Reactions of 1,4-bis(tetrazole)benzenes: formation of long chain alkyl halides

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Abstract—The reactions of 1,4-bis[2-(tributylstannyl)tetrazol-5-yl]benzene with α,ω-dibromoalkanes were carried out in order to synthesise pendant alkyl halide derivatives of the parent bis-tetrazole. This led to the formation of several alkyl halide derivatives, substituted variously at N1 or N2 on the tetrazole ring. The crystal structures of 1,4-bis[(2-(4-bromobutyl)tetrazol-5-yl)]benzene (2-N1,2-N0), 1,4-bis[(2-(4-bromo-octyl)tetrazol-5-yl)]benzene (1-N1,2-N0) and 1,4-bis[(2-(8-bromooctyl)tetrazol-5-yl)]benzene (2-N1,2-N0) are reported. Further discussion involves the structure of 1,4-bis[2-(6-bromohexyl)-2H-tetrazol-5-yl]benzene (2-N1,2-N0) previously reported.

1. Introduction

The synthesis of tetrazoles from a cycloaddition reaction between a nitrile and an azide is well documented1–6 since tetrazoles have roles in coordination chemistry as ligands, in medicinal chemistry as metabolically stable surrogates for carboxylic acids and in materials science applications, including photography and explosives. The interest in the ability of tetrazoles to mimic the carboxylic acid group has motivated the incorporation of tetrazoles into biologically active molecules.2 This potential use has led to the incorporation in therapeutic applications, including their incorporation in pharmacologically active compounds with anti-hypertensive, anti-allergic and antibiotic activities.3

In recent years, particular attention has been directed towards the use of polydentate aromatic nitrogen heterocycles, specifically ligands with five-membered rings (azoles). Among these, imidazoles and triazoles have been extensively used for their ability to construct open framework networks with a wide variety of topologies. Tetrazoles exhibit a strong networking ability usually acting as mono- or bidentate ligands in most of the reported complexes.7–9 A possible application for these materials as molecular hosts is in generating supramolecular arrays, which embody additional functional groups capable of metal complexation. This would result in a metalotetrazole framework with potential as new catalysts, anti-bacterial or therapeutic agents. Our interest in macrorcycles containing tetrazoles surrounds their use as precursors for the formation of new functionalised poly-tetrazoles as, for example, sensors or in molecular recognition.

Molloy et al.,5 Butler and Fleming10 have synthesised bis-(bromoalkyltetrazolyl)benzenes from either tributylstannyl-substituted bis-tetrazoles or N-unsubstituted tetrazoles with dihaloalkanes with the 2-N,2-N’-isomer again being the predominant product; Molloy et al. studied both the 1,2- and 1,3-substituted bis-tetrazole while Butler and Fleming looked only at the 1,3-unsubstituted bis-tetrazoles. In fact, Butler has succeeded in using these bis-(bromoalkyltetrazolyl)-benzenes to generate the tetra-tetrazolomacrocycle (Fig. 1), which include a cavity of variable dimensions tailored by both the length and flexibility of the alkyl chain and also the substitution position on the benzene ring.10–12 Furthermore, the X-ray crystal structure of one such macrocycle has been reported.13

We have previously reported our initial findings regarding the addition of pendant short-chain alkyl halide arms of some bis-tetrazoles, which yielded not only bis-tetrazole

Keywords: Tetrazole; Organotin; X-ray; Alkyl halide; NMR spectroscopy.

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Figure 1. Schematic of tetra-tetrazolomacrocycle with X= substituted benzene and Y= alkyl chain.
derivatives with pendant alkyl halide arms but also, and rather surprisingly, bis-tetrazole derivatives with pendant vinyl arms. The X-ray crystal structure of 1,4-bis(tetrazolyl)benzene with bromohexyl pendant arms has been reported, but with limited structural and spectroscopic discussion. In this paper, we report the reactions of 1,4-bis(tetrazolyl)benzenes with various long chain α,ω-dibromoalkanes and discuss their spectroscopic results. The crystal structures of three derivatives are also presented herein.

