organic papers

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

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Key indicators

Single-crystal X-ray study
T = 150 K
Mean σ(C–C) = 0.004 Å
R factor = 0.048
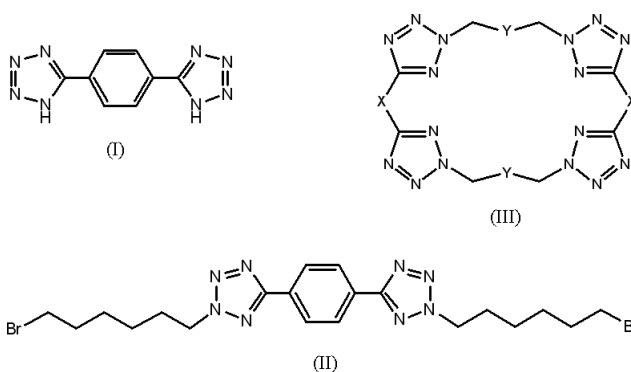wR factor = 0.131
Data-to-parameter ratio = 23.1

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

The 150 K structure of the title compound, $C_{20}H_{28}Br_2N_8$, has been shown to exhibit liquid-crystal alignment in the gross array, enhanced by the presence of intermolecular Br···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
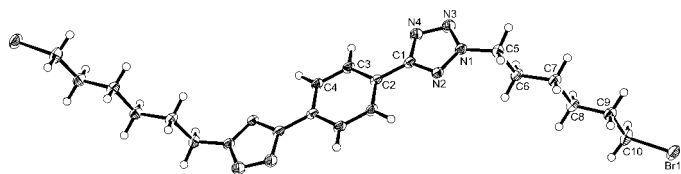
Figure 1
Plot of the title molecule. Displacement ellipsoids are drawn at the 30% probability level. Unlabelled atoms are related to labelled atoms by the symmetry operator $(-x, -y, 1 - z)$.
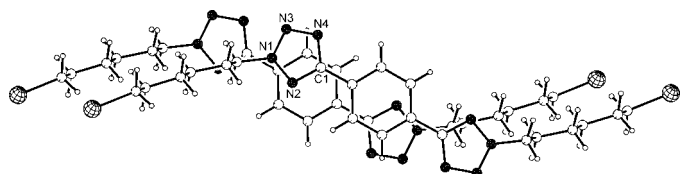

Figure 2
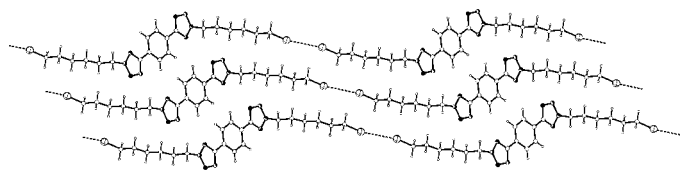Plot of two neighbouring molecules in the crystal structure of (II), showing π stacking.

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

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

Data collection

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

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$+ 0.1247P]$
$wR(F^2) = 0.131$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	$(\Delta/\sigma)_{max} = 0.001$
3144 reflections	$\Delta\rho_{max} = 1.11$ e Å^{-3}
136 parameters	$\Delta\rho_{min} = -1.18$ e Å^{-3}
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_{iso}(H) = 1.2U_{eq}(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: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *ORTEX* (McArdle, 1995); software used to prepare material for publication: *SHELXL*97.

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supporting information

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Crystal data

$C_{20}H_{28}Br_2N_8$	$Z = 1$
$M_r = 540.32$	$F(000) = 274$
Triclinic, $P\bar{1}$	$D_x = 1.604$ Mg m^{-3}
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
$a = 4.6290$ (1) Å	Cell parameters from 25 reflections
$b = 5.7030$ (1) Å	$\theta = 12–18°$
$c = 21.7110$ (6) Å	$\mu = 3.65$ mm^{-1}
$\alpha = 87.494$ (1)°	$T = 150$ K
$\beta = 85.631$ (1)°	Irregular tablet, colourless
$\gamma = 78.312$ (2)°	$0.60 \times 0.40 \times 0.12$ mm
$V = 559.40$ (2) Å^3	

