,3-Bis{[2-(bromomethyl)benzyl]tetrazol-5-yl}benzene (2-*N*,2-*N*′:12a) and 1,3-bis{[2-(bromomethyl)benzyl]tetrazol-5-yl}benzene (1-*N*,2-*N*′:12b). These compounds were prepared by heating **23** (1 g, 1.26 mmol) and α,α′-dibromo-*m*-xylene (3.3 g, 12.6 mmol) as a melt at 120 °C for two hours. The opaque mass which formed on cooling was then chromatographed as previously described to yield **12a** and **12b** as a crystalline solid and a viscous oil respectively. **12a**: Analysis: Found(Calc. for $C_{24}H_{20}Br_2N_8$): C 49.2(49.6); H 3.53(3.45); N 18.3(19.3)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 4.39 [s, 4H, 2 CH_2Br], 5.74 [s, 4H, CH_2N^2, $CH_2N^{2\prime}$], 7.29 [m, 6H, 2 *o*,*m*-$C_6H_4(CH_2)_2$], 7.38 [s, 2H, 2 *o*-$C_6H_4(CH_2)_2$], 7.52 [t, 1H, H^1-C_6H_4], 8.16 [dd, 2H, 2 H^2-C_6H_4], 8.82 [s, 1H, H^3-C_6H_4]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 32.6 [2 CH_2Br], 56.5 [CH_2N^2, $CH_2N^{2\prime}$], 125.4, 128.4, 128.6 and 129.0 [3 *o*, 1 *m*-$C_6H_4(CH_2)_2$], 128.1 [2 i-C_6H_4], 129.5 [C^1-C_6H_4], 129.6 [2 C^2-C_6H_4], 129.7 [C^3-C_6H_4], 133.8 and 138.8 [2 i-$C_6H_4(CH_2)_2$], 165.0 [2 CN_4]. **12b**: Analysis: Found(Calc. for $C_{24}H_{20}Br_2N_8$): C 50.4(49.6); H 3.66(3.45); 19.3(19.3)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 4.32 [s, 2H, CH_2Br], 4.38 [s, 2H, CH_2Br], 5.56 [s, 2H, CH_2N^1], 5.73 [s, 2H, $CH_2N^{2\prime}$], 7.16–8.78 [m, 8H, *o*,*m*-C_6H_4, *o*,*m*-$C_6H_4(CH_2)_2$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 32.5 [2 CH_2Br], 51.3 [CH_2N^1], 56.6 [$CH_2N^{2\prime}$], 124.4 [i^1-C_6H_4], 127.9 [i^2-C_6H_4], 126.9, 127.5, 128.2, 128.3, 128.6, 128.9, 129.5, 129.5, 129.6, 129.7, 129.9 and 130.6 [2 *o*,*m*-C_6H_4, 2 *o*,*m*-$C_6H_4(CH_2)_2$], 133.6, 134.0, 138.8 and 138.9 [4 i-$C_6H_4(CH_2)_2$], 153.9 [CN_4 (N$^1CH_2$)], 164.8 [CN_4 (N$^{2\prime}CH_2$)].

