

Benzene-1,4-diboronic acid–  
4,4'-bipyridine–water (1/2/2)Araceli Vega, Maria Zarate, Hugo Tlahuext and Herbert  
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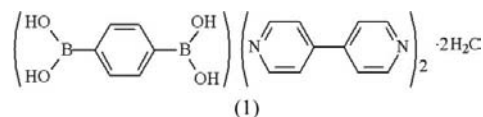
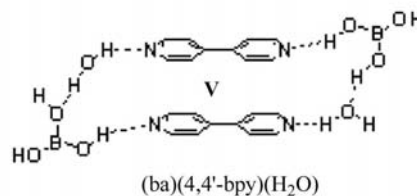
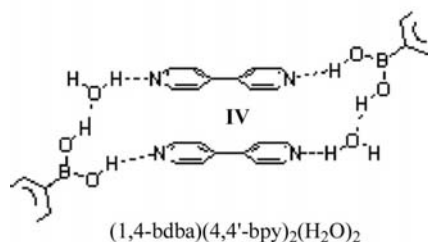
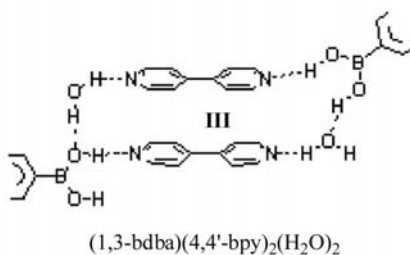
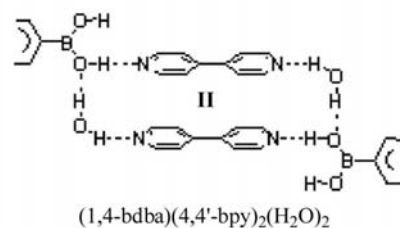
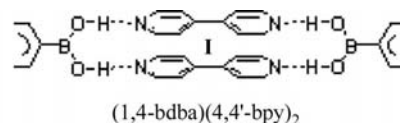
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In the presence of water, benzene-1,4-diboronic acid (1,4-bdba) and 4,4'-bipyridine (4,4'-bpy) form a cocrystal of composition  $(1,4\text{-bdba})(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2$ , in which the molecular components are organized in two, so far unknown, cyclophane-type hydrogen-bonding patterns. The asymmetric unit of the title compound,  $\text{C}_6\text{H}_8\text{B}_2\text{O}_4 \cdot 2\text{C}_{10}\text{H}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$ , contains two 4,4'-bpy, two water molecules and two halves of 1,4-bdba molecules arranged around crystallographic inversion centers. The occurrence of  $\text{O}-\text{H} \cdots \text{O}$  and  $\text{O}-\text{H} \cdots \text{N}$  hydrogen bonds involving the water molecules and all O atoms of boronic acid gives rise to a two-dimensional hydrogen-bonded layer structure that develops parallel to the  $(01\bar{4})$  plane. This supramolecular organization is reinforced by  $\pi-\pi$  interactions between symmetry-related 4,4'-bpy molecules.