Data collection

Nonius KappaCCD diffractometer	8752 measured reflections
Radiation source: fine-focus sealed tube	3144 independent reflections
Graphite monochromator	2680 reflections with $I > 2\sigma(I)$
KappaCCD scans	$R_{int} = 0.075$
Absorption correction: multi-scan (Blessing, 1995)	$\theta_{max} = 29.9°$, $\theta_{min} = 3.7°$
$T_{min} = 0.187$, $T_{max} = 0.65$	$h = -6 \rightarrow 6$
	$k = -7 \rightarrow 7$
	$l = -30 \rightarrow 30$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: inferred from neighbouring sites
$R[F^2 > 2\sigma(F^2)] = 0.048$	H-atom parameters constrained
$wR(F^2) = 0.131$	$w = 1/[\sigma^2(F_o^2) + (0.0798P)^2 + 0.1247P]$ where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.05$	
3144 reflections	$(\Delta/\sigma)_{max} = 0.001$
136 parameters	$\Delta\rho_{max} = 1.11$ e Å^{-3}
0 restraints	$\Delta\rho_{min} = -1.18$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	

Special details

Experimental. 'multi-scan from symmetry-related measurements (Blessing, 1995)'

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R-factor wR and goodness of fit S are based on F^2, conventional R-factors R are based on F, with F set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. R-factors based on F^2 are statistically about twice as large as those based on F, and R- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

	x	y	z	U_{iso}*/U_{eq}
Br1	1.40358 (6)	−1.26534 (5)	0.050985 (12)	0.03308 (13)
N1	0.7930 (5)	−0.0980 (4)	0.33633 (10)	0.0217 (4)
N2	0.6453 (5)	−0.1849 (4)	0.38397 (10)	0.0217 (4)
N3	0.6840 (6)	0.1309 (4)	0.32191 (11)	0.0292 (5)
N4	0.4560 (5)	0.1999 (4)	0.36189 (11)	0.0273 (5)
C1	0.4356 (6)	0.0064 (4)	0.39922 (11)	0.0207 (5)
C2	0.2114 (6)	0.0045 (4)	0.45048 (11)	0.0206 (5)
C3	0.0010 (6)	0.2117 (4)	0.46491 (12)	0.0233 (5)
H3	0.0004	0.3552	0.4409	0.028*
C4	−0.2067 (6)	0.2067 (4)	0.51438 (12)	0.0229 (5)
H4	−0.3472	0.3482	0.5245	0.027*
C5	1.0312 (6)	−0.2472 (5)	0.29910 (12)	0.0246 (5)
H5A	1.1472	−0.3700	0.3260	0.030*
H5B	1.1656	−0.1467	0.2794	0.030*
C6	0.9040 (6)	−0.3692 (5)	0.24945 (13)	0.0252 (5)
H6A	0.8035	−0.2459	0.2205	0.030*
H6B	0.7546	−0.4560	0.2691	0.030*
C7	1.1433 (6)	−0.5451 (5)	0.21343 (13)	0.0243 (5)
H7A	1.2859	−0.4564	0.1917	0.029*
H7B	1.2521	−0.6622	0.2427	0.029*
C8	1.0156 (6)	−0.6788 (5)	0.16645 (13)	0.0252 (5)
H8A	0.9235	−0.5629	0.1348	0.030*
H8B	0.8587	−0.7541	0.1876	0.030*
C9	1.2497 (6)	−0.8726 (5)	0.13441 (13)	0.0256 (5)
H9A	1.4096	−0.7988	0.1141	0.031*
H9B	1.3374	−0.9921	0.1657	0.031*
C10	1.1181 (7)	−0.9966 (5)	0.08686 (14)	0.0318 (6)
H10A	1.0477	−0.8797	0.0535	0.038*
H10B	0.9454	−1.0560	0.1064	0.038*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Br1	0.0440 (2)	0.02089 (17)	0.03148 (19)	0.00035 (12)	0.00067 (12)	−0.00647 (11)
N1	0.0283 (11)	0.0155 (9)	0.0208 (10)	−0.0037 (8)	−0.0010 (8)	0.0000 (7)