2. Results and discussion

While alkylation of 5-substituted mono-tetrazole derivatives is known to lead to mixtures of 1-N- and 2-N-substituted products, the regioselectivity being dependent on the reaction conditions and the nature of the C- and N-substituents, the alkylation of bis-tetrazole derivatives can lead to several products,1 the regioselectivity being dependent on the reaction conditions and the nature of the N-substituents. Our strategy was to use both of these approaches, that is, the use of both 1,4-bis(tetrazolyl)benzenes, either the 2-N,2'-N'- or the 1-N,2'-N'-isomer, with the 2-N,2'-N'-isomer predominating in a ratio of ca. 3:1. We have recently reported the reactions of either 1,4-bis(tetrazolyl)benzene with long chain α,ω-dibromoalkanes, either the 2-N,2'-N'- or the 1-N,2'-N'-isomer forming either a cyclophane or bis(bromoethyltetrazolyl)benzenes, depending on the ratio of the dibromoethane used in the reaction. When using a 10-fold excess, the cyclophane was obtained; a larger excess (25:1) resulted in the formation of the bis(bromoethyltetrazolyl)benzenes, either the 2-N,2'-N'- or the 1-N,2'-N'-isomer predominating in a ratio of ca. 3:1. We have recently reported the reactions of either 1,4-bis(tetrazolyl)benzene with long chain α,ω-dibromoalkanes, either the 2-N,2'-N'- or the 1-N,2'-N'-isomer forming either a cyclophane or bis(bromoethyltetrazolyl)benzenes, depending on the ratio of the dibromoethane employed in the reaction. When using a 10-fold excess, the cyclophane was obtained; a larger excess (25:1) resulted in the formation of the bis(bromoethyltetrazolyl)benzenes, either the 2-N,2'-N'- or the 1-N,2'-N'-isomer, with the 2-N,2'-N'-isomer predominating in a ratio of ca. 3:1.

Our strategy was to use both of these approaches, that is, the use of both 1,4-bis(tetrazolyl)benzene and 1,4-bis[2-(tributylstannyl)tetrazolyl]benzene, to obtain sufficient quantities of the 2-N,2'-N'-isomer of various bis(bromoalkyltetrazolyl)benzenes with a view towards generating derivatised tetra-tetrazole macrocycles. One approach involved the reactions of the 1,4-bis(tetrazole)benzene with long chain α,ω-dibromoalkanes. When the reactions of 1,4-bis(tetrazolyl)benzene (1,4-(HN=NC)2C6H4) with either 1,4-dibromobutane, 1,6-dibromohexane or 1,8-dibromo-octane were heated as neat suspensions, two products were obtained in reflux for 24 h, we found that the recovered material, after work-up, contained mainly starting bis-tetrazoles, with approx. 30% of products. We were able to grow crystals of the 1,4-bis[2-bromohexyl]tetrazolyl-5-yl]benzene, prepared by this method, which we have already reported. However, when the reactions of 1,4-bis[2-(tributylstannyl)tetrazolyl-5-yl]benzene (1,4-(Bu3SnN=C)2C6H4) with either 1,4-dibromobutane, 1,6-dibromohexane or 1,8-dibromo-octane were heated as neat suspensions, two products were obtained in relatively high yields, in all the reactions, as well as some recovered starting material (Scheme 1), suggesting that the organotin route was the better method for the synthesis of this particular type of material. It should be pointed out that neither the cyclophane product nor any products containing additions on one ring only were obtained.

