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Tetrahedron 61 (2005) 7002–7011
Tetrahedron

Reactions of bis(tetrazole)phenylenes. Surprising formation of vinyl compounds from alkyl halides

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Received 4 February 2005; revised 25 April 2005; accepted 5 May 2005

Available online 6 June 2005

Abstract—The reactions of 1,2-bis(tetrazol-5-yl)benzene (**1**), 1,3-bis(tetrazol-5-yl)benzene (**2**), 1,4-bis(tetrazol-5-yl)benzene (**3**), 1,2-$(Bu_3SnN_4C)_2C_6H_4$ (**4**), 1,3-$(Bu_3SnN_4C)_2C_6H_4$ (**5**) and 1,4-$(Bu_3SnN_4C)_2C_6H_4$ (**6**) with 1,2-dibromoethane were carried out by two different methods in order to synthesise pendant alkyl halide derivatives of the parent bis-tetrazoles. This lead to the formation of several alkyl halide derivatives, substituted at either N1 or N2 on the tetrazole ring, as well as the surprising formation of several vinyl derivatives. The crystal structures of both 1,2-[(2-vinyl)tetrazol-5-yl)]benzene (1-*N*,2-*N*′) (**1b**) and 1,3-bis[(2-bromoethyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′) (**5d**) are discussed.

1. Introduction

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.[1,2] The synthesis of tetrazoles from the cycloaddition reaction between a nitrile and an azide is well documented.[1–6] The three main synthetic approaches towards this type of transformation involve the use of tin azides,[4,5] strong Lewis acids,[7] and employment of acidic media.[8] Our interest in tetrazoles surrounds their potential as precursors in the formation of new functionalised poly-tetrazoles which can be used in other areas of chemistry, for example—sensors or molecular recognition. In this paper, we report our initial findings regarding the addition of pendant alkyl halide arms of some bis-tetrazoles. Earlier investigations by Molloy et al. revealed the formation of bis-tetrazole derivatives either with pendant alkyl halide arms or with a cyclophane structure.[5] In our hands, syntheses have yielded not only bis-tetrazole derivatives with pendant alkyl halide arms but also, and rather surprisingly, bis-tetrazole derivatives with pendant vinyl arms. The crystal structure of one such derivative is presented herein and discussed.

Keywords: Tetrazole; Organotin; X-ray; Vinyl; NMR.
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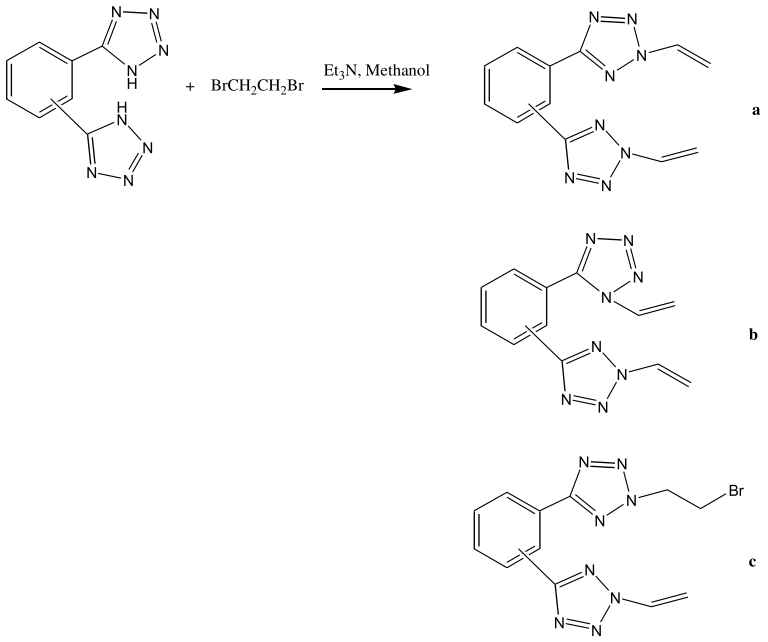
0040–4020/$ - see front matter © 2005 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tet.2005.05.013

2. Results and discussion

The reaction of 1,2-$(Bu_3SnN_4C)_2C_6H_4$ (**4**) with 1,2-dibromoethane has been shown to form either a cyclophane or bis(bromoalkyltetrazolyl)benzenes, depending on the ratio of the dibromoethane employed in the reaction.[5] When using a 10-fold excess, the cyclophane was obtained; a larger excess (25:1) resulted in the formation of the bis(bromoalkyltetrazolyl)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 3:1. Butler and Fleming have also synthesised bis(bromoalkyltetrazolyl)benzenes from *N*-unsubstituted tetrazoles and dihaloalkanes in the presence of Et_3N with the 2-*N*, 2-*N*′-isomer again predominating.[9] Our strategy was to use both of these approaches to obtain sufficient quantities of the 2-*N*,2-*N*′-isomer of various bis(bromoalkyltetrazolyl)benzenes with a view to subsequently generating derivatised tetra-tetrazole marcocycles.

The reaction of either 1,2-bis[tetrazol-5-yl]benzene (**1**), 1,3-bis[tetrazol-5-yl]benzene (**2**) or 1,4-bis[tetrazol-5-yl]benzene (**3**) with Et_3N and 1,2-dibromoethane in methanol at reflux temperature for 24 h (see Scheme 1) yielded four spots by TLC; the largest spot, in all cases, being the starting bis-tetrazole. In all reactions undertaken, on average, 50% of the starting bis-tetrazole was uniformly recovered. Our initial belief was that both the 2-*N*, 2-*N*′- and the 1-*N*, 2-*N*′-isomers of the bis(bromoethyltetrazolyl)benzene and the cyclophane had formed in the reaction, based solely on



Isomer	**a**	**b**	**c**
1,2-	1a (13.8 %)	1b (10.5 %)	1c (8.1 %)
1,3-	2a (15.6 %)	2b (10.2 %)	2c (8.3 %)
1,4-	3a (12.8 %)	3b (11.6 %)	3c (9.8 %)

* % Yield in parenthesises

Scheme 1.

published results in the literature,[5,9] and that longer reaction time would increase the yields of the three products. Unfortunately, increasing the reaction time, in some cases up to 120 h, did not improve the yield in any instance. Column chromatography, using a hexane/ethyl acetate mixture as eluent, separated the products. ^{1}H and ^{13}C NMR spectra were obtained for all samples. The isomeric 2-*N*, 2-*N*′- and the 1-*N*, 2-*N*′-derivatives should be readily distinguishable from their respective ^{1}H and ^{13}C NMR spectra, as described by Molloy et al.[5]

Surprisingly, all three products showed the distinct signal pattern for the presence of vinyl groups, while in the cases of **1c**, **2c** and **3c**, the presence of a bromoalkyl group was also observed. The formation of the vinyl group must be due to the presence of unreacted triethylamine abstracting HBr from the initially formed alkylbromo compound in all cases, although no sign of this initial bis-alkylbromotetrazole derivative was observed by TLC. Thus, the three products formed were the symmetrical 2-*N*,2-*N*′-bis(vinyl)-derivative, the unsymmetrical 1-*N*,2-*N*′-bis(vinyl)-derivative and the 2-*N*,2-*N*′-vinyl-bromoethyl-derivative. No obvious reason was apparent for the difference between these results and those published previously by Butler and Fleming.[9] Crystals of compound **1b**, suitable for an X-ray diffraction study, were obtained from chloroform and the X-ray structure obtained confirmed the presence of the pendant vinyl groups (see Fig. 1). It is notable that in the molecule the two tetrazole rings are not co-planar with each other, the angle between the least-squares planes of these two rings being 87.9°.

