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1,4-Bis(1*H*-benzotriazol-1-ylmethyl)benzene tetrahydrate

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Molecules of the title compound, $C_{20}H_{16}N_6.4H_2O$, lie across crystallographic inversion centres. The dihedral angle between each benzotriazole moiety and the central benzene ring is 74.95 (9)°. In the crystal structure, the molecular organization is stabilized by well defined weak C—H$\cdots\pi$, π–π, O—H$\cdots$O and O—H$\cdots$N intermolecular interactions, leading to the formation of a two-dimensional network.

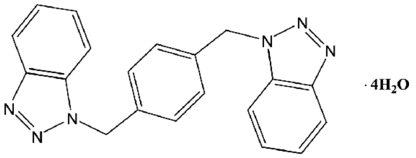
Key indicators

Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.069
wR factor = 0.228
Data-to-parameter ratio = 16.7

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

Comment

The controlled design of molecules that can be organized into specific supramolecular assemblies in the solid state is an area of increasing interest in recent years (Gardner *et al.*, 1995). Since the incorporation of well ordered structural components into a crystal structure may lead to advanced new materials with designed physico-chemical properties, such work will provide a foundation for the understanding of how molecules can be organized and how functions can be exhibited. Much effort has been devoted to the use of supramolecular contacts, such as halogen–halogen, N–halogen, S$\cdots$S, π–π and $M\cdots M$ interactions, and various types of weak hydrogen bonding (C—H$\cdots$O, C—H$\cdots$N, O—H$\cdots\pi$ and C—H$\cdots\pi$), in addition to the traditional hydrogen bonds (X—H$\cdots Y$; X, Y = F, O and N) which play important roles in the construction of ordered organic networks (Desiraju, 1995). We have been interested in utilizing benzimidazolyl-substituted bi/tripodal ligands with nitrogen/arene cores to construct supramolecules, which could provide hydrogen-bond-donor NH groups and π–π stacking interactions. Using these ligands, we were able to prepare model complexes with well defined trigonal or tetragonal prismatic shapes and a series of dinuclear rectangular macrocycles, as well as a series of one-dimensional chains/two-dimensional layers that have been partially reported in preliminary communications or articles (Cai, Chen *et al.*, 2003; Cai, Su *et al.*, 2003; Cai *et al.*, 2002; Su *et al.*, 2002, 2003). As part of the structural studies of the benzimidazolyl series, we report here the synthesis and structure of the semi-rigid arylheterocyclic bidentate ligand 1,4-bis(benztriazol-1-ylmethyl)benzene, (I).



(I)

The asymmetric unit contains of one-half of the organic molecule and two water molecules, the other half being

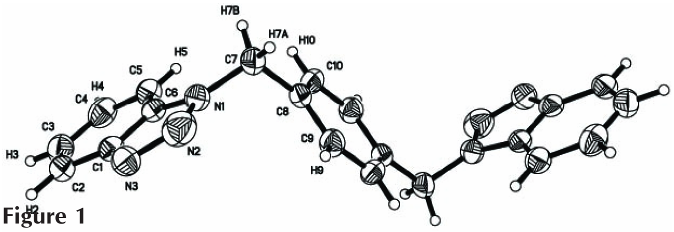


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 30% probability level. Solvent water molecules have been omitted for clarity. Unlabelled atoms are related to labelled atoms by $1 - x, -y, 1 - z$.

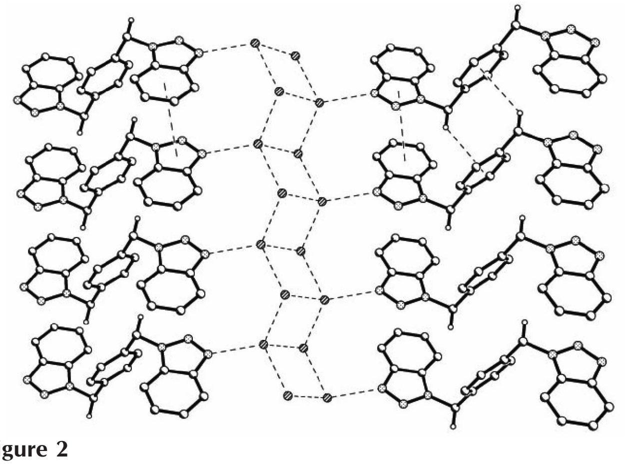


Figure 2
The two-dimensional network viewed down the *b* axis. Intermolecular interactions are shown as dashed lines.

