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Assembly of a two-dimensional layer structure with 1,4-bis(1*H*-benzimidazol-1-ylmethyl)benzene dihydrate *via* hydrogen bonds and π–π interactions

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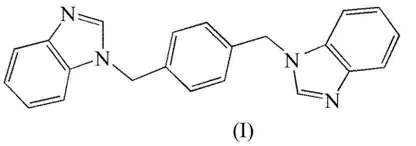
In the title compound, $C_{22}H_{18}N_4\cdot 2H_2O$, the organic fragment lies across a centre of inversion in the $P2_1/n$ space group. The water molecules form $C(2)$-type hydrogen-bonded chains which are linked to the 1,4-bis(1*H*-benzimidazol-1-ylmethyl)benzene molecules through O—H···N hydrogen bonds, forming sheets reinforced by π–π stacking interactions between the aromatic rings within the layers.

Comment

Benzimidazole-based organic ligands have been widely used in supramolecular coordination chemistry to generate various discrete and one- to three-dimensional coordination architectures (Wahon *et al.*, 1994; Berends & Stephan, 1984; Su *et al.*, 2002, 2003; Zhang, Guo, Yang, Lu *et al.*, 2007; Zheng *et al.*, 2007; Chen *et al.*, 2007). Bis-benzimidazole ligands, with two benzimidazole groups connected by an organic spacer at the 1-positions, can take either *trans* or *cis* conformations (Liu *et al.*, 2007; Lü, Pan *et al.*, 2006). Besides acting as coordination donors, the imino N atoms of the two benzimidazole groups can also act as hydrogen-bond acceptors (Zheng *et al.*, 2005). We describe here the title dihydrated compound, (I), which forms a hydrogen-bonded layer structure in the crystal structure, displaying π–π interactions between the aromatic groups.


$\cdot 2H_2O$

(I)

The organic component (Fig. 1) lies across an inversion centre, so that the asymmetric unit consists of one-half of an organic component and one water molecule. The organic molecule adopts a *trans* conformation, with the two benzimidazole arms arranged up and down on the two sides of the central benzene ring, showing a dihedral angle of 75.5° with each other (Fig. 1). The imino N atoms of the two benzimidazole arms form O—H···N hydrogen bonds with the water molecules (Table 1; Li *et al.*, 2007). Furthermore, the three aromatic rings are stacked in a parallel fashion, displaying π–π interactions (Chen *et al.*, 2003; Zhang, Guo, Yang, Wang *et al.*, 2007). Therefore, the crystal packing of the organic molecules is directed by these intermolecular interactions (Su *et al.*, 1998, 2001; Chen *et al.*, 2005, 2006).

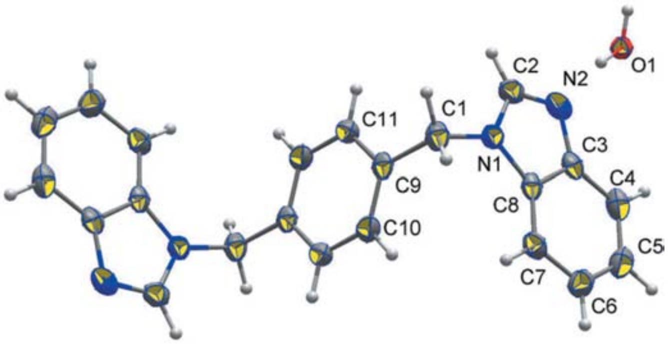


Figure 1
The molecular structure and crystallographic numbering scheme for (I). Displacement ellipsoids are shown at the 30% probability level. Unlabelled atoms are related to labelled atoms by the symmetry code $(-x, -y + 1, -z + 1)$.

One H atom of the water component is disordered over two sites due to the presence of inversion centres relating pairs of adjacent water molecules. The water molecules are linked through O—H···O hydrogen bonds (Table 1). Each water molecule is involved in three hydrogen bonds, one of which links the molecular components *via* an O—H···N hydrogen bond, while the other two, involving the disordered H atom, link pairs of water molecules. The water molecules alone are hydrogen bonded into zigzag chains along [100]. Since each pair of water molecules forms the unit-cell repeat unit of the chain, this one-dimensional water chain can be described as a $C(2)$ chain (Infantes & Motherwell, 2002). The zigzag arrangement of the water chain is directed by the intrinsic angles of the hydrogen bonds around the water molecule. The organic molecules are connected through the O—H···N hydrogen bonds to water chains on both sides to generate two-dimensional layers parallel to (010).

The 1,4-bis(1*H*-benzimidazol-1-ylmethyl)benzene molecule is composed of three aromatic rings and adopts a *trans* conformation. The whole molecule is nonplanar. The organic molecules overlap each other in the *a* direction and π–π interactions are formed between adjacent aromatic rings (Fig. 2). The centroid-to-centroid distance between the benzimidazole benzene ring and the imidazole ring of an adjacent benzimidazole ring system at $(-1 + x, y, z)$ is 3.9796 (9) Å, with an interplanar angle of 0.4 (2)°, and this interaction reinforces the hydrogen-bonded sheet.