The reaction of 1,2-$(Bu_3SnN_4C)_2C_6H_4$ (**4**), 1,3-$(Bu_3SnN_4C)_2C_6H_4$ (**5**) or 1,4-$(Bu_3SnN_4C)_2C_6H_4$ (**6**) with 1,2-dibromoethane forms either a cyclophane or bis(bromoalkyltetrazolyl)benzenes, depending on the ratio of the dibromoethane employed in the reaction.[5] In all the reactions that we tried, no evidence for a cyclophane was detected. Generally, four products were obtained from each reaction, with compounds **a**, **b** and **c** always being present (see Scheme 2) and either **d** or **e** being the remaining product. In these reactions also, not all the starting bis-tetrazole was consumed in the reaction, with the largest spot by TLC being the starting tin tetrazole. What is intriguing is the presence of vinyl groups in these products as well as

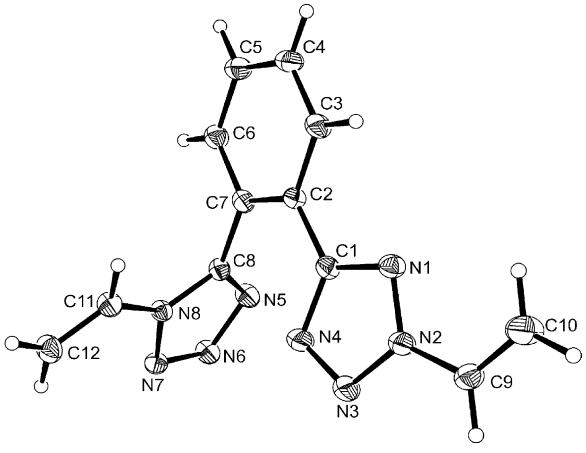
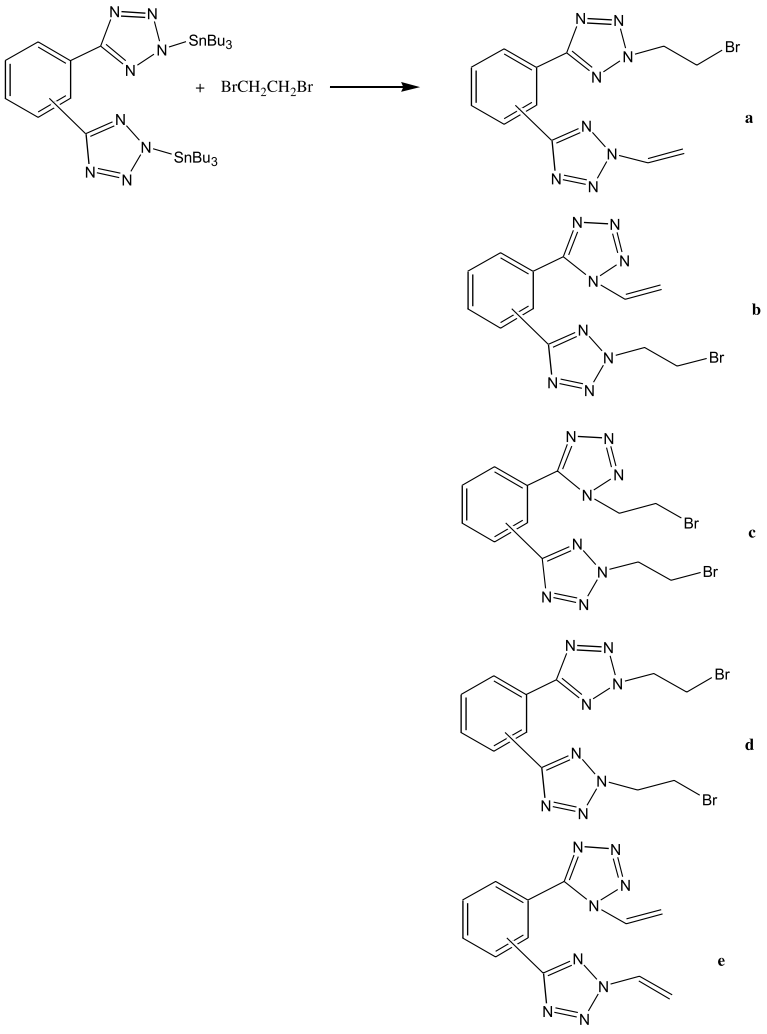


Figure 1. Molecular structure of **1b**, showing the labelling scheme used. Ellipsoids are represented at 30% probability.



Isomer	**a**	**b**	**c**	**d**	**e**
1,2-	4a (10.6 %)	4b (10.2 %)	4c (8.3 %)	-	4e (6.4 %)
1,3-	5a (11.8 %)	5b (9.8 %)	5c (7.6 %)	5d (6.3 %)	-
1,4-	6a (10.9 %)	6b (10.1 %)	6c (8.1 %)	-	6e (7.3 %)

* % Yield in parenthesises

Scheme 2.

those products already discussed above. In the previous set of reactions, described above, it was easier to rationalise the presence of the vinyl group as a result of excess base being present, resulting from not all the starting bis-tetrazole being consumed in the reaction.

There are three 'plausible' explanations for the formation of the N-vinyl compound in the absence of triethylamine. First, it is a thermal elimination (pyrolysis) of the hydrogen halide. This is unlikely as the reaction temperature is only 120 °C, and the fact that not all the bromoethyl arms are converted to vinyl groups would rule this out as a possibility. Secondly, the tributyltin bromide by-product under the reaction conditions produces the tributyltin radical, which then abstracts a bromide radical with subsequent loss of a proton to give the vinyl. While this appears plausible, the reaction conditions are very mild (120 °C reflux) compared to those published in the literature (for example, in the presence of a catalytic amount of azobisisobutyronitrile (AIBN) or UV irradiation in toluene).[10,11] On that basis, we believe that this pathway, though plausible, is not a possibility. The final plausible explanation is that the bromide ion formed in the first displacement acts as a base in 1,2-dibromoethane, as there is no solvent present to solvate the ion. It immediately abstracts a hydrogen from the product containing the bromoethyl arm resulting in a negative charge residing on the carbon atom. Loss of bromide ion removes the negative charge and also results in the formation of the vinyl group. Of the three possible routes, this final route appears the most plausible.

Despite our best endeavours, we were unable to grow suitable crystals of any of the **a** or **b** compounds but we did manage to grow suitable crystals of **5d**. The X-ray structure for this compound has been previously published[5] but this compound **5d** is a different polymorph. The major difference between the two sets of structural data is that the structure already published showed that the crystal was

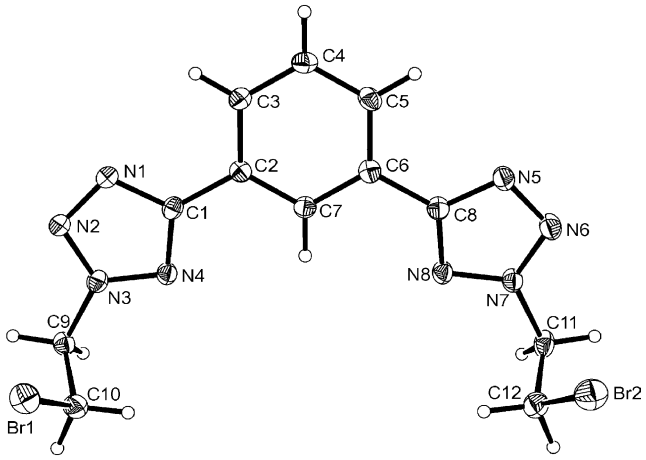


Figure 2. Molecular structure of **5d**, showing the labelling scheme used. Ellipsoids are represented at 30% probability.

monoclinic in the *C*2/*c* space group whereas in this case the structure is triclinic in the *P*-1 space group. This difference manifests itself in the orientation of the pendant bromoethyl arms. In the previously reported structure,[5] the pendant bromoethyl arms are pointing in opposite directions relative to the central phenyl ring, whereas in **5d**, the pendant bromoethyl arms are directed in the same direction (see Fig. 2).

The tetrazole rings and the phenyl ring are almost co-planar, with both bromoethyl arms on the same face of the phenyl ring. The packing diagram (see Fig. 3) illustrates this feature to greater effect. Here, distinct channels of bis-tetrazole units are evident with intermolecular interactions between adjacent units. Analysis of the supramolecular array reveals the presence of slipped π-stacking between the phenyl ring and the tetrazole based on C8, the distance between most proximate pairs of such rings in the supramolecular array being 3.36 Å. The tetrazoles based on C1 are also involved in π-stacking with each other. In this case an interplane distance of 3.36 Å is observed between said rings in closest lattice neighbours. The closest Br···Br distance of 3.854 Å mitigates against the presence of any significant bromine–bromine interactions.