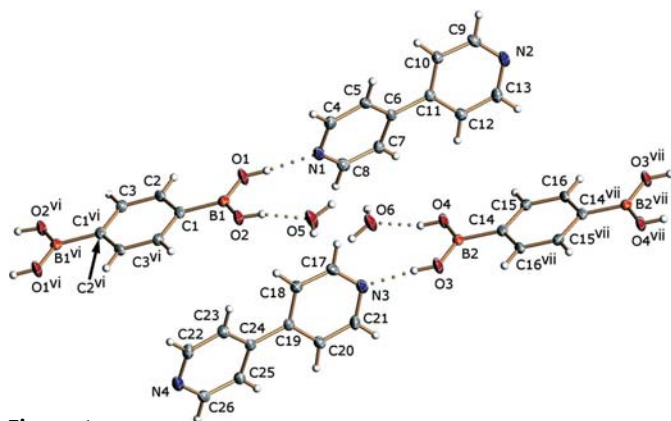
## Comment

Boronic acids form dimeric synthons of composition  $\text{PhB}(\text{OH})_2 \cdots (\text{HO})_2\text{BPh}$ , which are structurally related to the well known carboxylic acid and carboxamide homodimeric motifs (Rodríguez-Cuamatzi, Vargas-Díaz & Höpfel, 2004; Rodríguez-Cuamatzi, Vargas-Díaz, Maris *et al.*, 2004). Since the  $-\text{B}(\text{OH})_2$  function can also be integrated into neutral and charged heterodimeric motifs, boronic acids have become interesting building blocks for crystal engineering (Filthaus *et al.*, 2008; Fournier *et al.*, 2003; Kara *et al.*, 2006; Maly *et al.*, 2006; Rodríguez-Cuamatzi *et al.*, 2005; Rogowska *et al.*, 2006; SeethaLekshmi *et al.*, 2006, 2007; Shimpi *et al.*, 2007). In contrast to carboxylic acids, pyridine adducts of boronic acids show a larger structural variety of hydrogen-bonding motifs, which have been studied systematically during the last few years by different research groups (Aakeröy *et al.*, 2004, 2005; Braga *et al.*, 2003). It has been shown that the cocrystallization of boric and boronic acids with 4,4'-bipyridine (4,4'-bpy) gives one- or two-dimensional hydrogen-bonded supramolecular structures, in which water molecules are frequently incorporated to allow for an optimization of  $\pi-\pi$  interactions between

the 4,4'-bpy molecules (Pedireddi *et al.*, 2004; Rodríguez-Cuamatzi *et al.*, 2009). When combining benzene-1,4-diboronic acid (1,4-bdba) with 4,4'-bpy in benzene, cocrystals of the composition  $(1,4\text{-bdba})(4,4'\text{-bpy})_2$  have been obtained (Rodríguez-Cuamatzi *et al.*, 2009), in which the  $-\text{B}(\text{OH})_2$  groups are hydrogen bonded to the two pyridyl fragments of the 4,4'-bpy molecules to give one-dimensional chains containing hydrogen-bonded cyclophane-type macrocycles (motif I in the Scheme).



We report herein the single-crystal X-ray diffraction analysis of  $(1,4\text{-bdba})(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2$ , (1), obtained by a self-assembly reaction of 1,4-bdba and 4,4'-bpy in a 1:2 stoichiometric ratio in methanol containing small quantities of water. The unit cell of (1) contains four 4,4'-bpy and four

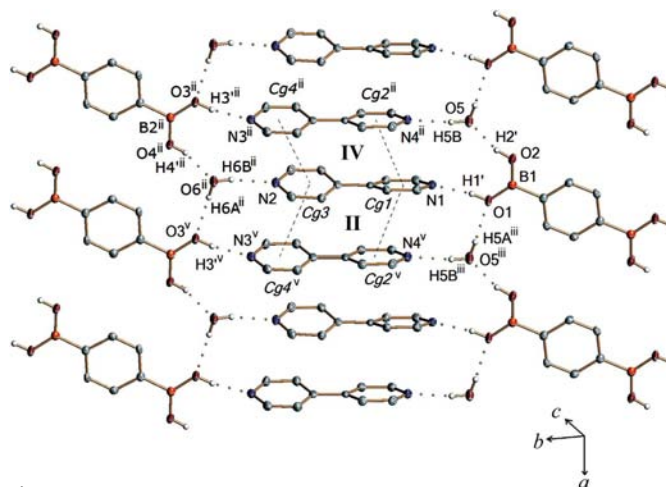


**Figure 1**

The independent moieties in the crystal structure of (1,4-bdba)(bpy)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>, showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (vi)  $-x + 2, -y, -z$ ; (vii)  $-x + 1, -y + 2, -z + 1$ .]

water molecules, of which two are independent in each case. Further, there are two independent 1,4-bdba molecules, which are both located at crystallographic inversion centers (Fig. 1). In the crystal structure, each  $-B(OH)_2$  group is involved in one  $(B)O-H \cdots N$  and one  $(B)O-H \cdots O_{\text{water}}$  hydrogen-bonding interaction, thus showing an asymmetric hydrogen-bonding behavior. Similarly, each 4,4'-bpy molecule participates in two different types of  $O-H \cdots N$  interactions, of which the first is formed with a BOH group and the second with a water molecule, which is further connected to a  $-B(OH)_2$  moiety.