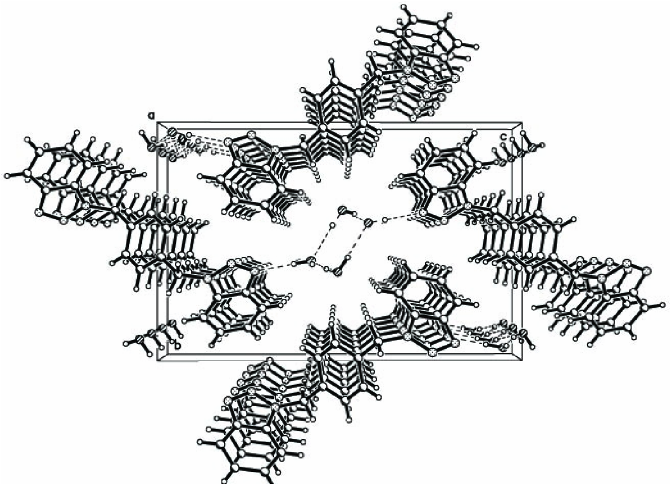


Figure 3
The packing of the molecules, viewed down the *a* axis.

inversion-related. The zigzag-like structure of (I) is shown in Fig. 1. The dihedral angle between the planes of each benzotriazole moiety and central benzene ring is 74.95 (9)°.

Each molecule is involved in two C—H$\cdots\pi$ (Table 1; *Cg*1 denotes the centroid of the central benzene ring) and two π–π interactions [$Cg2\cdots Cg3^{\rm v}$ = 3.716 (2) Å; *Cg*2 and *Cg*3 denote the centroids of the benzotriazole six- and five-membered rings, respectively; symmetry code: (v) $1 + x, y, z$], interlocking the molecules along the **a** direction to form infinite one-dimensional chains. These chains are linked through O—H$\cdots$N and O—H$\cdots$O hydrogen bonds involving the water molecules (Table 1), to form zigzag layered structures which extend along the *c* axis (Fig. 2 and Fig. 3).

Experimental

The title compound was prepared under an argon atmosphere. *n*-Butyllithium (9.0 mmol, 1.6 *M* solution in hexane) was added slowly with stirring to a solution of benzotriazole (1.064 g, 9.0 mmol) in 20 ml of THF at 273 K over a period of 30 min. A solution of 1,4-bis(bromomethyl)benzene (1.188 g, 4.5 mmol) in THF (20 ml) was then added slowly over 1 h with stirring at 273 K. After stirring for a further 3 h, H_2O (10 ml) was added dropwise to quench the reaction. The solvents were removed under reduced pressure and H_2O (30 ml) was added to the residue to precipitate the product. The resulting pale-yellow powder was recrystallized from hot anhydrous alcohol to afford a white powder. The crystal used for the data collection was obtained by slow evaporation from a saturated acetone–ethanol (1:4) solution at room temperature (yield 83%; m.p. 444–445 K)). The assigned structure was substantiated by EA and MS data. Elemental analysis calculated for $C_{20}H_{24}N_6O_4$: C 58.19, H 5.82, N 20.37%; found: C 58.11, H 5.93, N 20.41%. FAB–MS *m*/*z* (%): 413 (M^+, 1,68), 412 (M^+, 100).

Crystal data

$C_{20}H_{16}N_6 \cdot 4H_2O$
$M_r = 412.45$
Monoclinic, $P2_1/n$
$a = 4.8087$ (17) Å
$b = 12.043$ (4) Å
$c = 18.481$ (6) Å
$\beta = 91.160$ (8)°
$V = 1070.1$ (6) Å^3
$Z = 2$
$D_x = 1.280$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1599 reflections
$\theta = 4.0$–$55.2°$
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
Prism, colourless
0.28 × 0.12 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1997)
$T_{\rm min} = 0.975$, $T_{\rm max} = 0.991$
6843 measured reflections
2471 independent reflections
1044 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\rm max} = 27.6°$
$h = -6 \rightarrow 6$
$k = -15 \rightarrow 15$
$l = -12 \rightarrow 24$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.228$
$S = 0.89$
2471 reflections
148 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.1329P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.29$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.32$ e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1*W*—H1*WA*$\cdots$O2*W*$^{\rm i}$	0.85 (3)	1.98 (3)	2.833 (4)	175 (2)
O1*W*—H1*WB*$\cdots$O2*W*$^{\rm ii}$	0.86 (4)	1.91 (3)	2.743 (4)	161 (3)
O2*W*—H2*WA*$\cdots$O1*W*$^{\rm iii}$	0.85 (3)	2.02 (2)	2.791 (4)	148 (3)
O2*W*—H2*WB*$\cdots$N3	0.85 (2)	1.89 (2)	2.730 (4)	174 (4)
C7—H7*A*$\cdots$*Cg*1$^{\rm iv}$	0.97	3.01	3.790 (3)	138

Symmetry codes: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $x - \frac{1}{2}, \frac{1}{2} - y, \frac{1}{2} + z$; (iii) $x - \frac{1}{2}, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $x - 1, y, z$. *Cg*1 denotes the centroid of the central benzene ring.

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The water H atoms were located and isotropically refined, with the O—H and H···H distances restrained to 0.84 (1) and 1.37 (2) Å, respectively. All other H atoms were placed in calculated positions (C—H = 0.93–0.97 Å), and were included in the refinement in the riding-model approximation. $U_{\rm iso}$ values were set equal to $1.5U_{\rm eq}$(parent atom) for water H atoms and to $1.2U_{\rm eq}$(parent atom) for all other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SAINT* (Bruker, 1998); data reduction: *SAINT* and *SHELXTL* (Bruker, 1998); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* in *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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