Crystallographic data for the structural analysis on **1b** and **5d** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 261954 and 261955, respectively. Copies of this information may be obtained free of charge from deposit@ccdc.cam.ac.uk or www:http://www.ccdc.cam.ac.uk

3. Conclusions

The reactions of either 1,*n*-$(HN_4C)_2C_6H_4$ or 1,*n*-$(Bu_3SnN_4C)_2C_6H_4$ ($n=2$, 3, 4) with 1,2-dibromoethane yields compounds containing pendant bromoethyl or vinyl groups with substitution occurring at either 1-*N*,2-*N*′ or 2-*N*,2-*N*′, respectively. This is not in agreement with previously published work in this area. The next objective is to improve the reaction yields with a view to attaining our goal of synthesising tetra-tetrazole macrocycles.

4. Experimental

^1H and ^{13}C NMR (δ ppm; *J* Hz) spectra were recorded on a JOEL JNM-LA300 FT-NMR spectrometer using saturated $CDCl_3$ solutions with Me_4Si reference, unless indicated otherwise, with resolutions of 0.18 Hz and 0.01 ppm, respectively. Infrared spectra (cm^{-1}) were recorded as KBr discs or liquid films between KBr plates using a Nicolet

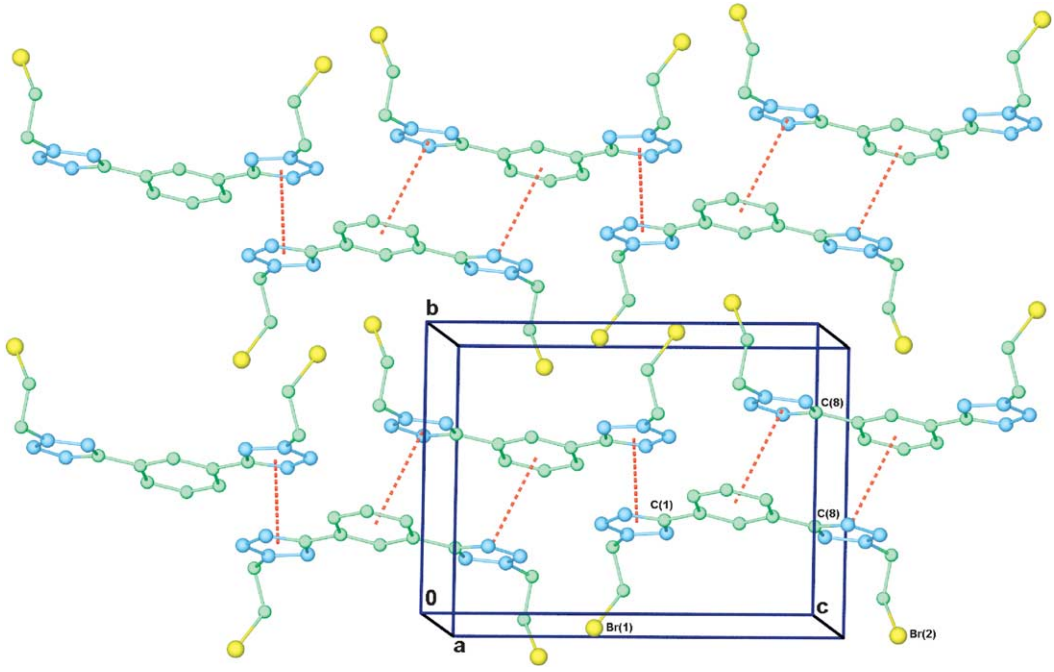


Figure 3. Partial packing diagram for structure **5d**, to illustrate the relative orientation of the pendant groups on the tetrazole rings and the π-stacking interactions.

Impact 410 FT-IR. All uv/vis spectra were recorded on a Shimadzu UV-160A spectrometer. Melting 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.

4.1. Syntheses

1,2-$(Bu_3SnN_4C)_2C_6H_4$ (**4**), 1,3-$(Bu_3SnN_4C)_2C_6H_4$ (**5**) and 1,4-$(Bu_3SnN_4C)_2C_6H_4$ (**6**) were prepared as described previously.[4] 1,2-Bis(tetrazol-5-yl)benzene (**1**), 1,3-bis(tetrazol-5-yl)benzene (**2**) and 1,4-bis(tetrazol-5-yl)benzene (**3**) were prepared by a different method to that of Molloy et al.[5] but the analytical data in all cases were the same. 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 were conducted under an inert atmosphere behind a rigid safety screen.

The numbering scheme for the 1,2-, 1,3- and 1,4-bis-tetrazoles are shown in the figures below and all NMR assignments are based on these diagrams (Figs. 4–6).

4.1.1. 1,2-Bis(tetrazol-5-yl)benzene (1)[5] A suspension of 1,2-dicyanobenzene (12.8 g, 0.10 mol), sodium azide (14.3 g, 0.22 mol), ammonium chloride (11.76 g, 0.22 mol) and lithium chloride (3.0 g, 0.07 mol) in anhydrous dimethylformamide (100 ml) was stirred at 110 °C for 10 h. After this time, the solution was cooled and the insoluble salts were removed by filtration. The solvent was then evaporated under reduced pressure and the residue was dissolved in deionised water (200 ml) and acidified with concentrated HCl (3 ml), to initiate precipitation. The product was filtered, washed with water (3×40 ml) and dried to give a white solid. Recrystallisation from ethanol gave white needle-like crystals (14.55 g, 68% yield), mp 234–236 °C. Analysis: δ_H (300 MHz, d_6-DMSO): 7.85 (2H, dd, aromatic-H), 7.91 (2H, d, aromatic-H); δ_C (300 MHz, d_6-DMSO): 124.5 (2 i-C_6H_4), 130.8 (2 C^2-C_6H_4), 131.3 (2 C^1-C_6H_4), 155.5 (2 CN_4).

Compounds **2** and **3** were also prepared by the same methodology.

4.1.2. 1,3-Bis(tetrazol-5-yl)benzene (2)[5] Recrystallisation from ethanol gave white needle-like solid (67.5% yield), mp 268–270 °C. Analysis: δ_H (300 MHz, d_6-DMSO): 7.86 (1H, t, H^1), 8.24 (2H, dd, H^2), 8.78 (1H, s, H^3); δ_C (300 MHz, d_6-DMSO): 125.3 (C^1–C_6H_4), 125.7 (2*i*–C_6H_4), 129.3 (2C^2–C_6H_4), 130.8 (C^3–C_6H_4), 155.5 (2 CN_4).

4.1.3. 1,4-Bis(tetrazol-5-yl)benzene (3)[5] Recrystallisation from ethanol gave white needle-like solid (69.7% yield), mp 291–294 °C. Analysis: δ_H (300 MHz, d_6-DMSO): 8.27 (4H, 6, H^1); δ_C (300 MHz, d_6-DMSO): 126.7 (2*i*-C_6H_4), 127.9 (2C^1–C_6H_4), 155.5 (2CN_4).

4.2. Synthesis of compounds 1a, 1b and 1c

1,2-Bis[tetrazol-5-yl]benzene (**1**), (1.0 g, 4.7 mmol) was dissolved in methanol (30 ml), and to the stirred solution was added triethylamine (3.0 ml, 2.8 mmol). The resulting solution was heated to reflux for half an hour, and to the hot solution was added 1,2-dibromoethane (2.6 g, 1.4 mmol). The reaction mixture was then heated to reflux for a further 24 h. After cooling, the solvent was removed under reduced pressure to afford the mixture of isomers **1a**, **1b** and **1c**. These isomers were separated by column chromatography on silica gel (initially at the ratio of hexane–ethyl acetate 80:20, followed by the ratio 60:40).