In the hydrogen-bonding pattern (Table 1), a cyclophane-type macrocycle with the graph set  $R_6^6(30)$  (Bernstein *et al.*, 1995) can be distinguished, involving two 4,4'-bpy molecules, two  $-B(OH)_2$  groups and two water molecules (motif IV in the Scheme) (Fig. 2). Although structurally related, this arrangement is different from motifs I, III and V, which have been observed previously for boric and boronic acid adducts with 4,4'-bpy (see Scheme) (Pedireddi *et al.*, 2004; Rodríguez-Cuamatzi *et al.*, 2009). In motif III, one  $-B(OH)_2$  group interacts only with one of its two OH groups in the hydrogen-bonding pattern. In motif V, each  $-B(OH)_2$  group participates also with both hydroxy functions; however, at the same time the configuration of the  $-B(OH)_2$  group changes, one has a *syn-anti* and the other a *syn-syn* orientation. In the present case (Fig. 2) (motif IV), both  $-B(OH)_2$  functions have *syn-syn* orientation, with the consequence that both water molecules act as simultaneous hydrogen-bonding donors and acceptors within the macrocycle. In the crystal structure, these cyclophane-type macrocycles are connected further through additional  $O_{\text{water}}-H \cdots O(H)B$  interactions to give a two-dimensional hydrogen-bonded layer structure (Fig. 2). Interestingly, this association generates an additional novel hydrogen-bonded macrocyclic motif that can be described by the graph set  $R_6^6(26)$ , in which two 4,4'-bpy and two water molecules, but only two BOH hydroxy groups are involved (Fig. 2, motif II). This motif is therefore an additional member of a series of cyclophane-type hydrogen-bonding motifs, I–V (see Scheme), containing a varying number of BOH hydroxy



**Figure 2**

Fragment of the two-dimensional hydrogen-bonded layer found in the crystal structure of (1), showing the cyclophane-type hydrogen-bonding motifs (II and IV). Dashed lines indicate  $\pi$ – $\pi$  interactions between the 4,4'-bpy molecules along the *a* axis. Displacement ellipsoids are drawn at the 30% probability level and H atoms not involved in hydrogen bonding have been omitted for clarity. [Symmetry codes: (ii)  $x, 1 + y, z$ ; (iii)  $1 + x, y, z$ ; (v)  $1 + x, 1 + y, z$ .]

groups ( $n = 2, 3$  and  $4$ ) and water molecules ( $n = 0$  and  $2$ ) found in various structures. Analogous patterns containing only one water molecule have not been described so far. As described previously (Rodríguez-Cuamatzi *et al.*, 2009), it is probable that the differences in the supramolecular structure of motifs I–V result from the optimization of  $\pi$ – $\pi$  interactions between the 4,4'-bpy molecules within the crystal structure. Indeed, in the two-dimensional layers of the title compound the 4,4'-bpy molecules are stacked along the *a* axis (Fig. 2). Thereby, the pyridine rings of opposite 4,4'-bpy molecules have slightly displaced parallel-sandwich geometries and are almost coplanar with each other, having perpendicular distances varying from 3.26 to 3.40 Å, centroid–centroid distances in the range 3.59–3.65 Å, N $\cdots$ N distances in the range 3.59–3.67 Å and interplanar angles of 2.7 and 4.4 Å (Table 2). Within the 4,4'-bpy molecules, the pyridine rings are twisted about the central C–C bonds, as can be seen from the C5–C6–C11–C10 [ $-21.4(2)^\circ$ ] and C23–C24–C19–C18 [ $-14.3(2)^\circ$ ] torsion angles.

## Experimental

A solution of benzene-1,4-diboronic acid (0.250 g, 1.50 mmol) and 4,4'-bipyridine (0.470 g, 3.01 mmol) in methanol (20 ml) was refluxed for 1 h. A precipitate formed upon cooling that was recrystallized from a mixture of methanol and water (25 ml, 10:1 v/v) to give crystals suitable for X-ray diffraction analysis (m.p. >573 K).

