

Supramolecular interactions in the
2,6-bis(benzimidazol-2-yl)pyridine–
terephthalic acid–water (2/1/4)
cocrystalHailian Xiao,^a Guixue Wang^a and Fangfang Jian^{b*}^aCollege of Materials Science and Engineering, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China, and ^bNew Materials and Function Coordination Chemistry Laboratory, Qingdao University of Science and Technology, Qingdao 266042, People's Republic of China
Correspondence e-mail: xiaohailian@163.com

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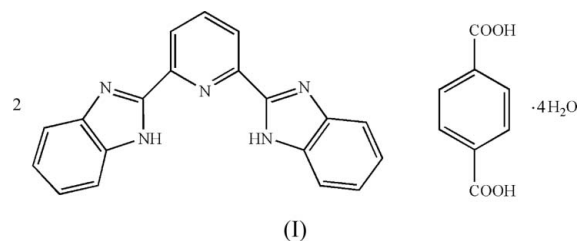
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In the title compound, $2C_{19}H_{13}N_5 \cdot C_8H_6O_4 \cdot 4H_2O$, the terephthalic acid molecule lies on a crystallographic inversion centre and the H atoms of one water molecule exhibit disorder. The maximum deviation of any atom from the mean plane through the C and N atoms of the 2,6-bis(benzimidazol-2-yl)pyridine molecule is only 0.161 (4) Å. In the crystal structure, the water molecules play an important role in linking the other molecules *via* hydrogen bonding. The structure forms a three-dimensional framework *via* strong intermolecular hydrogen bonding. In addition, there are π – π stacking interactions between the imidazole, pyridine and benzene rings.

Comment

Supramolecular interactions such as hydrogen bonding, C–H $\cdots\pi$ interactions, π – π stacking and metal–ligand coordination have all been utilized in recent years to manipulate the way in which molecules are arranged in crystal structures (Desiraju, 2005; Burrows, 2004; Stephenson & Hardie, 2007). In contrast with cases where potentially active metal centres are utilized for creating supramolecular materials, the prediction of the solid-state packing of simple organic cocrystals still remains an ongoing challenge (Dunitz, 2003; Dale *et al.*, 2004). Organic molecules bearing hydrogen-bond donor and/or acceptor groups capable of participating in supramolecular synthons (Desiraju, 1995) have probably received the most interest, many using a combination of both strong and weak hydrogen-bond interactions (Steiner, 2002). Complexes of 2,6-bis(benzimidazol-2-yl)pyridine and its derivatives have been studied for more than 30 years because of their unusual coordination and magnetic properties (Boča *et al.*, 2000). However, the structures of supramolecular complexes consisting of this ligand and other organic mol-

ecules have been reported only occasionally. Chetia & Iyer (2006) demonstrated that 2,6-bis(benzimidazol-2-yl)pyridine is an efficient receptor for binding urea with high affinity, and it forms hydrogen-bonded complexes with various metabolites of benzene, even in a competitive solvent environment, which is proof of its potential application in chemical and biological sensing (Chetia & Iyer, 2007). In order to research the supramolecular chemistry of this compound, we synthesized the 2,6-bis(benzimidazol-2-yl)pyridine–terephthalic acid–water (2/1/4) cocrystal, (I), and report its crystal structure here. This work forms part of a wider study of the supramolecular structures and properties of this compound being undertaken by our research group.



The asymmetric unit of (I) consists of one 2,6-bis(benzimidazol-2-yl)pyridine molecule, half a terephthalic acid molecule on a centre of symmetry (symmetry code: $-x + 1, -y + 1, -z + 1$) and to water molecules (Fig. 1). The aromatic C–C and C–N distances in both the benzimidazole and pyridine rings are within the usual ranges, and this confirms the aromatic character of the pyridine and benzimidazole moieties. The C and N atoms of the 2,6-bis(benzimidazol-2-yl)pyridine molecule lie in a plane with an r.m.s. deviation of 0.079 (4) Å, with the largest individual deviation being 0.161 (4) Å for atom C4. This planarity of the 2,6-bis(benzimidazol-2-yl)pyridine moiety is similar to other compounds containing 2,6-bis(benzimidazol-2-yl)pyridine and organic

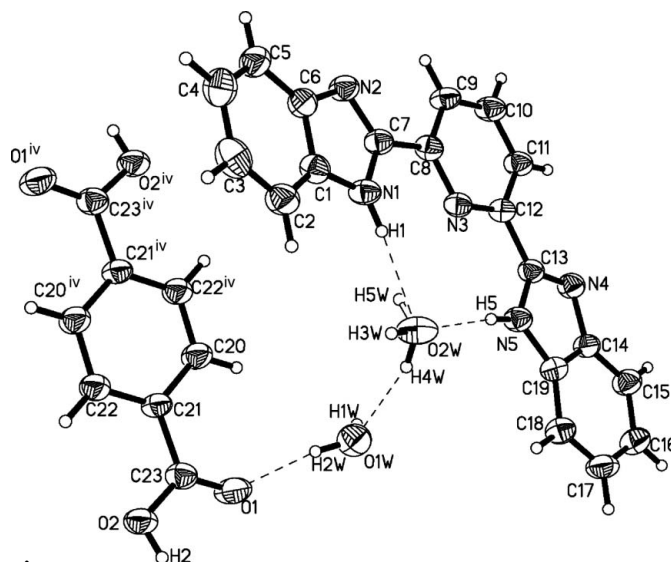


Figure 1
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms are shown as small spheres of arbitrary radii. Dashed lines indicate hydrogen bonds. [Symmetry code: (iv) $1 - x, 1 - y, 1 - z$.]