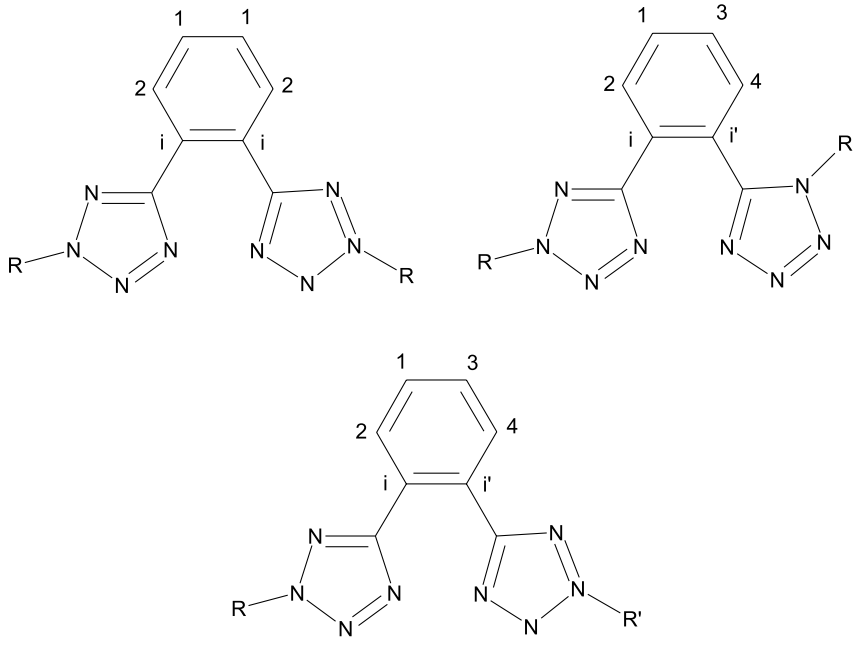


Figure 4. Labelling scheme used for central core in the 1,2-bis(tetrazole) derivatives.

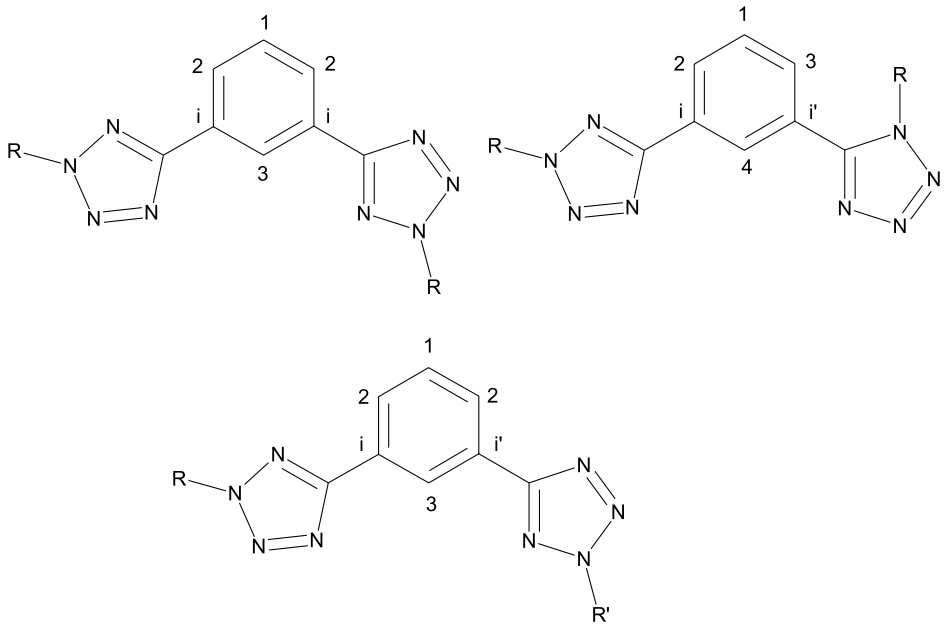


Figure 5. Labelling scheme used for central core in the 1,3-bis(tetrazole) derivatives.

4.2.1. 1,2-Bis[(2-vinyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′) (1a). White solid. Analysis: Found: C, 54.52; H, 3.96; N, 42.35. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 13.8%. Mp 95–98 °C; ν_{max} (KBr) 3150, 3090, 2910, 1610, 1648, 1490, 1102, 986, 910, 800 cm^{-1}; δ_H: 5.25 [dd, $2H_{cis}$, $J_{trans}=8.8$ Hz, $J_{gem}=1.8$ Hz, $N^2CH{=}CH_2$, $N^{2'}CH{=}CH_2$], 6.35 [dd, $2H_{trans}$, $J_{cis}=15.5$ Hz, $J_{gem}=1.6$ Hz, $N^2CH{=}CH_2$, $N^{2'}CH{=}CH_2$], 7.59 [dd, $2H_{gem}$, $J_{trans}=15.5$ Hz, $J_{cis}=8.8$ Hz, $N^2CH{=}CH_2$, $N^{2'}CH{=}CH_2$], 7.65 [d, 2H, $J=6.6$ Hz, H^1-C_6H_4], 7.85 [d, 2H, $J=6.5$ Hz, H^2–C_6H_4]; δ_C: 29.6 [CH_2], 109.9 [*i*-C_6H_4], 130.6 [C^1–C_6H_4], 134.8 [C^2–C_6H_4], 164.2 [CN_4].

4.2.2. 1,2-Bis[(2-vinyl)tetrazol-5-yl)]benzene (1-*N*,2-*N*′) (1b). White solid. Analysis: Found: C, 54.45; H, 4.01; N, 42.29. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 10.5%. Mp 110–112 °C; ν_{max} (KBr) 3169, 3109, 2910, 2896, 1615, 1589, 1475, 1090, 956, 910, 779 cm^{-1}; δ_H: 5.04 [dd, 1H, H_{cis}, $J_{trans}=8.8$ Hz, $J_{gem}=1.5$ Hz, $N^1CH{=}CH_2$], 5.25 [dd, 1H, H_{cis}, $J_{trans}=8.6$ Hz, $J_{gem}=1.6$ Hz, $N^{2'}CH{=}CH_2$], 5.78 [dd, 1H, H_{trans}, $J_{cis}=15.5$ Hz, $J_{gem}=1.8$ Hz, $N^1CH{=}CH_2$], 5.88 [dd, 1H, H_{trans}, $J_{cis}=13.9$ Hz, $J_{gem}=1.3$ Hz, $N^{2'}CH{=}CH_2$], 6.59 [dd, 1H, H_{gem}, $J_{trans}=15.5$ Hz, $J_{cis}=8.8$ Hz, $N^1CH{=}CH_2$], 7.30 [dd, 1H, H_{gem}, $J_{trans}=15.5$ Hz, $J_{cis}=8.8$ Hz, $N^{2'}CH{=}CH_2$], 7.53 [d, 1H, $J=6.5$ Hz, H^1–C_6H_4], 7.62 [t, 1H, $J=6.5$ Hz, H^2–C_6H_4], 7.78 [t, 1H, $J=6.5$ Hz, H^3–C_6H_4], 8.41 [d, 1H, $J=6.5$ Hz, H^4–C_6H_4]; δ_C: 109.3 [CH_2], 109.5 [CH_2], 122.5 [*i*-C_6H_4], 125.6 [$CHN^{2'}$], 127.0 [*i*′-C_6H_4], 128.8 [CHN^1], 129.6 [C^1–C_6H_4], 130.9 [C^2–C_6H_4], 131.6 [C^3–C_6H_4], 132.0 [C^4–C_6H_4], 152.6 [N^1CN_4], 162.4 [$N^{2'}CN_4$].

4.2.3. 1,2-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (2-*N*,2-*N*′) (1c). White solid. Analysis: Found: C, 41.76; H, 3.45; N, 32.35. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 8.1%. Mp 102–104 °C; ν_{max} (KBr) 3150, 3100, 2890, 1755, 1650, 1648, 1459, 1210, 1175, 1005, 996, 907, 746, 650 cm^{-1}; δ_H: 3.66 [t, 2H, $J=6.6$ Hz, CH_2Br], 4.38 [t, 2H, $J=6.6$ Hz, NCH_2], 5.27 [dd, 1H, H_{cis}, $J_{trans}=8.8$ Hz, $J_{gem}=1.5$ Hz, $NCH{=}CH_2$], 5.88 [dd, 1H, H_{trans}, $J_{cis}=15.4$ Hz, $J_{gem}=1.6$ Hz, $NCH{=}CH_2$], 7.35 [dd, 1H, H_{gem}, $J_{trans}=15.5$ Hz,

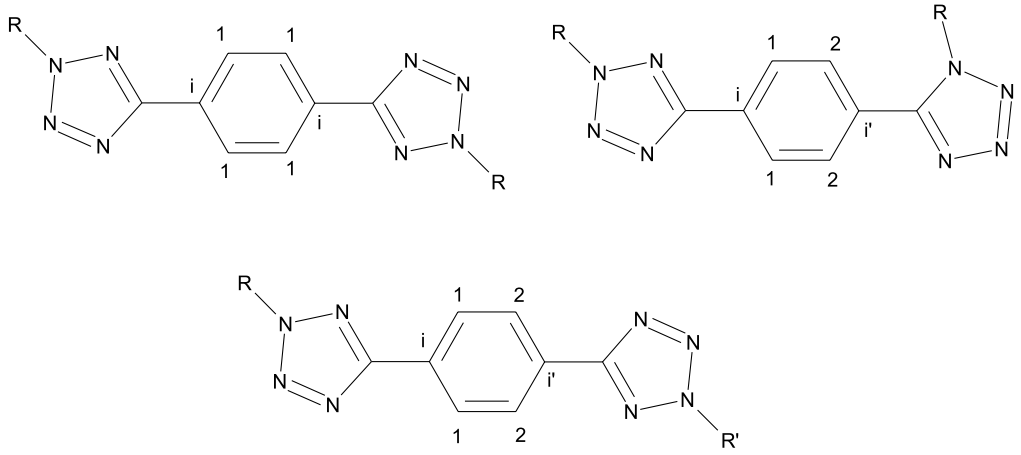


Figure 6. Labelling scheme used for central core in the 1,4-bis(tetrazole) derivatives.