1,3-Bis[2-(3-cyanopropyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′: 13). Compound **23** (6.0 g, 7.6 mmol) and 4-bromobutyronitrile (*ca*. 20 g, 133 mmol) were heated at 120 °C for two hours giving an amber oil. Elution with a gradient of petrol (bp 40–60 °C) to acetone on silica gel yielded a single fraction, **13**, as a viscous oil which solidified on standing to an amorphous solid. Purification was by column chromatography (petroleum ether (bp 40–60 °C) to 40% acetone on silica gel) followed by recrystallisation from acetone–petroleum ether. Mp 82–84 °C. Analysis: Found(Calc. for $C_{16}H_{16}N_{10}$): C 55.2(55.2); H 4.82(4.60); N 39.6(40.2)%. ^{1}H NMR [δ (ppm), $CDCl_3$]: 2.32–2.56 [m, 8H, 2 CH_2CH_2CN], 4.84 [t, 4H, CH_2N^2, CH_2N$^{2\prime}$], 7.64 [t, 1H, H^1-C$_6H_4$], 8.22 [dd, 2H, 2 H^2-C$_6H_4$], 8.85 [s, 1H, H^3-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 14.8 [2 *C*H$_2$CH$_2$CN], 25.2 [2 *C*H$_2$CN], 51.2 [*C*H$_2$N^2, *C*H$_2$N$^{2\prime}$], 117.9 [2 CH$_2$*C*N], 127.9 [2 i-*C*$_6$H$_4$], 128.7 [C^1-*C*$_6$H$_4$], 129.6 [2 C^2-*C*$_6$H$_4$], 130.3 [C^3-*C*$_6$H$_4$], 164.8 [2 *C*N$_4$]. Mass spectrum (*m*/*z*, CI): 349 [M + 1], 292 [M − 2N$_2$]. IR [(cm^{-1}), Nujol mull]: 2249 [*ν*(CN)].

1,3-Bis[(2-3-[(2-tributylstannyl)tetrazol-5-yl]propyl}tetrazol-5-yl)benzene (2-*N*,2-*N*′:14). Compound **13** (0.5 g, 1.44 mmol) was heated as a neat suspension under nitrogen with tributyltin azide (0.93 g, 2.81 mmol) at 180 °C for 1 hour. This yielded a viscous amber oil which solidified to a brittle glass on cooling. Dissolution in methanol and filtration through activated carbon afforded a colourless solution which was evaporated and dried under vacuum to give **14** as a bis-methanol solvated glass. Analysis: Found(Calc. for $C_{42}H_{66}N_{16}O_2Sn_2$): C 46.9(47.3); H 7.43(7.25); 20.8(21.0)%. ^{1}H NMR [δ (ppm), DMSO-d$_6$]: 0.78 [t, 18H, 6 C*H*$_3$], 1.15–1.31 [m, 24H, 6 C*H*$_2$CH$_2$C*H*$_2$CH$_3$], 1.44–1.52 [m, 12H, 6 CH$_2$C*H*$_2$CH$_2$CH$_3$], 2.37–2.48 [m, 4H, 2 CH$_2$C*H*$_2$CH$_2$CN$_4$], 2.84 [t, 4H, C*H*$_2$CN$_4$], 4.88 [t, 4H, C*H*$_2$N^2, C*H*$_2$N$^{2\prime}$], 7.76 [t, 1H, H^1-C$_6H_4$], 8.20 [dd, 2H, 2 H^2-C$_6H_4$], 8.74 [s, 1H, H^3-C$_6H_4$]. ^{13}C NMR [δ (ppm), DMSO-d$_6$]: 13.3 [6 *C*H$_3$], 18.1 [Sn*C*H$_2$(CH$_2$)$_2$CH$_3$], 21.6 [2 *C*H$_2$CN$_4$], 26.2 [Sn(CH$_2$)$_2$-*C*H$_2$CH$_3$], 27.5 [SnCH$_2$*C*H$_2$CH$_2$CH$_3$], 27.7 [2 *C*H$_2$CH$_2$CN$_4$], 52.3 [2 *C*H$_2$N^2], 127.9 [C^1-*C*$_6$H$_4$], 128.0 [2 i-*C*$_6$H$_4$], 128.6 [2 C^2-*C*$_6$H$_4$], 130.2 [C^3-*C*$_6$H$_4$], 161.0 [2 *C*N$_4$SnBu$_3$], 163.4 [2 *C*N$_4$], ^1J[^{13}C–^{117,119}Sn] 478.0 Hz (unresolved); ^3J[^{13}C–^{117,119}Sn] 75.4 Hz (unresolved). ^{119}Sn NMR [δ (ppm), DMSO-d$_6$]: −55.1. ^{119m}Sn Mössbauer (mm s^{-1}): is (isomer shift) = 1.40; qs = 3.50.