Column chromatography, using hexane/ethyl acetate mixtures as eluent, separated the products from the reactants. 1H and 13C NMR spectra were obtained for all samples and revealed that both the 2-N,2'-N'- and the 1-N,2'-N'-isomers of the bis(bromoalkyltetrazolyl)benzene had formed in the reaction, but the expected cyclophane was not present. The isomeric 2-N,2'-N'- and 1-N,2'-N'-derivatives are readily distinguishable by their 1H and 13C NMR spectra, with the 13C NMR chemical shift of the tetrazole carbon atom appearing at ca. 154.0 and 164.0 ppm in 1,5- and 2,5-disubstituted tetrazoles, respectively. The symmetrical 2-N,2'-N'-substituted compounds thus gave rise to a single resonance at 164.0 ppm while both signals were apparent in the 1-N, 2-N'-substituted compounds. For example, 1,4-bis[2-bromobutyl]tetrazolyl-5-yl]benzene (2-N,2'-N') (2a) has a single peak at 164.6 ppm while 1,4-bis[2-bromobutyl]tetrazolyl-5-yl]benzene (1-N,2'-N') (2b) has two peaks at 153.8 and 164.0 ppm. The main difference in the 1H NMR spectra of the isomers was the doubling of signals in the case of the 1-N,2'-N'-derivatives.

Crystals of compounds 2a, 2b and 4a, suitable for an X-ray diffraction study, were obtained from chloroform and the structures confirmed the presence of the pendant bromoalkyl groups at the 2-N,2'-N'-positions for 2a and 4a and at the 1-N,2'-N'-positions for 2b (Figs. 2, 3 and 4). Table 1 shows important bond lengths and angles for the three structures. We have previously published the structure of 3a, allowing us to include this also in our comparison of the 2-N,2'-N'-compounds.

The structures of 2a, 3a and 4a exhibit regularity. In each case, the molecular unit is centrosymmetric in the solid state and is sited on a crystallographic inversion centre. The tetrazole rings are essentially coplanar with the benzene ring to
which they are attached, and the bromoalkyl groups adopt fully extended conformations, projecting to either side of this plane. The long axes of the alkyl chains form angles of ca. 145° to the molecular plane (measured by the N4–C9–C11 and N6–C13–C15 both ca. 95.5°), and the terminal CH2–Br bond vectors lie perpendicularly close to each other (Fig. 3). The arrangement of the central portions of the molecules in the crystal structure is closely comparable to that in 2a, 3a and 4a. The least-squares planes of the π-stacked molecules are separated by ca. 3.5 Å, with centroid–centroid separations of ca. 4.4 Å. Adjacent molecules in the stacks are related by centres of inversion. The molecules in adjacent stacks are again close to co-planar, but with a slightly greater lateral offset along the long axes of the molecules in 2b compared to 2a. The introduction of a short H⋯H contact (ca. 2.29 Å) between adjacent benzene rings, and the twisting of these rings from the planes of the tetrazole rings may be attributed at least in part to alleviation of the steric constraints associated with this close contact. The terminal CH2–Br bonds again form ‘Type I’ Br⋯Br interactions, as classified previously by Pedireddi et al. The intermolecular Br⋯Br distances lie in the range 3.4802(4)–3.5351(8) Å, considerably shorter than twice the bromine van der Waals radius (3.90 Å) and within the range of those values previously reported, 3.415–3.691 Å.

In the crystal structure of 2b, the two tetrazole rings in each molecule are essentially co-planar (rms deviation of 10 fitted atoms = 0.007 Å), but the plane of the central benzene ring forms a dihedral angle of 9.7(3)° with this plane. The bromobutyl chains form greater angles to the molecular plane (N4–C9–C11 and N6–C13–C15 both ca. 95.5°), and the terminal CH2–Br bond vectors lie perpendicularly close to each other (Fig. 3). The arrangement of the central portions of the molecules in the crystal structure is closely comparable to that in 2a, 3a and 4a. The least-squares planes of the π-stacked molecules are separated by ca. 3.5 Å, with centroid–centroid separations of ca. 4.4 Å. Adjacent molecules in the stacks are related by centres of inversion. The molecules in adjacent stacks are again close to co-planar, but with a slightly greater lateral offset along the long axes of the molecules in 2b compared to 2a. The introduction of a short H⋯H contact (ca. 2.29 Å) between adjacent benzene rings, and the twisting of these rings from the planes of the tetrazole rings may be attributed at least in part to alleviation of the steric constraints associated with this close contact. The terminal CH2–Br bonds again form ‘Type I’ Br⋯Br interactions, as classified previously by Pedireddi et al. The intermolecular Br⋯Br distances lie in the range 3.4802(4)–3.5351(8) Å, considerably shorter than twice the bromine van der Waals radius (3.90 Å) and within the range of those values previously reported, 3.415–3.691 Å.