J_{cis}=8.6 Hz, NCH=CH_2], 7.54 [d, 1H, J=7.0 Hz, H^1-C_6H_4], 7.62 [t, 1H, J=7.0 Hz, H^2–C_6H_4], 7.71 [d, 1H, J=6.5 Hz, H^3–C_6H_4], 8.37 [t, 1H, J=6.5 Hz, H^4–C_6H_4]; δ_C: 27.0 [CH_2Br], 48.6 [CH_2N], 109.4 [CH_2], 122.5 [i-C_6H_4], 126.9 [i'-C_6H_4], 128.7 [C^1–C_6H_4], 129.2 [CHN], 129.6 [C^2–C_6H_4], 130.8 [C^3–C_6H_4], 131.9 [C^4–C_6H_4], 162.6 [CN_4].

4.3. Synthesis of compounds 2a, 2b and 2c

These compounds were prepared by the same general method from 1,3-bis[tetrazol-5-yl]benzene (**2**), triethylamine and 1,2-dibromoethane, resulting in a mixture of **2a**, **2b** and **2c** which were isolated from each other by column chromatography on silica gel as described previously.

4.3.1. 1,3-Bis[(2-vinyl)tetrazol-5-yl]benzene (2-*N*,2-*N'*) (2a). White solid. Analysis: Found: C, 54.23; H, 3.69; N, 42.45. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 15.6%. Mp 112–116 °C; ν_{max} (KBr) 3124, 3100, 2921, 2848, 1699, 1649, 1458, 1213, 1182, 1003, 905, 910, 738 cm^{-1}; δ_H: 5.43 [dd, 2H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.6 Hz, NCH=CH_2], 6.33 [dd, 2H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.6 Hz, NCH=CH_2], 7.62 [dd, 2H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, NCH=CH_2], 7.66 [t, 1H, J=7.0 Hz, H^1-C_6H_4], 8.34 [d, 2H, J=7.0 Hz, H^2-C_6H_4], 9.03 [s, 1H, H^3-C_6H_4]; δ_C: 108.8 [CH_2], 125.6 [C^1–C_6H_4], 127.8 [i-C_6H_4], 129.1 [C^2–C_6H_4], 129.6 [CHN], 129.8 [C^3–C_6H_4], 164.2 [CN_4].

4.3.2. 1,3-Bis[(2-vinyl)tetrazol-5-yl]benzene (1-*N*,2-*N'*) (2b). White solid. Analysis: Found: C, 54.26; H, 3.85; N, 42.32. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 10.2%. Mp 120–122 °C; ν_{max} (KBr) 3179, 3067, 2897, 1605, 1596, 1470, 1105, 998, 905, 805 cm^{-1}; δ_H: 5.46 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.6 Hz, N^1CH=CH_2], 5.52 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.6 Hz, $N^{2'}CH$=CH_2], 6.27 [dd, 1H, H_{trans}, J_{cis}=13.2 Hz, J_{gem}=1.6 Hz, N^1CH=CH_2], 6.32 [dd, 1H, H_{trans}, J_{cis}=13.6 Hz, J_{gem}=1.6 Hz, $N^{2'}CH$=CH_2], 7.15 [dd, 1H, H_{gem}, J_{trans}=15.4 Hz, J_{cis}=8.8 Hz, N^1CH=CH_2], 7.59 [dd, 1H, H_{gem}, J_{trans}=15.7 Hz, J_{cis}=8.8 Hz, $N^{2'}CH$=CH_2], 7.75 [t, 1H, J=7.7 Hz, H^2–C_6H_4], 7.87 [d, 1H, J=7.4 Hz, H^1–C_6H_4], 8.45 [d, 1H, J=7.2 Hz, H^3–C_6H_4], 8.55 [s, 1H, H^4–C_6H_4]; δ_C: 109.3 [CH_2], 111.8 [CH_2], 124.4 [i-C_6H_4], 125.0 [i'-C_6H_4], 126.0 [C^3–C_6H_4], 127.6 [C^2–C_6H_4], 128.4 [C^1–C_6H_4], 130.0 [$CHN^{2'}$], 131.2 [CHN^1], 135.2 [C^4–C_6H_4], 152.4 [CN_4], 163.6 [CN_4].

4.3.3. 1,3-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (2-*N*,2-*N'*) (2c). White solid. Analysis: Found: C, 41.68; H, 3.33; N, 32.46. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 8.3%. Mp 104–106 °C; ν_{max} (KBr) 3150, 3100, 2890, 1755, 1650, 1459, 1210, 1175, 1005, 907, 746, 650 cm^{-1}; δ_H: 3.80 [t, 2H, J=6.6 Hz, CH_2Br], 4.95 [t, 2H, J=6.6 Hz, CH_2N^2], 5.29 [dd, 1H, H_{cis}, J_{trans}=9.0 Hz, J_{gem}=1.6 Hz, $N^{2'}CH$=CH_2], 6.18 [dd, 1H, H_{trans}, J_{cis}=15.9 Hz, J_{gem}=1.6 Hz, $N^{2'}CH$=CH_2], 7.45 [dd, 1H, H_{gem}, J_{trans}=15.9 Hz, J_{cis}=9.1 Hz, $N^{2'}CH$=CH_2], 7.53 [d, 2H, J=8.4 Hz, H^2–C_6H_4], 8.18 [t, 1H, J=7.9 Hz, H^1–C_6H_4], 8.85 [s, 1H, H^3–C_6H_4]; δ_C: 27.0 [CH_2Br], 54.1 [CH_2N^2], 109.1 [CH_2], 125.6 [C^1–C_6H_4], 127.8 [i-C_6H_4], 129.1 [C^2–C_6H_4], 129.5 [CHN], 129.8 [C^3–C_6H_4], 164.2 [CN_4].

4.4. Synthesis of compounds 3a, 3b and 3c

These compounds were prepared by the same general method from 1,4-bis[tetrazol-5-yl]benzene (**3**), triethylamine and 1,2-dibromoethane resulting in a mixture of **3a**, **3b** and **3c** which were individually isolated by column chromatography on silica gel as previously described.

4.4.1. 1,4-Bis[(2-vinyl)tetrazol-5-yl]benzene (2-*N*,2-*N'*) (3a). White solid. Analysis: Found: C, 54.36; H, 4.18; N, 42.08. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 12.8%. Mp 124–126 °C; ν_{max} (KBr) 3148, 3108, 2910, 2894, 1690, 1650, 1429, 1150, 1005, 990, 913, 810 cm^{-1}; δ_H: 5.44 [dd, 2H, H_{cis}, J_{trans}=9.7 Hz, J_{gem}=1.6 Hz, NCH=CH_2], 6.32 [dd, 2H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.2 Hz, NCH=CH_2], 7.56 [dd, 2H, H_{gem}, J_{trans}=12.2 Hz, J_{cis}=8.8 Hz, NCH=CH_2], 7.81 [s, 4H, C_6H_4]; δ_C: 108.9 [CH_2], 127.5 [C^1–C_6H_4], 129.0 [i-C_6H_4], 129.8 [CHN], 164.3 [CN_4].

