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Key indicators

Single-crystal X-ray study
T = 150 K
Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
R factor = 0.048
wR factor = 0.131
Data-to-parameter ratio = 23.1

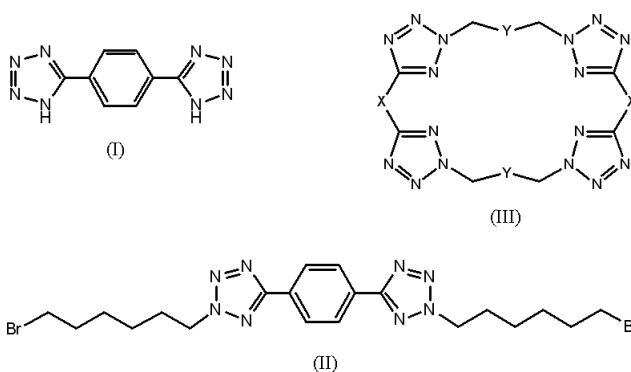
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1,4-Bis[2-(6-bromohexyl)-2H-tetrazol-5-yl]benzene

The 150 K structure of the title compound, $\text{C}_{20}\text{H}_{28}\text{Br}_2\text{N}_8$, has been shown to exhibit liquid-crystal alignment in the gross array, enhanced by the presence of intermolecular $\text{Br} \cdots \text{Br}$ interactions. The asymmetric unit consists of one-half of a molecule, the remainder being generated *via* a crystallographic inversion centre located at the centre of the benzene ring.

Comment

The synthesis of tetrazoles from the cycloaddition reaction between an azide and a nitrile is well established (Butler, 1996). Regioselective alkylation of tetrazoles has been the subject of several investigations during the last 20 years (Bethel *et al.*, 1999; Goodger *et al.*, 1996; Hill *et al.*, 1996; Zubarev & Ostrovskii, 2000). Our group has recently studied the alkylation of 1,4-bis(1H-tetrazol-5-yl)benzene, (I), with various alkyl halides to give bifunctional products of type (II) with N-2 substitution in both tetrazole rings (Fleming *et al.*, 2004). These compounds are intermediates in the generation of tetratetrazole macrocycles of general formula (III) which include a cavity of variable dimensions tailored by both the length and flexibility of the bridging groups X and Y (Butler & NíBhrádaigh, 1994; Butler *et al.*, 1992, 2001; Butler & Fleming, 1997). As part of our ongoing studies on this family of compounds, the structure of 1,4-bis[2-(6-bromohexyl)-2H-tetrazol-5-yl]benzene, (II), is now reported (Fig. 1).



The asymmetric unit consists of one half of a molecule, the remainder being generated *via* a crystallographic inversion centre located at the centre of the benzene ring. Both tetrazole rings are coplanar with the benzene ring to which they are attached (the largest deviation from the least-squares plane is 0.023 Å for atom C4). Analysis of the gross structure reveals slipped π stacking, with a distance of 3.38 Å between the least-squares planes of the tetrazole ring and the benzene ring of its closest neighbour (Fig. 2). It is also probable that liquid crystal

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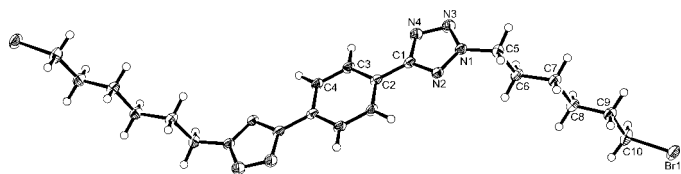


Figure 1
Plot of the title molecule. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, -y, 1 - z)$.

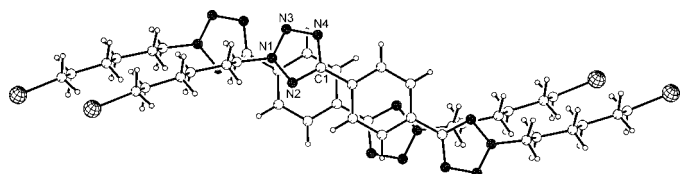


Figure 2
Plot of two neighbouring molecules in the crystal structure of (II), showing π stacking.

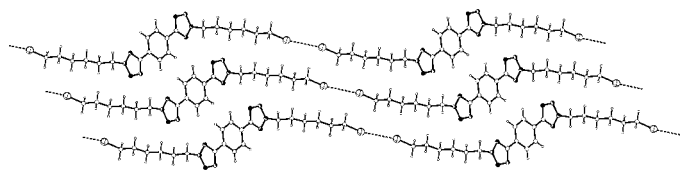


Figure 3
Partial packing diagram for (II), illustrating intermolecular interactions and liquid-crystal alignment.

alignment is present along the c axis in this structure, evidenced by an intermolecular distance of 3.4802 (4) Å between proximate terminal Br atoms (Fig. 3). This distance is considerably shorter than twice the bromine van der Waals radius (3.90 Å) and is within the range of those values previously reported, 3.415–3.691 Å (Christofi *et al.*, 2000; Kuhn *et al.*, 2004; Ruthe *et al.*, 1997; Savinsky *et al.*, 2001).