### Crystal data

C<sub>6</sub>H<sub>8</sub>B<sub>2</sub>O<sub>4</sub>·2C<sub>10</sub>H<sub>8</sub>N<sub>2</sub>·2H<sub>2</sub>O  
 $M_r = 514.14$   
 Triclinic,  $P\bar{1}$   
 $a = 6.8262(9)$  Å  
 $b = 10.1914(13)$  Å  
 $c = 18.834(2)$  Å  
 $\alpha = 98.825(2)^\circ$   
 $\beta = 90.804(2)^\circ$

$\gamma = 98.000(2)^\circ$   
 $V = 1281.3(3)$  Å<sup>3</sup>  
 $Z = 2$   
 Mo  $K\alpha$  radiation  
 $\mu = 0.09$  mm<sup>-1</sup>  
 $T = 100$  K  
 $0.44 \times 0.41 \times 0.34$  mm

## Data collection

Bruker SMART APEX CCD area-detector diffractometer	12443 measured reflections
Absorption correction: multi-scan (SADABS; Sheldrick, 1996)	4495 independent reflections
$T_{\min} = 0.960$ , $T_{\max} = 0.969$	3542 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.029$

## Refinement

$R[F^2 > 2\sigma(F^2)] = 0.048$	343 parameters
$wR(F^2) = 0.129$	H-atom parameters constrained
$S = 1.04$	$\Delta\rho_{\text{max}} = 0.29 \text{ e } \text{\AA}^{-3}$
4495 reflections	$\Delta\rho_{\text{min}} = -0.23 \text{ e } \text{\AA}^{-3}$

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O1—H1' $\cdots$ N1	0.84	1.86	2.6846 (18)	168
O2—H2' $\cdots$ O5	0.84	1.89	2.7058 (17)	164
O3—H3' $\cdots$ N3	0.84	1.85	2.6753 (18)	169
O4—H4' $\cdots$ O6	0.84	1.93	2.7398 (16)	163
O5—H5A $\cdots$ O1 <sup>i</sup>	0.84	2.12	2.9574 (18)	176
O5—H5B $\cdots$ N4 <sup>ii</sup>	0.84	2.01	2.8371 (19)	170
O6—H6A $\cdots$ O3 <sup>iii</sup>	0.84	2.12	2.9533 (17)	174
O6—H6B $\cdots$ N2 <sup>iv</sup>	0.84	2.04	2.8591 (19)	164

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

Table 2

Parameters of the  $\pi$ - $\pi$  stacking interactions in (1).

Cg1, Cg2, Cg3 and Cg4 are the centroids of rings N1/C4–C8, N4/C22–C26, N2/C9–C13 and N3/C17–C21, respectively.

	$Cg1\cdots Cg2$ ( $\text{\AA}$ )	Dihedral angle ( $^\circ$ )	$Cg1$ to plane ( $\text{\AA}$ )	$Cg2$ to plane ( $\text{\AA}$ )
$Cg1\cdots Cg2^{ii}$	3.6479 (11)	4.43 (8)	3.3379 (7)	−3.2566 (7)
$Cg1\cdots Cg2^v$	3.5880 (11)	4.43 (8)	−3.4065 (7)	3.3863 (7)
$Cg3\cdots Cg4^{ii}$	3.6103 (11)	2.69 (8)	3.3948 (7)	−3.3756 (8)
$Cg3\cdots Cg4^v$	3.6392 (11)	2.69 (8)	−3.3976 (7)	3.3776 (8)

Symmetry codes: (ii)  $x, y + 1, z$ ; (v)  $x + 1, y + 1, z$ .

H atoms bonded to C atoms were positioned geometrically and constrained using the riding-model approximation [aryl C—H = 0.93  $\text{\AA}$  and  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ ]. H atoms bonded to O (H1', H2', H3', H4', H5A, H5B, H6A and H6B) were initially located in difference Fourier maps, then their positions were refined with an O—H distance restraint of 0.84 (1)  $\text{\AA}$  and with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . In the final cycles of refinement, these H atoms were constrained to ride on their parent O atoms.

Data collection: SMART (Bruker, 2000); cell refinement: SAINT-Plus NT (Bruker, 2001); data reduction: SAINT-Plus NT; program(s) used to solve structure: SHELXTL-NT (Sheldrick, 2008); program(s) used to refine structure: SHELXTL-NT; molecular graphics: SHELXTL-NT; software used to prepare material for publication: PLATON (Spek, 2009) and publCIF (Westrip, 2010).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DN3139). Services for accessing these data are described at the back of the journal.

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