4.4.2. 1,4-Bis[(2-vinyl)tetrazol-5-yl]benzene (1-*N*,2-*N'*) (3b). White solid. Analysis: Found: C, 54.26; H, 3.56; N, 42.33. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 11.6%. Mp 116–120 °C; ν_{max} (KBr) 3105, 3089, 2928, 2890, 1603, 1567, 1470, 1096, 980, 905, 803 cm^{-1}; δ_H: 5.47 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.5 Hz, N^1CH=CH_2], 5.51 [dd, 1H, H_{cis}, J_{trans}=8.6 Hz, J_{gem}=1.5 Hz, $N^{2'}CH$=CH_2], 6.27 [dd, 1H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.6 Hz, N^1CH=CH_2], 6.33 [dd, 1H, H_{trans}, J_{cis}=15.4 Hz, J_{gem}=1.3 Hz, $N^{2'}CH$=CH_2], 7.12 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.7 Hz, N^1CH=CH_2], 7.59 [dd, 1H, H_{gem}, J_{trans}=15.4 Hz, J_{cis}=8.8 Hz, $N^{2'}CH$=CH_2], 7.89 [d, 2H, J=8.2 Hz, H^2-C_6H_4], 8.42 [d, 2H, J=8.2 Hz, H^1-C_6H_4]; δ_C: 109.2 [CH_2], 111.8 [CH_2], 125.4 [i-C_6H_4], 126.0 [i'-C_6H_4], 127.9 [C^1–C_6H_4], 128.2 [C^2–C_6H_4], 129.9 [$CHN^{2'}$], 133.1 [CHN^1], 152.4 [CN_4], 163.6 [CN_4].

4.4.3. 1,4-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl))]benzene (2-*N*,2-*N'*) (3c). White solid. Analysis: Found: C, 41.44; H, 3.36; N, 32.45. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 9.8%. Mp 128–130 °C; ν_{max} (KBr) 3128, 3094, 2905, 1610, 1548, 1460, 1238, 1100, 1003, 960, 838, 610 cm^{-1}; δ_H: 3.94 [t, 2H, J=6.6 Hz, CH_2Br], 5.08 [t, 2H, J=6.6 Hz, CH_2N^2], 5.45 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.6 Hz, $N^{2'}CH$=CH_2], 6.31 [dd, 1H, H_{trans}, J_{cis}=15.6 Hz, J_{gem}=1.5 Hz, $N^{2'}CH$=CH_2], 7.58 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, $N^{2'}CH$=CH_2], 8.30 [d, 2H, J=8.8 Hz, C^1–C_6H_4], 8.34 [d, 2H, J=8.8 Hz, C^2–C_6H_4]; δ_C: 27.0 [CH_2Br], 54.1 [CH_2N], 108.8 [CH_2], 127.5 [C^1–C_6H_4], 127.7 [C^2–C_6H_4], 128.8 [i-C_6H_4], 129.1 [i'-C_6H_4], 129.8 [CHN], 164.8 [CN_4].

4.5. Synthesis of compounds 4a, 4b, 4c and 4e

1,2-Bis[2-(tributylstannyl)tetrazol-5-yl]benzene (**4**) (1.0 g, 1.25 mmol) was heated to 120 °C in 1,2-dibromoethane (5.5 ml) for 24 h. A viscous solution resulted which, on cooling, yielded a mixture of **4a**, **4b**, **4c** and **4e**. These were individually isolated by column chromatography on silica gel as previously described.

4.5.1. 1,2-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (2-*N*,2-*N*′) (4a). White solid. Analysis: Found: C, 41.69; H, 3.42; N, 32.08. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 10.6%. Mp 102–104 °C; ν_{max} (KBr) 3100, 3098, 2954, 2879, 1605, 1545, 1460, 1256, 1100, 1010, 990, 905, 850, 602 cm^{-1}; δ_H: 3.66 [t, 2H, J=6.6 Hz, CH_2Br], 4.38 [t, 2H, J=6.6 Hz, N^2CH_2], 5.27 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 5.88 [dd, 1H, H_{trans}, J_{cis}=15.4 Hz, J_{gem}=1.6 Hz, $N^{2'}CH{=}CH_2$], 7.35 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.6 Hz, $N^{2'}CH{=}CH_2$], 7.54 [d, 1H, J=7.0 Hz, H^1–C_6H_4], 7.62 [t, 1H, J=7.0 Hz, H^2–C_6H_4], 7.71 [t, 1H, J=6.5 Hz, H^3–C_6H_4], 8.37 [d, 1H, J=6.5 Hz, H^4–C_6H_4]; δ_C: 27.0 [CH_2Br], 48.6 [CH_2N], 109.4 [CH_2], 122.5 [i-C_6H_4], 126.9 [i'-C_6H_4], 128.7 [C^1–C_6H_4], 129.2 [CHN], 129.6 [C^2–C_6H_4], 130.8 [C^3–C_6H_4], 131.9 [C^4–C_6H_4], 162.6 [CN_4].

4.5.2. 1,2-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (1-*N*,2-*N*′) (4b). White solid. Analysis: Found: C, 41.89; H, 3.36; N, 32.42. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 10.2%. Mp 108–112 °C; ν_{max} (KBr) 3100, 3098, 2954, 2879, 1605, 1545, 1460, 1256, 1100, 1010, 990, 905, 850, 602 cm^{-1}; δ_H: 3.92 [t, 2H, J=6.6 Hz, CH_2Br], 4.92 [t, 2H, J=6.6 Hz, CH_2N^1], 5.50 [dd, 1H, H_{cis}, J_{trans}=8.6 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 6.28 [dd, 1H, H_{trans}, J_{cis}=15.4 Hz, J_{gem}=1.3 Hz, $N^{2'}CH{=}CH_2$], 7.15 [dd, 1H, H_{gem}, J_{trans}=15.3 Hz, J_{cis}=8.6 Hz, $N^{2'}CH{=}CH_2$], 7.61 [d, 1H, J=7.0 Hz, H^1–C_6H_4], 7.69 [t, 1H, J=7.0 Hz, H^2–C_6H_4], 7.78 [t, 1H, J=7.0 Hz, H^3–C_6H_4], 8.38 [d, 1H, J=7.0 Hz, H^4–C_6H_4]; δ_C: 27.0 [CH_2Br], 54.0 [CH_2N^1], 112.0 [CH_2], 123.4 [i-C_6H_4], 126.1 [i'-C_6H_4], 127.5 [C^1–C_6H_4], 129.8 [C^2–C_6H_4], 130.2 [$CHN^{2'}$], 132.2 [C^3–C_6H_4], 132.3 [C^4–C_6H_4], 152.6 [CN_4], 162.4 [CN_4].

4.5.3. 1,2-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′) (4c). White solid. Analysis: Found: C, 33.50; H, 2.96; N, 26.25. Calcd for $C_{12}H_{12}N_8Br_2$: C, 33.70; H, 2.81; N, 26.10. Yield: 8.3%. Mp 124–126 °C; ν_{max} (KBr) 3099, 3087, 2850, 1543, 1460, 1276, 1090, 1005, 830, 605 cm^{-1}; δ_H: 3.70 [t, 2H, J=6.6 Hz, CH_2Br], 3.74 [t, 2H, J=6.6 Hz, CH_2Br], 4.42 [t, 2H, J=6.6 Hz, CH_2N^1], 4.89 [t, 2H, J=6.6 Hz, $CH_2N^{2'}$], 7.61 [d, 1H, J=7.0 Hz, H^1–C_6H_4], 7.69 [t, 1H, J=7.0 Hz, H^2–C_6H_4], 7.78 [t, 1H, J=7.0 Hz, H^3–C_6H_4], 8.38 [d, 1H, J=7.0 Hz, H^4–C_6H_4]; δ_C: 27.2 [CH_2Br], 48.9 [CH_2N], 54.4 [$CH_2N^{2'}$], 122.7 [i-C_6H_4], 127.5 [i'-C_6H_4], 129.8 [C^1–C_6H_4], 131.0 [C^2–C_6H_4], 132.2 [C^3–C_6H_4], 132.3 [C^4–C_6H_4], 154.8 [CN_4], 163.6 [CN_4].