### Table 1. Selected bond lengths (Å) and angles (°) for 2a, 3a and 4a

<table>
<thead>
<tr>
<th>Bond lengths</th>
<th>2a</th>
<th>3a</th>
<th>4a</th>
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<tbody>
<tr>
<td>C(1)–C(2)</td>
<td>1.389(4)</td>
<td>1.389(4)</td>
<td>1.378(3)</td>
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<tr>
<td>C(2)–C(3)</td>
<td>1.399(4)</td>
<td>1.402(3)</td>
<td>1.395(3)</td>
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<td>1.340(3)</td>
<td>1.323(3)</td>
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<td>1.321(3)</td>
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<td>1.333(3)</td>
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<tr>
<td>N(4)–C(5)</td>
<td>1.472(4)</td>
<td>1.463(3)</td>
<td>1.458(3)</td>
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<table>
<thead>
<tr>
<th>Bond angles</th>
<th>2a</th>
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<th>4a</th>
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<tbody>
<tr>
<td>C(4)–N(1)–N(3)</td>
<td>106.1(3)</td>
<td>106.2(2)</td>
<td>105.7(2)</td>
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<tr>
<td>N(1)–N(3)–N(4)</td>
<td>105.9(2)</td>
<td>106.2(2)</td>
<td>106.35(19)</td>
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<tr>
<td>N(3)–N(4)–N(2)</td>
<td>114.2(2)</td>
<td>113.8(2)</td>
<td>113.7(2)</td>
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<td>N(4)–N(2)–C(4)</td>
<td>101.4(3)</td>
<td>102.2(2)</td>
<td>102.1(2)</td>
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<tr>
<td>N(2)–C(4)–N(1)</td>
<td>112.4(3)</td>
<td>112.2(2)</td>
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3. Conclusions

The reactions of 1,4-(Bu3SnN4C)2C6H4 with 1,4-dibromo-butane, 1,6-dibromo-hexane and 1,8-dibromo-octane yield compounds containing pendant bromoalkyl groups with
substitution occurring at either 1-N,2-N' or 2-N,2'-N'. The crystal structures of three derivatives were obtained, including both the 1-N,2-N' and 2-N,2'-N'-isomers of one derivative. No cyclophanes were observed from any of the reactions. Similar reactions involving 1,3-dibromopropane, 1,5-dibromopentane and 1,7-dibromoheptane are currently being investigated, as are macrocyclic ring closure reactions with 1,4-(Bu3SnN4C)2C6H4 and metal complexation reactions with the resulting macrocyclic ring.

4. Experimental

4.1. General

1H and 13C NMR (δ ppm; J Hz) spectra were recorded on a JOEL JNM-LA300 FT-NMR spectrometer using saturated CDC13 solutions with Me4Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm. Infra-red spectra (cm⁻¹) were recorded as KBr discs or liquid films by a Nicolet Impact 410 FT-IR. Meltind points were measured with a Stuart Scientific melting point apparatus (SMP1) without correction. Microanalysis was carried out at the Microanalytical Laboratory of University College, Dublin. Standard Schlenk techniques were used throughout.

4.2. Syntheses

1,4-(Bu3SnN4C)2C6H4 (1) was prepared as described previously. All other reagents were commercially obtained and used without further purification. Caution: owing to their potentially explosive nature, all preparations of and subsequent reactions with organotin azides and tetrazoles were conducted under an inert atmosphere behind a rigid safety screen.