In the *ac* plane, the water chains and organic arrays are aligned alternately *via* O—H···N hydrogen bonds to give a two-dimensional layer (Fig. 2). The layers display a woven feature due to the *trans* conformation of the organic mol-

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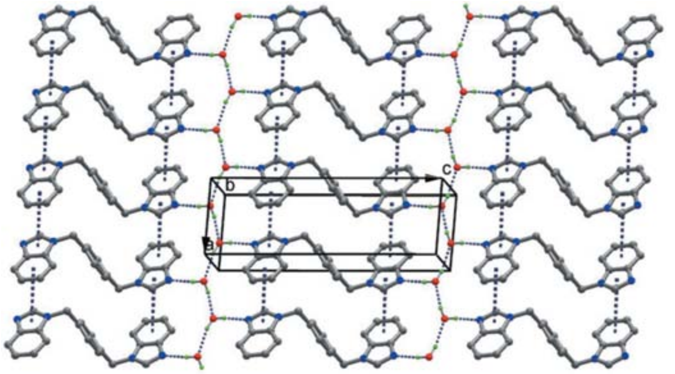

Figure 2
A view of the two-dimensional layers, showing hydrogen bonds and π–π stacking interactions as dashed lines.

ecules. Therefore, the overall crystal packing is sustained by offset stacking of the two-dimensional layers in the *b* direction.

The title compound crystallizes in a slightly different manner to the previously reported compound 1,4-bis(1*H*-benzotriazol-1-ylmethyl)benzene (Cai *et al.*, 2004). These two compounds have rather similar molecular structures but with a modest difference between their five-membered N-heterocyclic rings. In addition, the title compound is a dihydrate, while the previously reported structure is a tetrahydrate. 1,4-Bis(1*H*-benzotriazol-1-ylmethyl)benzene has two free N atoms to act as potential hydrogen-bond donors, although only one N atom is involved in hydrogen bonding, quite similar to the present compound. Nevertheless, 1,4-bis(1*H*-benzotriazol-1-ylmethyl)benzene crystallizes as a tetrahydrate adduct with the water molecules forming a one-dimensional O—H···O hydrogen-bonded tape, while in (I) the dihydrate crystallizes with the water molecules forming a *C*(2)-type hydrogen-bonded chain. In both cases, the organic molecules are connected by the water chain or tape in essentially the same way through O—H···N hydrogen bonds to generate similar two-dimensional layers. These results indicate that similar organic molecules can display similar intermolecular interactions, which play important roles in directing molecular arrangement and crystal packing.

In summary, cocrystallization of the nonplanar linear organic molecule 1,4-bis(1*H*-benzimidazol-1-ylmethyl)benzene and water affords a layered structure which is consolidated by co-operative O—H···O and O—H···N hydrogen bonds and π–π interactions. This is an example of the synergistic effect of different supramolecular interactions in directing the crystal packing, which is of significance to crystal engineering (Su *et al.*, 1998, 2001; Lü, Qiao *et al.*, 2006).

Experimental

The title compound was prepared according the literature method of Su *et al.* (2003). Single crystals were grown from an ethanol solution over a period of several days at room temperature.

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1*C*···O1^{i}	0.86	2.04	2.892 (3)	171
O1—H1*D*···O1^{ii}	0.84	2.13	2.955 (4)	165
O1—H1*E*···N2	0.87	2.01	2.8778 (17)	172

Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x, -y+1, -z+2$.

Crystal data

$C_{22}H_{18}N_4\cdot 2H_2O$
$M_r = 374.44$
Monoclinic, $P2_1/n$
$a = 5.4040$ (2) Å
$b = 10.7114$ (4) Å
$c = 16.5003$ (5) Å
$\beta = 94.079$ (3)°
$V = 952.69$ (6) Å^3
$Z = 2$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 150$ (2) K
0.25 × 0.20 × 0.18 mm

Data collection

Bruker SMART 1K CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.964$, $T_{\max} = 0.985$
7740 measured reflections
2275 independent reflections
1412 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.027$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.120$
$S = 1.03$
2275 reflections
127 parameters
6 restraints
Only H-atom coordinates refined
$\Delta\rho_{\max} = 0.53$ e Å^{-3}
$\Delta\rho_{\min} = -0.31$ e Å^{-3}

Water H atoms were located in the difference map and refined isotropically, with O—H distances restrained to about 0.86 (1) Å. Because the crystallographically imposed inversion centre is located in the middle of two adjacent water molecules, the H atom which forms the O—H···O hydrogen bond is required by symmetry to be distributed over two positions with half occupancy. All other H atoms were placed in calculated positions and included in the refinement in the riding-model approximation, with C—H distances in the range 0.95–0.99 Å, and with $U_{\rm iso}({\rm H}) = 1.5U_{\rm eq}({\rm O})$ for water H atoms or $1.2U_{\rm eq}({\rm C})$ for all other H atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD3187). Services for accessing these data are described at the back of the journal.

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