4.5.4. 1,2-Bis[(2-vinyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′) (4e). White solid. Analysis: Found: C, 54.33; H, 3.99; N, 42.35. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 6.4%. Mp 92–94 °C. ν_{max} (KBr) 3169, 3109, 2910, 2896, 1615, 1589, 1475, 1090, 956, 910, 779 cm^{-1}; δ_H: 5.04 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.5 Hz, $N^1CH{=}CH_2$], 5.25 [dd, 1H, H_{cis}, J_{trans}=8.6 Hz, J_{gem}=1.6 Hz, $N^{2'}CH{=}CH_2$], 5.78 [dd, 1H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.8 Hz, $N^1CH{=}CH_2$], 5.88 [dd, 1H, H_{trans}, J_{cis}=13.9 Hz, J_{gem}=1.3 Hz, $N^{2'}CH{=}CH_2$], 6.59 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, $N^1CH{=}CH_2$], 7.30 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, $N^{2'}CH{=}CH_2$], 7.53 [d, 1H, J=6.5 Hz, H^1–C_6H_4], 7.62 [t, 1H, J=6.5 Hz, H^2–C_6H_4], 7.78 [t, 1H, J=6.5 Hz, H^3–C_6H_4], 8.41 [d, 1H, J=6.5 Hz, H^4–C_6H_4]; δ_C: 109.3 [CH_2], 109.5 [CH_2], 122.5 [i-C_6H_4], 125.6 [$CHN^{2'}$], 127.0 [i'-C_6H_4], 128.8 [CHN^1], 129.6 [C^1–C_6H_4], 130.9 [C^2–C_6H_4], 131.6 [C^3–C_6H_4], 132.0 [C^4–C_6H_4], 152.6 [CN_4], 162.4 [CN_4].

4.6. Synthesis of compounds 5a, 5b, 5c and 5d

These compounds were prepared by the same method as above but using 1,3-bis[2-(tributylstannyl)tetrazol-5-yl]benzene (**5**) instead. A viscous solution resulted again which, on cooling, yielded a mixture of **5a**, **5b**, **5c** and **5d**. These were isolated by column chromatography on silica gel as previously described.

4.6.1. 1,3-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (2-*N*,2-*N*′) (5a). White solid. Analysis: Found: C, 41.45; H, 3.55; N, 32.25. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 11.8%. Mp 104–106 °C; ν_{max} (KBr) 3150, 3100, 2890, 1755, 1650, 1459, 1210, 1175, 1005, 907, 746, 650 cm^{-1}; δ_H: 3.93 [t, 2H, J=6.6 Hz, CH_2Br], 5.08 [t, 2H, J=6.6 Hz, CH_2N^2], 5.44 [dd, 1H, H_{cis}, J_{trans}=9.0 Hz, J_{gem}=1.7 Hz, $N^{2'}CH{=}CH_2$], 6.33 [dd, 1H, H_{trans}, J_{cis}=15.7 Hz, J_{gem}=1.6 Hz, $N^{2'}CH{=}CH_2$], 7.58 [dd, 1H, H_{gem}, J_{trans}=17.9 Hz, J_{cis}=7.7 Hz, $N^{2'}CH{=}CH_2$], 7.63 [d, 2H, J=8.4 Hz, H^2–C_6H_4], 8.39 [t, 1H, J=7.9 Hz, H^1–C_6H_4], 8.99 [s, 1H, H^3–C_6H_4]; δ_C: 27.0 [CH_2Br], 54.2 [CH_2N^2], 109.1 [CH_2], 125.6 [C^1–C_6H_4], 127.5 [i-C_6H_4], 129.0 [C^2–C_6H_4], 129.5 [CHN], 130.0 [C^3–C_6H_4], 164.2 [CN_4].

4.6.2. 1,3-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (1-*N*,2-*N*′) (5b). White solid. Analysis: Found: C, 41.54; H, 3.34; N, 32.48. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 9.8%. Mp 99–100 °C; ν_{max} (KBr) 3104, 3098, 2950, 1605, 1540, 1463, 1250, 1110, 1005, 998, 905, 856 cm^{-1}; δ_H: 3.90 [t, 2H, J=6.6 Hz, CH_2Br], 4.86 [t, 2H, J=6.6 Hz, CH_2N^1], 5.49 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.7 Hz, $N^{2'}CH{=}CH_2$], 6.28 [dd, 1H, H_{trans}, J_{cis}=15.3 Hz, J_{gem}=1.8 Hz, $N^{2'}CH{=}CH_2$], 7.15 [dd, 1H, H_{gem}, J_{trans}=15.4 Hz, J_{cis}=8.8 Hz, $N^{2'}CH{=}CH_2$], 7.71 [t, 1H, J=7.9 Hz, H^1–C_6H_4], 7.84 [d, 1H, J=8.4 Hz, H^2–C_6H_4], 8.42 [d, 1H, J=8.4 Hz, H^3–C_6H_4], 8.53 [s, 1H, H^4–C_6H_4]; δ_C: 27.1 [CH_2Br], 54.3 [CH_2N^1], 111.9 [CH_2], 125.2 [i-C_6H_4], 126.0 [i'-C_6H_4], 127.4 [C^3–C_6H_4], 127.6 [C^2–C_6H_4], 129.9 [C^1–C_6H_4], 130.2 [$CHN^{2'}$], 133.8 [C^4–C_6H_4], 156.4 [CN_4], 162.6 [CN_4].

4.6.3. 1,3-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′) (5c). White solid. Analysis: Found: C, 33.86; H, 3.01; N, 26.35. Calcd for $C_{12}H_{12}N_8Br_2$: C, 33.70; H, 2.81; N, 26.10. Yield: 7.6%. Mp 130–132 °C; ν_{max} (Nujol) (KBr) 3109, 3086, 2910, 2850, 1545, 1456, 1270, 1105, 1003, 850, 715, 615 cm^{-1}; δ_H: 3.87 [t, 2H, J=6.6 Hz, CH_2Br], 3.95 [t, 2H, J=6.6 Hz, CH_2Br], 4.87 [t, 2H, J=6.6 Hz, CH_2N^1], 5.10 [t, 2H, J=6.6 Hz, $CH_2N^{2'}$], 7.83 [t, 1H, J=7.9 Hz, H^1–C_6H_4], 7.88 [d, 1H, J=8.4 Hz, H^2–C_6H_4], 8.42 [d, 1H, J=8.4 Hz, H^3–C_6H_4], 8.51 [s, 1H, H^4–C_6H_4]; δ_C: 27.6 [CH_2Br], 27.9 [CH_2Br], 49.0 [CH_2N^1], 54.2 [$CH_2N^{2'}$], 124.6 [i-C_6H_4], 125.0 [i'-C_6H_4], 127.4 [C^1–C_6H_4], 128.6 [C^2–C_6H_4], 129.9 [$C^{2'}$–C_6H_4], 130.2 [C^3–C_6H_4], 154.5 [CN_4], 164.4 [CN_4].

4.6.4. 1,3-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (2-*N*,2-*N*′) (5d). White solid. Analysis: Found: C, 33.58; H, 2.98; N, 26.25. Calcd for $C_{12}H_{12}N_8Br_2$: C, 33.70; H, 2.81; N, 26.10. Yield: 6.3%. Mp 118–122 °C; ν_{max} (KBr) 3109, 3086, 2910, 2850, 1545, 1456, 1270, 1105, 1003, 850, 715, 615 cm^{-1}; δ_H: 3.94 [t, 4H, J=6.6 Hz, CH_2Br], 5.09 [t, 4H, J=6.6 Hz, CH_2N], 7.64 [t, 1H, J=7.9 Hz, H^1–C_6H_4], 8.29 [d, 2H, J=8.4 Hz, H^2–C_6H_4], 8.94 [s, 1H, H^3–C_6H_4]; δ_C: 27.7 [CH_2Br], 54.1 [CH_2N], 125.4 [*i*-C_6H_4], 128.0 [C^1–C_6H_4], 128.8 [C^2–C_6H_4], 129.6 [C^3–C_6H_4], 164.9 [CN_4].

4.7. Synthesis of compounds 6a, 6b, 6c and 6e

These compounds were prepared by the same method from 1,4-bis[2-(tributylstannyl)tetrazol-5-yl]benzene (**6**) and 1,2-dibromoethane. A viscous solution resulted again which, on cooling, yielded a mixture of **6a**, **6b**, **6c** and **6e**. These were isolated by column chromatography on silica gel as previously described.