Anhydrous material can be obtained if the initial glass is extracted with boiling hexane to extract any unreacted reagents. Analysis: Found(Calc. for $C_{40}H_{70}N_{16}Sn_2$): C 47.4(47.4); H 6.57(6.90); N 22.5(22.1)%. ^{119}Sn NMR [δ (ppm), CH$_3$OH-d^4]: −16.2. ^{119m}Sn Mössbauer (mm s^{-1}): is = 1.47; qs = 3.70.

1,3-Bis(2-{3-[2-(3-cyanopropyl)tetrazol-5-yl]propyl}tetrazol-5-yl)benzene (2-*N*,2-*N*′:15). A mixture of **14** (0.98 g, 0.97 mmol) and 4-bromobutyronitrile (1.72 g, 11.6 mmol) was heated at 120 °C for 3 h. Further 4-bromobutyronitrile (0.57 g, 3.88 mmol) was added and heating was continued for a further 7 h to yield an amber oil. Purification by column chromatography eluting with a gradient from petroleum ether (bp 40–60 °C) to 40% acetone on silica gel produced **15** as an orange oil (46 mg, 8%). ^{1}H NMR [δ (ppm), $CDCl_3$]: 2.30–2.70 [m, 12H, 2 C*H*$_2$CN, 4 CH$_2$C*H*$_2$CH$_2$], 3.00 [t, 4H, C*H*$_2$N^2], 4.72 [m, 3H, C*H*$_2$N$^{2\prime}$], 4.83 [m, 5H, C*H*$_2$N$^{2\prime}$], 7.63 [t, 1H, H^1-C$_6H_4$], 8.23 [d, 2H, 2 H^2-C$_6H_4$], 8.90 [s, 1H, H^3-C$_6H_4$]. ^{13}C NMR [δ (ppm), $CDCl_3$]: 14.8 [2 *C*H$_2$CH$_2$CN], 22.5 [2 *C*H$_2$CH$_2$CN$_4$], 25.1 [2 *C*H$_2$CN], 27.1 [2 *C*H$_2$CN$_4$], 51.2, 52.3 [2 CH$_2$N^2, 2 CH$_2$N$^{2\prime}$], 118.0 [2-CH$_2$*C*N], 125.2 [2 i-*C*$_6$H$_4$], 128.6 [C^1-*C*$_6$H$_4$], 128.7 [2 C^2-*C*$_6$H$_4$], 129.7 [C^3-*C*$_6$H$_4$], 164.6 [2 *C*N$_4$], 165.4 [2 CH$_2$*C*N$_4$]. IR [(cm^{-1}), Nujol mull]: 2249 [*ν*(CN)].

2-(Tributystannyl)-5-(azidomethyl)tetrazole (16). Tributyltin azide (2.66 g, 8 mmol) and azidoacetonitrile[15] (1.00 g, 12 mmol) were heated together under vacuum for 1 h at 100 °C. The resulting dark oil showed an azide band *ν*(N$_3$) at 2102 cm^{-1} differing from that in either reagent. Analysis: Found(Calc. for $C_7H_{29}N_7Sn$): C 41.2(40.6); H 7.21(7.06); N 21.8(23.7). ^{1}H NMR [δ (ppm), $CDCl_3$]: 0.81 (m, 9H, *C*H$_3$), 1.29 (m, 6H, SnC*H*$_2$), 1.55 (m, 12H, SnCH$_2$C*H*$_2$C*H*$_2$), 4.59 (s, 2H, N$_3$C*H*$_2$). ^{13}C NMR [δ (ppm), $CDCl_3$]: 13.5 (*C*H$_3$), 18.4 (Sn*C*H$_2$), 26.9 (*C*H$_2$CH$_3$), 28.1 (SnCH$_2$*C*H$_2$), 37.2 (N$_3$*C*H$_2$), 157.5 (*C*N$_4$). ^{119}Sn [δ (ppm), $CDCl_3$]: −27.9. ^{119m}Sn Mössbauer (mm s^{-1}): is = 1.42; qs = 3.61.