Figure 5. Labelling scheme used for central core in the 1,4-bis(tetrazole) derivatives.

4.3. General synthesis of compounds

1,4-(Bu3SnN4C)2C6H4 (1) (10 g, 126.2 mmol) and the appropriate αβ-dibromoalkane (300 mmol) were heated to 120 °C for 24 h, under nitrogen. After cooling, the excess αβ-dibromoalkane was removed under reduced pressure to afford the mixture of isomers a and b, as well as some starting bis-tetrazole. These were separated by column chromatography on silica gel (initially at the ratio of hexane/ethyl acetate 80:20, followed by the ratio 60:40). All compounds were recrystallised from chloroform.

4.3.1. 1,4-Bis[2-(4-bromobutyl)tetrazol-5-yl]benzene (2-N,2'-N) (2a). White solid. Anal. Calcd for C25H28Br2N8: C, 39.69; H, 4.16; N, 23.14. Found: C, 39.61; H, 4.15; N, 22.85; Yield: 64%; 3.91 g, 8.11 mmol; νmax (KBr) 2985, 1609, 1584, 1538, 1503, 1443, 1384, 1357, 1254, 1222, 1190, 1035, 1006, 875, 782, 753 cm⁻¹; mp 138–142 °C; δH: 1.95 [4H, CH2], 2.75 [4H, CH2], 3.47 [4H, J = 6.6 Hz, CH2Br], 4.74 [4H, J = 6.6 Hz, NCH2], 8.28 [8s, 4H, H1–C6H4]; δC: 27.8 [CH2], 29.2 [CH2], 32.2 [CH2], 52.9 [CH2N], 127.4 [1C–C6H4], 129.1 [i–C6H4], 164.6 [CN].

4.3.2. 1,4-Bis[2-(4-bromobutyl)tetrazol-5-yl]benzene (1-N,2-N') (2b). White solid. Anal. Calcd for C25H28Br2N8: C, 39.69; H, 4.16; N, 23.14. Found: C, 39.92; H, 4.13; N, 23.04; Yield: 21%; 1.28 g, 2.6 mmol; mp 108–112 °C; νmax (KBr) 2929, 2853, 1628, 1558, 1538, 1469, 1438, 1370, 1307, 1260, 1225, 1195, 1112, 1037, 1005, 847, 744, 645 cm⁻¹; δH: 1.95 [4, CH2Br], 2.15 [2, CH2], 2.28 [2, CH2], 2.30 [2H, J = 6.6 Hz, CH2Br], 2.47 [2H, J = 6.6 Hz, CH2Br]. All other reagents were commercially obtained and used throughout.

Figure 5. Labelling scheme used for central core in the 1,4-bis(tetrazole) derivatives.

4.3.3. 1,6-Bis[2-(6-bromohexyl)tetrazol-5-yl]benzene (2-N,2'-N) (2c). White solid. Anal. Calcd for C27H38Br2N8: C, 39.69; H, 4.16; N, 23.14. Found: C, 39.69; H, 4.16; N, 23.14. The numbering scheme for the 1,4-bis-tetrazoles is shown in Figure 5 and all NMR assignments are based on these diagrams.