4.7.1. 1,4-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (2-*N*,2-*N*′) (6a). White solid. Analysis: Found: C, 41.69; H, 3.39; N, 32.05. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 10.9%. Mp 128–130 °C; ν_{max} (KBr) 3128, 3094, 2905, 1610, 1548, 1460, 1238, 1100, 1003, 960, 838, 610 cm^{-1}; δ_H: 3.94 [t, 2H, J=6.6 Hz, CH_2Br], 5.08 [t, 2H, J=6.6 Hz, CH_2N^2], 5.45 [dd, 1H, H_{cis}, J_{trans}=8.6 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 6.33 [dd, 1H, H_{trans}, J_{cis}=15.7 Hz, J_{gem}=1.6 Hz, $N^{2'}CH{=}CH_2$], 7.58 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, $N^{2'}CH{=}CH_2$], 8.30 [d, 2H, J=8.8 Hz, C^1–C_6H_4], 8.33 [d, 2H, J=8.8 Hz, C^1–C_6H_4]; δ_C: 26.9 [CH_2Br], 54.3 [CH_2N^2], 108.8 [CH_2], 127.6 [C^1–C_6H_4], 127.9 [C^2–C_6H_4], 128.8 [*i*-C_6H_4], 129.1 [*i*′-C_6H_4], 129.8 [$CHN^{2'}$], 164.8 [CN_4].

4.7.2. 1,4-Bis[((2-bromoethyl)tetrazol-5-yl)((2-vinyl) tetrazol-5′-yl)]benzene (1-*N*,2-*N*′) (6b). White solid. Analysis: Found: C, 41.69; H, 3.28; N, 32.11. Calcd for $C_{12}H_{11}N_8Br$: C, 41.50; H, 3.17; N, 32.28. Yield: 10.1%. Mp 122–126 °C; ν_{max} (Nujol) (KBr) 3128, 3094, 2905, 1610, 1548, 1460, 1238, 1100, 1003, 960, 838, 610 cm^{-1}; δ_H: 3.94 [t, 2H, J=6.6 Hz, CH_2Br], 5.10 [t, 2H, J=6.6 Hz, CH_2N^1], 5.52 [dd, 1H, H_{cis}, J_{trans}=8.6 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 6.27 [dd, 1H, H_{trans}, J_{cis}=15.4 Hz, J_{gem}=1.3 Hz, $N^{2'}CH{=}CH_2$], 7.14 [dd, 1H, H_{gem}, J_{trans}=15.3 Hz, J_{cis}=8.6 Hz, $N^{2'}CH{=}CH_2$], 7.88 [d, 2H, J=8.8 Hz, C^1-C_6H_4], 8.38 [d, 2H, J=8.8 Hz, C^2–C_6H_4]; δ_C: 26.9 [CH_2Br], 54.2 [CH_2N^1], 111.8 [CH_2], 125.1 [*i*-C_6H_4], 126.1 [*i*′-C_6H_4], 127.6 [C^1-C_6H_4], 129.8 [C^2–C_6H_4], 130.2 [$CHN^{2'}$], 152.4 [CN_4], 164.2 [CN_4].

4.7.3. 1,4-Bis[(2-bromoethyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′) (6c). White solid. Analysis: Found: C, 33.33; H, 2.74; N, 26.08. Calcd for $C_{12}H_{12}N_8Br_2$: C, 33.70; H, 2.81; N, 26.10. Yield: 8.1%. Mp 156–160 °C; ν_{max} (KBr) 3105, 3090, 2897, 1543, 1459, 1225, 1108, 1010, 897, 776, 609 cm^{-1}; δ_H: 3.92 [t, 2H, J=6.6 Hz, CH_2Br], 3.94 [t, 2H, J=6.6 Hz, CH_2Br], 4.38 [t, 2H, J=6.6 Hz, CH_2N^1], 5.07 [t, 2H, J=6.6 Hz, $CH_2N^{2'}$], 8.15 [d, 2H, J=8.8 Hz, H^1-C_6H_4], 8.22 [d, 2H, J=8.8 Hz, H^2–C_6H_4]. δ_C: 27.7 [CH_2Br], 54.2 [CH_2 N^1], 54.4 [$CH_2N^{2'}$], 116.8 [i-C_6H_4], 117.0 [*i*′-C_6H_4], 130.2 [C^1–C_6H_4], 132.8 [C^2–C_6H_4], 156.3 [CN_4], 164.1 [CN_4].

4.7.4. 1,4-Bis[(2-vinyl)tetrazol-5-yl]benzene (1-*N*,2-*N*′) (6e). White solid. Analysis: Found: C, 54.08; H, 3.49; N, 42.28. Calcd for $C_{12}H_{10}N_8$: C, 54.13; H, 3.76; N, 42.10. Yield: 7.3%. Mp 116–120 °C; ν_{max} (KBr) 3099, 3089, 2928, 2894, 1610, 1568, 1475, 1106, 1008, 980, 905, 810 cm^{-1}; δ_H: 5.49 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.5 Hz, $N^1CH{=}CH_2$], 5.52 [dd, 1H, H_{cis}, J_{trans}=8.8 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 6.29 [dd, 1H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.6 Hz, $N^1CH{=}CH_2$], 6.36 [dd, 1H, H_{trans}, J_{cis}=15.5 Hz, J_{gem}=1.5 Hz, $N^{2'}CH{=}CH_2$], 7.11 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.6 Hz, $N^1CH{=}CH_2$], 7.35 [dd, 1H, H_{gem}, J_{trans}=15.5 Hz, J_{cis}=8.8 Hz, $N^{2'}CH{=}CH_2$], 7.90 [d, 2H, J=8.2 Hz, H^2–C_6H_4], 8.43 [d, 2H, J=8.2 Hz, H^1–C_6H_4]; δ_C: 109.3 [CH_2], 111.9 [CH_2], 125.4 [*i*-C_6H_4], 126.1 [*i*′-C_6H_4], 127.9 [C^1–C_6H_4], 128.2 [C^2–C_6H_4], 129.9 [$CHN^{2'}$], 133.1 [CHN^1], 152.0 [CN_4], 165.0 [CN_4].

4.8. X-ray crystallography

Suitable crystals of **1b** and **5d** for X-ray study were obtained by recrystallisation from chloroform and acetonitrile solutions, respectively. Crystallographic details are given below. In each case, refinement was full-matrix least-squares on F^2. Data for compounds **1b** and **5d** were collected at room temperature on an Enraf–Nonius CAD4 diffractometer. In both cases, data were corrected for Lp and absorption. Hydrogen atoms were added at calculated positions. Software used was SHELXS86,[12] SHELXL97[13] and ORTEX.[14]

4.8.1. Compound 1b. *Crystal data*: $C_{12}H_{10}N_8$, M=266.28, orthorhombic, a=12.9010(3) Å, b=12.9580(3) Å, c=7.5620(2) Å, U=4264.15(5) $Å^3$, space group $P2_12_12_1$, Z=4, μ(Mo Kα)=0.095 mm^{-1}. Crystallographic measurements were made at 150(2) K on a Nonius kappaCCD diffractometer in the range $4.14<\theta<27.42°$. The solution of the structure (SHELXS86) and refinement (SHELXL97) converged to a conventional [i.e., based on 2775F data with $F_o>4\sigma(F_o)$] R_1=0.0393 and wR_2=0.0836. Goodness of fit=1.019. CCDC No. 261954.

4.8.2. Compound 5d. *Crystal data*: $C_{12}H_{12}Br_2N_8$, M=428.12, triclinic, a=6.5230(4) Å, b=9.7510(6) Å, c=12.7850(9) Å, α=88.149(3)°, β=75.839(3)°, γ=84.759(2)°, U=785.15(9) $Å^3$, space group P-1 (No. 2), Z=2, μ(Mo Kα)=5.172 mm^{-1}. Crystallographic measurements were made at 150(2) K on a Nonius kappaCCD diffractometer in the range $3.70<\theta<27.57°$. The solution of the structure (SHELXS86) and refinement (SHELXL97) converged to a conventional [i.e., based on 2441F data with $F_o>4\sigma(F_o)$] R_1=0.0498 and wR_2=0.1044. Goodness of fit=1.029. CCDC No. 261955.

Acknowledgements

We would like to thank Prof. D. Cunningham and Dr. B. A. Murray for useful discussions. VP would like to thank the Postgraduate R&D Skills programme (Technological Sector Research, Strand III) for financial assistance.

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