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Key indicators

Single-crystal X-ray study
 T = 294 K
 Mean $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$
 R factor = 0.050
 wR factor = 0.155
 Data-to-parameter ratio = 15.9

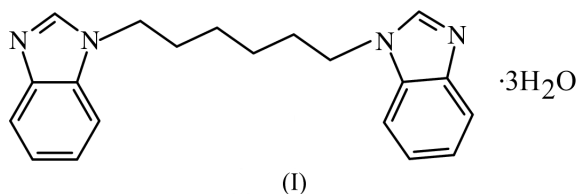
For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

1,6-Bis(1-benzimidazolyl)hexane trihydrate

In the title compound, $\text{C}_{20}\text{H}_{22}\text{N}_4 \cdot 3\text{H}_2\text{O}$, the asymmetric unit contains one half of the organic molecule, the other half being related by twofold rotational symmetry. The O atom of one of the solvent water molecules lies on a twofold axis. In the crystal, the molecular organization is stabilized by well-defined weak intermolecular interactions that lead to the formation of a three-dimensional network.

Comment

For the last three decades, selective recognition of metal cations has been one of the central research themes in host-guest chemistry, and many targets are achieved using either naturally occurring ionophores or synthetic receptors, such as crown ethers, cryptands and spherands, whose ligating heteroatoms are sp^2 -hybridized N atoms, because these atoms can be incorporated into strong and selective host systems as the planar lone pair has directionality and can occur in different positions in aromatic rings (Bell & Drew, 1991). This type of N atom has been incorporated in imines (Bell & Drew, 1991), pyridine (Wang & Wasielewski, 1997), benzimidazole (Kang & Su, 2001) *etc.*, to give good hosts for transition metals or organic guests. As part of our efforts to investigate this area, we present the crystal structure of 1,6-bis(1-benzimidazolyl)hexane trihydrate, (I).



The asymmetric unit contains one half of the organic molecule, the other half generated by twofold rotational symmetry ($3/2-x, 1/2-y, z$). The solvent water oxygen, O2W, lies on a twofold axis. The balance-like structure is shown in Fig. 1. The benzimidazole moiety is planar, with the maximum deviation being $0.016 (2) \text{ \AA}$ for atom N1. The two symmetry-related benzimidazole groups in the molecule form a dihedral angle of $22.8 (2)^\circ$. Each molecule is involved in four weak C—H $\cdots\pi$ interactions (only two are independent), interlocking the molecules along the *c* direction to form infinite one-dimensional chains [Table 1; Cg(A) and Cg(B) denote the centroids of the six- and five-membered rings, respectively]. These chains are linked through O—H \cdots N and O—H \cdots O hydrogen bonds (Table 1) involving the water molecules, to form sheet-like structures parallel to (011) (Fig. 2). The $\pi\cdots\pi$ interactions between the benzimidazole moieties (the shortest

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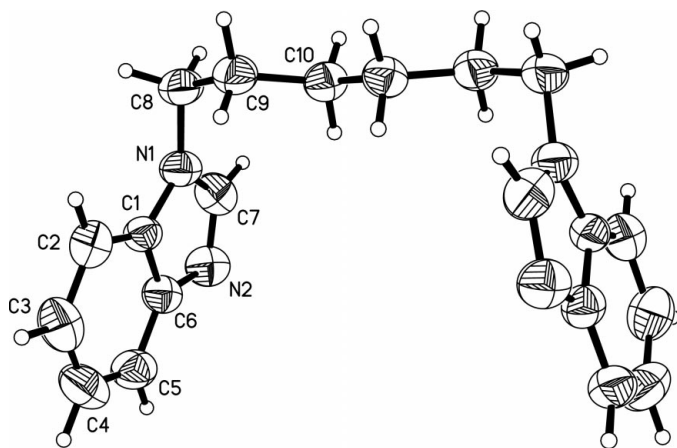


Figure 1
The structure of (I) showing 50% probability displacement ellipsoids. The atom-numbering scheme is shown only for one-half of the molecule as the other half is generated by $(3/2-x, 1/2-y, z)$. Solvent water molecules have been omitted.

distance between two benzimidazole rings is 3.589 Å) of adjacent sheets result in a three-dimensional molecular network (Fig. 3).

Experimental

The title compound was prepared under an argon atmosphere. *n*-Butyllithium (9.0 mmol, 1.2 M solution in Et₂O) was added slowly, with stirring, to a solution of benzimidazole (1.063 g, 9.0 mmol) in 20 ml of THF at 273 K over a period of 30 min. A solution of 1,6-dibromohexane (1.098 g, 4.5 mmol) in THF (20 ml) was then added slowly over 1 h with stirring, also at 273 K. After stirring for a further 3 h, 10 ml of H₂O was added dropwise to quench the reaction. The solvents were removed under reduced pressure and 30 ml of H₂O was added to the residue to precipitate the product. The resulting pale-