Experimental

A suspension of 1,4-bis(1*H*-tetrazol-5-yl)benzene (1.0 g, 4.7 mmol), methanol (30 ml) and triethylamine (1.90 g, 19 mmol) was stirred at 333 K for an hour. 1,6-Dibromohexane (3.6 g, 14 mmol) was then added and the mixture was heated under reflux for 5 h. The solvent was removed and the product was purified using column chromatography (hexane/ethyl acetate 80/20 initially followed by 60/40). Crystals suitable for X-ray diffraction were grown from acetonitrile.

Crystal data

$C_{20}H_{28}Br_2N_8$	$Z = 1$
$M_r = 540.32$	$D_x = 1.604 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 4.6290$ (1) Å	Cell parameters from 20 025 reflections
$b = 5.7030$ (1) Å	$\theta = 12\text{--}18^\circ$
$c = 21.7111$ (6) Å	$\mu = 3.65 \text{ mm}^{-1}$
$\alpha = 87.494$ (1)°	$T = 150$ (2) K
$\beta = 85.631$ (1)°	Irregular tablet, colourless
$\gamma = 78.312$ (2)°	$0.60 \times 0.40 \times 0.12 \text{ mm}$
$V = 559.40$ (2) Å ³	

Data collection

Nonius KappaCCD diffractometer	2680 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{\text{int}} = 0.075$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{\text{max}} = 29.9^\circ$
$T_{\text{min}} = 0.187$, $T_{\text{max}} = 0.65$	$h = -6 \rightarrow 6$
8752 measured reflections	$k = -7 \rightarrow 7$
3144 independent reflections	$l = -30 \rightarrow 30$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.1247P]$
$R[F^2 > 2\sigma(F^2)] = 0.048$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.131$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.05$	$\Delta\rho_{\text{max}} = 1.11 \text{ e \AA}^{-3}$
3144 reflections	$\Delta\rho_{\text{min}} = -1.18 \text{ e \AA}^{-3}$
136 parameters	
H-atom parameters constrained	

H atoms were included at calculated positions and constrained to an ideal geometry, with C–H distances of 0.98 Å and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. The largest peak and deepest hole in the final difference map are located 849 and 0.769 Å, respectively, from atom Br1.

Data collection: *COLLECT* (Hooft, 1998); cell refinement: *HKL DENZO* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP* (McArdle, 1995); software used to prepare material for publication: *SHELXL97*.

References

- Bethel, P. A., Hill, M. S., Mahon, M. F. & Molloy, K. C. (1999). *J. Chem. Soc. Perkin Trans. 1*, pp. 3507–3514.
- Blessing, R. H. (1995). *Acta Cryst. A* **51**, 33–37.
- Butler, R. N. (1996). *Comprehensive Heterocyclic Chemistry*, Vol. 4, edited by A. R. Katritzky, C. W. Rees & E. F. V. Scriven. Oxford: Pergamon.
- Butler, R. N. & Fleming, A. F. M. (1997). *J. Heterocycl. Chem.* **34**, 691–693.
- Butler, R. N., McGinley, J., Mahon, M. F., Molloy, K. C. & NíBhrádaigh, E. P. (2001). *Acta Cryst. E* **57**, o195–o197.
- Butler, R. N. & NíBhrádaigh, E. P. (1994). *J. Chem. Res. (S)*, pp. 148–149.
- Butler, R. N., Quinn, K. F. & Welke, B. (1992). *J. Chem. Soc. Chem. Commun.* pp. 1481–1482.
- Christofi, A. M., Garratt, P. J., Hogarth, G. & Steed, J. W. (2000). *J. Chem. Soc. Dalton Trans.* pp. 2137–2144.
- Fleming, A. F. M., Kelleher, F., Mahon, M. F., McGinley, J. & Prajapati, V. (2004). Unpublished work.
- Goodger, A., Hill, M. S., Mahon, M. F., McGinley, J. & Molloy, K. C. (1996). *J. Chem. Soc. Dalton Trans.* pp. 847–852.
- Hill, M. S., Mahon, M. F., McGinley, J. & Molloy, K. C. (1996). *J. Chem. Soc. Dalton Trans.* pp. 835–845.
- Hooft, R. (1998). *COLLECT*. Nonius BV, Delft, The Netherlands.
- Kuhn, N., Abu-Rayyan, A., Eichele, K., Schwarz, S. & Steimann, M. (2004). *Inorg. Chim. Acta*, **357**, 1799–1804.
- McArdle, P. (1995). *J. Appl. Cryst.* **28**, 65.
- Otwinowski, Z. & Minor, W. (1997). *Methods in Enzymology*, Vol. 276, *Macromolecular Crystallography*, Part A, edited by C. W. Carter Jr and R. M. Sweet, pp. 307–326. New York: Academic Press.
- Ruthe, F., Du Mont, W.-W. & Jones, P. G. (1997). *Chem. Commun.* p. 1947.
- Savinsky, R., Hopf, H., Dix, I. & Jones, P. G. (2001). *Eur. J. Org. Chem.* pp. 4595–4606.
- Sheldrick, G. M. (1990). *Acta Cryst. A* **46**, 467–473.
- Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.
- Zubarev, V. Y. & Ostrovskii, V. A. (2000). *Chem. Heterocycl. Compds*, **53**, 1421–1448.