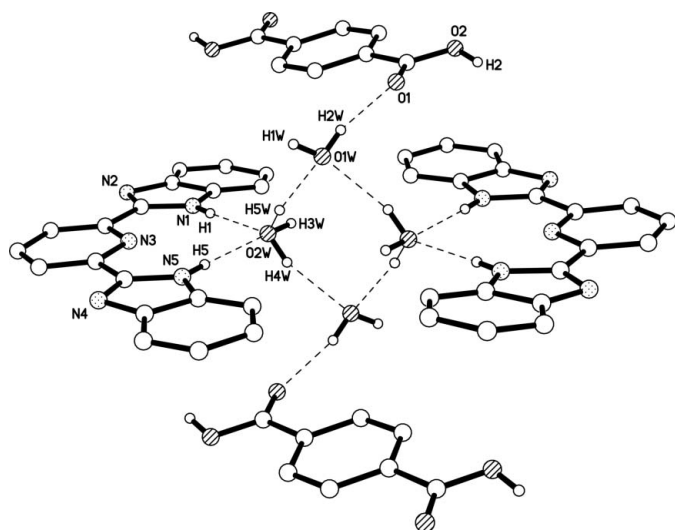


Figure 2

Hydrogen-bond interactions in (I) (dashed lines). The thin bond is to atom H5W, the minor disorder component. Terephthalic acid molecules lie on centres of symmetry at $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ for the molecule involving atom O1 and at $(\frac{1}{2}, \frac{1}{2}, -\frac{1}{2})$ for the unlabelled molecule at the bottom.

molecules, for example, 2-[6-(1*H*-benzimidazol-2-yl)-2-pyridyl]-1*H*-benzimidazol-3-ium perchlorate monohydrate (Boča *et al.*, 2000), 2,6-bis(benzimidazol-2-yl)pyridine urea (Chetia & Iyer, 2006) and 2,6-bis(benzimidazol-2-yl)pyridine hydroquinone (Chetia & Iyer, 2007). In contrast, the corresponding moiety in 2-(1-methyl-3-benzimidazolinium-2-yl)-6(1-methylbenzimidazol-2-yl)pyridine perchlorate is quite bent, with the planes of the benzimidazole forming dihedral angles of 30.5 (2) and 45.3 (1)° with the pyridine ring (Petoud *et al.*, 1997). The dihedral angles formed by the benzimidazoles and the pyridine ring are 7.61 (1) and 3.64 (2)° in (I).

The intermolecular interactions in (I) are listed in Table 2 and shown in Fig. 2. Each 2,6-bis(benzimidazol-2-yl)pyridine molecule is hydrogen bonded to a water molecule *via* a pair of N–H...O hydrogen bonds (involving atoms N1, N5 and O2W) in an $R_2^1(10)$ motif (Bernstein *et al.*, 1995). Two 2,6-bis(benzimidazol-2-yl)pyridine molecules are linked face-to-face by four water molecules in an $R_2^2(8)$ diamond motif *via* the two interactions mentioned above, plus pairs of O2W–H4W...O1Wⁱⁱⁱ and O2W–H5W...O1W hydrogen bonds [symmetry code: (iii) $-x + 1, -y + 1, -z$]. It should be noted that the H atoms in this diamond are subject to some disorder (see *Refinement*). The 2,6-bis(benzimidazol-2-yl)pyridine molecules are also linked back-to-back by one terephthalic acid molecule *via* strong intermolecular O2–H2...N2ⁱ and C9–H9...O1^{iv} hydrogen bonds [symmetry code: (iv) $x - 1, y, z$] in an $R_2^2(9)$ motif, closely related to the carboxylic acid–pyridine motif Y described by Dale *et al.* (2004), but here using the closest available CH group rather than the CH adjacent to the pyridyl N atom. The diamonds of water molecules not only link to the 2,6-bis(benzimidazol-2-yl)pyridine molecules, but also to the terephthalic acid molecules *via* O1W–H2W...O1 hydrogen bonds. The remaining strong hydrogen-bond donors and acceptors also act as bridges between the planes *via* an O1W–H1W...N4ⁱⁱ hydrogen bond [symmetry code: (ii) $-x,$

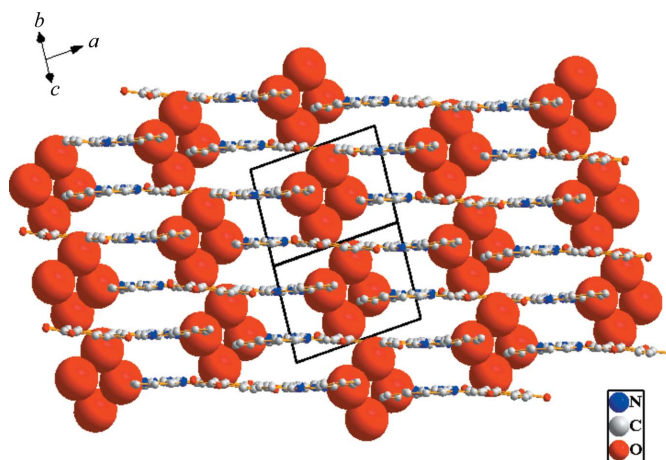


Figure 3

A view of the three-dimensional network in the structure of (I), showing the layer structure.