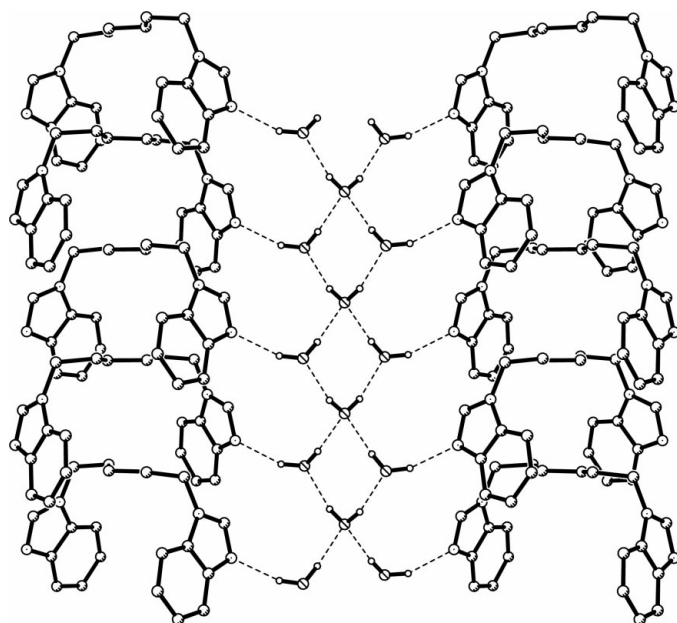


Figure 2
A view of the molecular network parallel to (011).

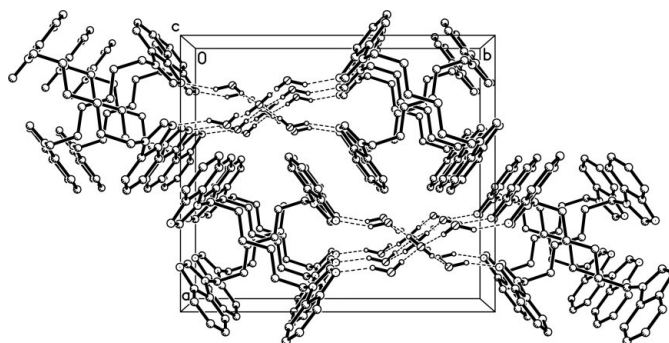


Figure 3
Packing of the molecules viewed down the *c* axis.

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–alcohol (1:4) solution at room temperature (yield: 78%; m.p. 421–423 K). Found: C 64.31, H 7.64, N 14.92%. Calculated for C₂₀H₂₈N₄O₃: C 64.52, H 7.53, N 15.05%. IR (cm⁻¹): 3306–3540 (*m*), 3122 (*m*), 2939 (*m*), 1612 (*m*), 1460 (*m*), 1282 (*m*), 1240 (*m*), 753 (*m*). FAB–Ms *m/z*(%): 318 [*M*+1-3H₂O]⁺ (100%). ¹H NMR δ(p.p.m.): 8.210 (*s*, 2H, H²), 7.648 (*d*, 2H, H²), 7.557 (*d*, 2H, H⁶), 7.216 (*m*, 4H, H^{2,3}), 4.202 (*t*, 4H, H⁸), 1.757 (*t,br*, 4H, H⁹), 1.261 (*m*, 4H, H¹⁰).

Crystal data

C₂₀H₂₈N₄·3H₂O
M_r = 372.46
Orthorhombic, *Pccn*
a = 14.4368 (19) Å
b = 16.426 (2) Å
c = 8.3834 (12) Å
V = 1988.0 (5) Å³
Z = 4
D_x = 1.244 Mg m⁻³

Mo *K*α radiation
Cell parameters from 1646 reflections
θ = 2.4–27.5°
μ = 0.09 mm⁻¹
T = 294 (2) K
Block, colourless
0.20 × 0.18 × 0.16 mm

Data collection

Bruker CCD area-detector diffractometer
φ and *ω* scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.983, *T_{max}* = 0.987
11 751 measured reflections

2120 independent reflections
721 reflections with *I* > 2σ(*I*)
R_{int} = 0.105
θ_{max} = 26.8°
h = -18 → 15
k = -20 → 20
l = -10 → 10

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.050
wR (*F*²) = 0.155
S = 0.81
2120 reflections
133 parameters

H atoms treated by a mixture of independent and constrained refinement
 $w = 1/[\sigma^2(F_o^2) + (0.0685P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
(Δ/σ)_{max} < 0.001
Δρ_{max} = 0.19 e Å⁻³
Δρ_{min} = -0.20 e Å⁻³

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

<i>D</i> –H... <i>A</i>	<i>D</i> –H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> –H... <i>A</i>
O1W–H1O1...N2 ⁱ	0.92 (3)	2.00 (4)	2.838 (3)	151 (4)
O2W–H1O2...O1W ⁱⁱ	0.91 (5)	1.97 (4)	2.844 (4)	161 (4)
O1W–H2O1...O2W	0.91 (5)	1.92 (5)	2.822 (4)	170 (4)
C9–H9A...Cg(<i>A</i> ⁱⁱⁱ)	0.97	3.26	3.754 (3)	114
C10–H10B...Cg(<i>B</i> ^{iv})	0.97	2.86	3.729 (3)	150

Symmetry codes: (i) $x - \frac{1}{2}, \frac{1}{2} + y, 1 - z$; (ii) $\frac{1}{2} - x, y, \frac{1}{2} + z$; (iii) $x, \frac{1}{2} - y, z - \frac{1}{2}$; (iv) $\frac{1}{2} - x, y, z - \frac{1}{2}$.

All C-bound H atoms were geometrically positioned and allowed to ride on their parent atoms and refined isotropically. The H atoms of the two water molecules were located from a difference map and refined isotropically with their O—H distances restrained to be equal. The high R_{int} value (0.11) and low ratio of observed to unique reflections (34%) may be due to the poor diffraction quality of the crystal.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SHELXTL* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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