Hydrated 1,2-ditetrazol-5-ylbenzene (17). Compound **22** (3.0 g, 3.8 mmol) in methanol (100 ml) was treated with 12 M HCl (1 ml, 12 mmol) and was refluxed for 1 h during which time the suspension dissolved. After solvent removal *in vacuo* the residue was washed with hexane to remove Bu_3SnCl and recrystallised from methanol to give **17** in quantitative yield. Microanalysis was consistent with the incorporation of 1.5 H_2O. Analysis: Found(Calc. for $C_8H_9N_8O_{1.5}$): C 40.2(39.5); H 2.76(3.70); N 46.5(46.1)%. ^{1}H NMR [δ (ppm), DMSO-d$_6$]: 5.74 [br s, 2H, *H*$_2$O], 7.81 [m, 2H, *o*-C$_6H_4$], 7.90 [m, 2H, *m*-C$_6H_4$], 9.97 [br s, 2H, N*H*]. ^{13}C NMR [δ (ppm), DMSO-d$_6$]: 124.7 [2 i-*C*$_6$H$_4$], 130.5 [2 *o*-*C*$_6$H$_4$], 131.5 [2 *m*-*C*$_6$H$_4$], 155.0 [2 *C*N$_4$].

Compounds **18**, **19** and **20** were also prepared by the same methodology.

Hydrated 1,3-ditetrazol-5-ylbenzene (18). From **23**, white needles of the monohydrate were produced in quantitative yield. Analysis: Found(Calc. for $C_8H_8N_8O$): C 41.7(41.3); H 2.77(2.61); N 47.9(48.2)%. ^{1}H NMR [δ (ppm), DMSO-d$_6$]: 7.79 [t, 1H, *m*-C$_6H_4$], 8.17 [dd, 2H, *o*-C$_6H_4$], 8.74 [t, 1H, *o*-C$_6H_4$]. ^{13}C NMR [δ (ppm), DMSO-d$_6$]: 125.4 [*m*-*C*$_6$H$_4$], 125.7 [2 i-*C*$_6$H$_4$], 129.4 [2 *o*-*C*$_6$H$_4$], 130.7 [2 *o*-*C*$_6$H$_4$], 155.6 [2 *C*N$_4$].

1,4-Ditetrazol-5-ylbenzene (19). From **24**, a white solid produced in quantitative yield. Analysis: Found(Calc. for $C_8H_6N_8$): C 44.5(44.8); H 2.68(2.81); N 51.8(52.3)%. ^{1}H NMR [δ (ppm), DMSO-d$_6$]: 8.21 [s, 4H, *o*-C$_6H_4$]. ^{13}C NMR [δ (ppm), DMSO-d$_6$]: 127.8 [2 i-*C*$_6$H$_4$], 128.0 [4 *o*-*C*$_6$H$_4$], 155.4 [2 *C*N$_4$].

Ditetrazol-5-ylmethane (20). From **25**, a white solid produced in quantitative yield. Analysis: Found(Calc. for $C_3H_4N_8$): C 23.5(23.7); H 2.58(2.65); N 74.0(73.7)%. ^{1}H NMR [δ (ppm), DMSO-d$_6$]: 3.20 [s, 2H, C*H*$_2$], 14.74 [s 2H, N*H*]. ^{13}C NMR [δ (ppm), DMSO-d$_6$]: 18.3 [*C*H$_2$], 151.6 [2 *C*N$_4$].