$-y + 1, -z$]. The overall packing has the 2,6-bis(benzimidazol-2-yl)pyridine, the terephthalic acid and the O2W water molecules in a layer, with these layers linked *via* the diamonds of water molecules to give a three-dimensional hydrogen-bonded supramolecular network (Figs. 2 and 3).

In addition, there are some fairly long π – π stacking interactions between the layers at separations in the range 3.6–3.8 Å. These are between overlapping rings in the 2,6-bis(benzimidazol-2-yl)pyridine molecules, suggesting that it is the hydrogen bonds, *via* the diamonds of water molecules, which predominantly dictate the interlayer separations. The centroid–centroid distances are $Cg1 \cdots Cg2 = 3.816$ (2) Å, $Cg3 \cdots Cg3 = 3.602$ (2) Å and $Cg2 \cdots Cg4 = 3.736$ (2) Å, where Cg1, Cg2, Cg3 and Cg4 are the centroids of imidazole ring N1/C1/C6/N2/C7, pyridine ring N3/C8–C12, imidazole ring N4/C13/N5/C19/C14 and benzene ring C14–C19, respectively.

Experimental

Single crystals of the title compound suitable for X-ray analysis were obtained from a mixture of solutions of 2,6-bis(benzimidazol-2-yl)pyridine (0.031 g, 0.10 mmol) in ethanol (10 ml) and terephthalic acid (0.017 g, 0.10 mmol) in ethanol (20 ml) and water (2 ml) after one week at room temperature.

Crystal data

$2C_{19}H_{13}N_5 \cdot C_8H_6O_4 \cdot 4H_2O$	$\gamma = 74.88$ (3)°
$M_r = 860.88$	$V = 1040.1$ (3) Å ³
Triclinic, $P\bar{1}$	$Z = 1$
$a = 9.5040$ (19) Å	Mo $K\alpha$ radiation
$b = 9.888$ (2) Å	$\mu = 0.10$ mm ⁻¹
$c = 11.713$ (2) Å	$T = 295$ K
$\alpha = 80.19$ (3)°	$0.25 \times 0.22 \times 0.18$ mm
$\beta = 81.13$ (3)°	

Data collection

Enraf–Nonius CAD-4 diffractometer	3660 independent reflections
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	1926 reflections with $I > 2\sigma(I)$
$T_{min} = 0.976, T_{max} = 0.983$	3 standard reflections every 100 reflections
3660 measured reflections	intensity decay: none

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O2W	0.86	2.14	2.985 (4)	169
N5—H5 \cdots O2W	0.86	2.27	3.125 (4)	174
O2—H2 \cdots N2 ⁱ	0.82	1.88	2.655 (3)	157
O1W—H1W \cdots N4 ⁱⁱ	0.82 (2)	1.98 (2)	2.787 (3)	167 (4)
O1W—H2W \cdots O1	0.84 (2)	1.94 (2)	2.766 (3)	167 (4)
O2W—H5W \cdots O1W	0.87 (2)	1.99 (3)	2.849 (5)	168 (6)
O2W—H4W \cdots O1W ⁱⁱⁱ	0.88 (2)	2.03 (3)	2.850 (4)	155 (5)
C9—H9 \cdots O1 ^{iv}	0.93	2.23	3.173 (2)	169

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

Refinement

$$R[F^2 > 2\sigma(F^2)] = 0.053$$

$$wR(F^2) = 0.171$$

$$S = 1.05$$

3660 reflections

305 parameters

9 restraints

H atoms treated by a mixture of independent and constrained refinement

$$\Delta\rho_{\max} = 0.29 \text{ e } \text{Å}^{-3}$$

$$\Delta\rho_{\min} = -0.23 \text{ e } \text{Å}^{-3}$$

The positions of all H atoms bonded to N or O atoms were initially found in a difference Fourier map. The H atoms on water molecule O2W were refined, with atom H3W fully occupied and the other (H4W/H5W) disordered over two positions, with a major component of 0.55 (6). Geometric restraints were applied to both water molecules, with O—H and H \cdots H distances restrained to 0.83 (2) and 1.35 (2) Å, respectively. All other H atoms were fixed geometrically and treated as riding on the parent C, O or N atom, with C—H = 0.93 Å, O—H = 0.82 Å and N—H = 0.86 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$ or $1.5U_{\text{eq}}(\text{O})$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *NRCVAX* (Gabe *et al.*,

1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *SHELXL97*; software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: EM3031). Services for accessing these data are described at the back of the journal.

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