4.3.4. 1,6-Bis[2-(6-bromohexyl)tetrazol-5-yl]benzene (1-N,2-N') (2d). White solid. Anal. Calcd for C27H38Br2N8: C, 39.69; H, 4.16; N, 23.14. Found: C, 39.69; H, 4.16; N, 23.14. The numbering scheme for the 1,4-bis-tetrazoles is shown in Figure 5 and all NMR assignments are based on these diagrams.
4.3.6. 1,8-Bis[2-(8-bromo-5-yl)tetrazol-5-yl]benzene (I-
N2-N') (4b). White solid. Anal. Calcd for C24H36Br2N8: C, 48.33; H, 6.08; N, 18.79. Found: C, 48.16; H, 6.07; N, 18.58; Yield: 10%; 0.75 g, 1.3 mmol; mp 64–68 °C; rDmax
(KBr) 2929, 2853, 1652, 1558, 1493, 1378, 3127, 1271, 1197, 1112, 1044, 1003, 848, 736,
645 cm⁻¹; δ: 1.29 [m, 8H, CH3], 1.37 [m, 8H, CH3], 1.82
[m, 4H, CH2], 1.95 [m, 2H, CH2], 2.09 [m, 2H, CH2], 3.38
[t, 2H, J = 6.6 Hz, CH2Br], 3.40 [t, 2H, J = 6.6 Hz, CH2Br],
4.46 [t, 2H, J = 6.6 Hz, N'CH2], 4.69 [t, 2H, J = 6.6 Hz,
N'CH2], 7.82 [d, 2H, J = 6.6 Hz, H–C6H4], 8.36 [d, 2H, J =
6.6 Hz, H1–C6H4]; δC: 26.2 [CH2], 26.3 [CH2], 27.9 [KZ],
28.0 [CH2], 28.4 [CH2], 28.5 [CH2], 28.7 [CH2], 29.3 [CH2],
29.7 [CH2], 32.6 [CH2], 32.7 [CH2], 33.8 [CH2], 48.2
[CH2N], 53.4 [CH2N], 125.7 [i–C6H4], 127.6 [C–C6H4],
129.3 [C–C6H4], 130.3 [i–C6H4], 153.8 [CN], 163.8 [CN].

4.4. X-ray crystallography

Suitable crystals of 2a, 2b and 4a for X-ray study were ob-
tained by recrystallisation from chloroform solutions. Data
were collected at 180(2) K on a Bruker Nonius X8 APEX
diffractometer,21 and a multi-scan correction was ap-
plied.22 The structures were refined against F² using all
data.23 Hydrogen atoms were placed at calculated positions
and refined using a riding model.

4.4.1. Compound 2a. Crystal data: C16H20Br2N6, M=
484.22, triclinic, a=4.5722(7), b=5.8805(9), c=
18.119(3) Å, α=96.943(6), β=96.426(6), γ=101.287(6),
U=469.61(13) Å³, space group P1, Z=1, μ(Mo–Kα)=
4.334 mm⁻¹. 7346 data (1717 unique, Rint=0.0386) were
measured in the range 3.59<θ<25.74°. R₁(½σ(I))=
0.0321 and wR2(all data)=0.0815. Goodness of fit on
F²=1.06. CCDC No. 604247.

4.4.2. Compound 2b. Crystal data: C16H20Br2N6, M=
484.22, triclinic, a=6.7256(14), b=8.1427(19), c=
17.186(4) Å, α=96.972(8), β=92.193(8), γ=90.034(8),
U=933.54(4) Å³, space group P1, Z=2, μ(Mo–Kα)=
4.361 mm⁻¹. 11127 data (3428 unique, Rint=0.0607) were
measured in the range 3.59<θ<25.84°. R₁(½σ(I))=
0.0906 and wR2(all data)=0.2519. Goodness of fit on
F²=1.04. CCDC No. 604248.

4.4.3. Compound 4a. Crystal data: C24H36Br2N8, M=
596.43, triclinic, a=4.6665(5), b=5.6593(5), c=
25.284(2) Å, α=92.812(3), β=90.773(4), γ=102.138(3),
U=651.82(10) Å³, space group P1, Z=1, μ(Mo–Kα)=
3.138 mm⁻¹. 11318 data (2448 unique, Rint=0.0477) were
measured in the range 3.69<θ<25.84°. R₁(½σ(I))=0.0338
and wR2(all data)=0.0863. Goodness of fit on F²=1.04.
CCDC No. 604249.

4.5. Crystallographic data

Crystallographic data for 2a, 2b and 4a have been deposited
with the Cambridge Crystallographic Data Centre. Copies of
this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk.

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