1,3-Bis{[3-(tetrazol-5-yl)propyl]tetrazol-5-yl}benzene–1.5MeOH (2-*N*,2-*N*′:21). From **14**, a white solid produced in 84%. Analysis: Found(Calc. for $C_{17.5}H_{24}N_{16}O_{1.5}$): C 43.2(43.5); H 4.42(4.90); N 46.8(46.5)%. ^{1}H NMR [δ (ppm), CH$_3$OH-d$_4$, 55 °C]: 2.45 [m, 1H], 2.62 [m, 4H], 3.12 [t, 3H] (all 2 C*H*$_2$C*H*$_2$), 4.89 [t, 4H, 2 CH$_2$N], 7.66 [t, 1H, H^1-C$_6H_4$], 8.21 [d, 2H, H^2-C$_6H_4$], 8.80 [s, 1H, H^3-C$_6H_4$]. ^{13}C NMR [δ (ppm), CH$_3$OH-d$_4$, 55 °C]: 22.4 [2 *C*H$_2$CH$_2$CN$_4$], 28.6 [2 *C*H$_2$CN$_4$], 54.2 [2 *C*H$_2$N], 126.8 [2 *i*-*C*$_6$H$_4$], 130.4 [2 C^{1,2}-*C*$_6$H$_4$], 131.7 [C^3-*C*$_6$H$_4$], 158.0 [2 *C*N$_4$], 166.6 [2 CH$_2$*C*N$_4$].

X-Ray crystallography

General. Software used was SHELX86,[19] SHELX93[20] and ORTEX.[21] CCDC reference number 207/368. See http://www.rsc.org/suppdata/p1/1999/3507 for crystallographic files in .cif format.

Compound 1. *Crystal data:* $C_{10}H_8N_8$, M = 480.49, tetragonal, a = 24.513(2), b = 24.513(2), c = 7.035(1) Å, U = 4227.2(8) Å^3, space group $I4_1cd$, Z = 8, μ(Mo-Kα) = 0.105 mm^{-1}. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.35 < \theta < 23.97°$. The solution of the structure (SHELX86) and refinement (SHELX93) converged to a conventional [*i.e.* based on 692F data with $F_o > 4\sigma(F_o)$] $R_1 = 0.0427$ and $wR_2 = 0.0907$. Goodness of fit = 1.092.

Compound 6a. *Crystal data:* $C_{12}H_{12}Br_2N_8$, $M = 428.12$, monoclinic, $a = 15.959(3)$, $b = 11.370(2)$, $c = 8.974(1)$ Å, $\beta = 102.82(1)°$, $U = 1587.8(4)$ Å^3, space group $C2/c$, $Z = 4$, μ(Mo-Kα) = 5.115 mm^{-1}. Crystallographic measurements were made at 293(2) K on a CAD4 automatic four-circle diffractometer in the range $2.22 < \theta < 23.98°$. The asymmetric unit in this structure consists of one half of the molecule above, the remainder of which is generated *via* the $1 - x$, y, $\frac{3}{2} - z$ symmetry operation. The solution of the structure (SHELX86) and refinement (SHELX93) converged to a conventional [*i.e.* based on 814F data with $F_o > 4\sigma(F_o)$] $R_1 = 0.0674$ and $wR_2 = 0.1566$. Goodness of fit = 1.234.

Compound 17. *Crystal data:* $C_8H_{14}N_8O_4$, $M = 286.27$, monoclinic, $a = 7.2650(6)$, $b = 12.408(2)$, $c = 14.529(2)$ Å, $\beta = 96.35(1)°$, $U = 1301.7(3)$ Å^3, space group $P2_1/a$, $Z = 4$, $D_c = 1.461$ g cm^{-3}, μ(Mo-Kα) = 0.119 mm^{-1}, $F(000) = 600$. Crystallographic measurements were made at 293(2) K on a CAD-4 automatic four-circle diffractometer in the range $2.16 < \theta < 23.92°$. The solution of the structure (SHELX86) and refinement (SHELX93) converged to a conventional [*i.e.* based on 1410F data with $F_o > 4\sigma(F_o)$] $R_1 = 0.0404$ and $wR_2 = 0.1489$. Goodness of fit = 1.244.

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