N2	0.0270 (11)	0.0158 (9)	0.0226 (10)	−0.0051 (8)	−0.0006 (8)	−0.0020 (7)
N3	0.0373 (13)	0.0183 (10)	0.0292 (12)	−0.0012 (9)	0.0015 (10)	0.0037 (9)
N4	0.0340 (13)	0.0184 (10)	0.0270 (11)	−0.0016 (9)	0.0014 (9)	0.0022 (8)
C1	0.0272 (12)	0.0150 (10)	0.0197 (11)	−0.0032 (9)	−0.0033 (9)	−0.0011 (8)
C2	0.0263 (12)	0.0137 (10)	0.0224 (11)	−0.0043 (8)	−0.0040 (9)	−0.0015 (8)
C3	0.0309 (13)	0.0133 (10)	0.0245 (12)	−0.0020 (9)	−0.0018 (10)	0.0005 (9)
C4	0.0283 (13)	0.0129 (10)	0.0251 (12)	0.0010 (9)	0.0001 (9)	−0.0014 (8)
C5	0.0261 (13)	0.0222 (12)	0.0245 (12)	−0.0028 (9)	0.0016 (9)	−0.0039 (9)
C6	0.0284 (13)	0.0193 (11)	0.0279 (13)	−0.0037 (9)	−0.0017 (10)	−0.0060 (9)
C7	0.0250 (13)	0.0196 (11)	0.0276 (13)	−0.0020 (9)	−0.0025 (10)	−0.0030 (9)
C8	0.0290 (13)	0.0194 (11)	0.0267 (13)	−0.0023 (9)	−0.0032 (10)	−0.0046 (9)
C9	0.0263 (13)	0.0197 (11)	0.0297 (14)	−0.0011 (9)	−0.0028 (10)	−0.0028 (10)
C10	0.0304 (14)	0.0283 (14)	0.0334 (15)	0.0048 (11)	−0.0036 (11)	−0.0113 (11)

Geometric parameters (Å, º)

Br1—C10	1.957 (3)	C5—H5B	0.9900
N1—N2	1.330 (3)	C6—C7	1.527 (4)
N1—N3	1.333 (3)	C6—H6A	0.9900
N1—C5	1.462 (3)	C6—H6B	0.9900
N2—C1	1.340 (3)	C7—C8	1.521 (4)
N3—N4	1.321 (3)	C7—H7A	0.9900
N4—C1	1.355 (3)	C7—H7B	0.9900
C1—C2	1.464 (4)	C8—C9	1.532 (4)
C2—C4^i	1.400 (3)	C8—H8A	0.9900
C2—C3	1.401 (3)	C8—H8B	0.9900
C3—C4	1.389 (4)	C9—C10	1.507 (4)
C3—H3	0.9500	C9—H9A	0.9900
C4—C2^i	1.400 (3)	C9—H9B	0.9900
C4—H4	0.9500	C10—H10A	0.9900
C5—C6	1.524 (4)	C10—H10B	0.9900
C5—H5A	0.9900		
N2—N1—N3	113.8 (2)	C5—C6—H6B	109.2
N2—N1—C5	122.8 (2)	C7—C6—H6B	109.2
N3—N1—C5	123.1 (2)	H6A—C6—H6B	107.9
N1—N2—C1	101.6 (2)	C8—C7—C6	112.2 (2)
N4—N3—N1	106.2 (2)	C8—C7—H7A	109.2
N3—N4—C1	106.1 (2)	C6—C7—H7A	109.2
N2—C1—N4	112.3 (2)	C8—C7—H7B	109.2
N2—C1—C2	123.4 (2)	C6—C7—H7B	109.2
N4—C1—C2	124.3 (2)	H7A—C7—H7B	107.9
C4^i—C2—C3	119.5 (2)	C7—C8—C9	112.6 (2)
C4^i—C2—C1	119.7 (2)	C7—C8—H8A	109.1
C3—C2—C1	120.8 (2)	C9—C8—H8A	109.1
C4—C3—C2	119.8 (2)	C7—C8—H8B	109.1
C4—C3—H3	120.1	C9—C8—H8B	109.1
C2—C3—H3	120.1	H8A—C8—H8B	107.8

C3—C4—C2^i	120.7 (2)	C10—C9—C8	111.3 (2)
C3—C4—H4	119.6	C10—C9—H9A	109.4
C2^i—C4—H4	119.6	C8—C9—H9A	109.4
N1—C5—C6	110.2 (2)	C10—C9—H9B	109.4
N1—C5—H5A	109.6	C8—C9—H9B	109.4
C6—C5—H5A	109.6	H9A—C9—H9B	108.0
N1—C5—H5B	109.6	C9—C10—Br1	112.1 (2)
C6—C5—H5B	109.6	C9—C10—H10A	109.2
H5A—C5—H5B	108.1	Br1—C10—H10A	109.2
C5—C6—C7	111.9 (2)	C9—C10—H10B	109.2
C5—C6—H6A	109.2	Br1—C10—H10B	109.2
C7—C6—H6A	109.2	H10A—C10—H10B	107.9

Symmetry code: (i) −*x*, −*y*, −*z*+1.