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A novel three-dimensional framework constructed by 2-[(1*H*-imidazol-1-yl)-methyl]-1*H*-benzimidazole and infinite chains of hydrogen-bonded water molecules

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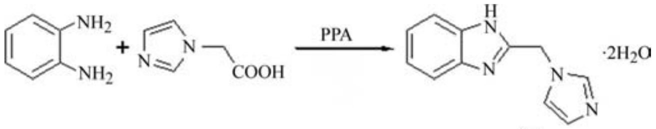
A novel three-dimensional framework of 2-[(1*H*-imidazol-1-yl)methyl]-1*H*-benzimidazole dihydrate, $C_{11}H_{10}N_4 \cdot 2H_2O$ or $L \cdot 2H_2O$, (I), in which *L* acts as both hydrogen-bond acceptor and donor in the supramolecular construction with water, has been obtained by self-assembly reaction of *L* with H_2O. The two independent water molecules are hydrogen bonded alternately with each other to form a one-dimensional infinite zigzag water chain. These water chains are linked by the benzimidazole molecules into a three-dimensional framework, in which each organic molecule is hydrogen bonded by three water molecules. This study shows that the diversity of hydrogen-bonded patterns plays a crucial role in the formation of the three-dimensional framework. More significantly, as water molecules are important in contributing to the conformation, stability, function and dynamics of biomacromolecules, the infinite chains of hydrogen-bonded water molecules seen in (I) may be a useful model for water in other chemical and biological processes.

Comment

Research on supramolecular compounds has become popular because of their potential applications in areas such as gas storage (Rowsell *et al.*, 2005), selective absorption (Dong *et al.*, 2007), catalysis (Wu *et al.*, 2007), magnetics (Zhao *et al.*, 2003; Wang *et al.*, 2006; Neville *et al.*, 2008) and optics (Huang *et al.*, 2007). Many strategies have been developed to achieve supramolecular compounds with predefined structures (Yaghi *et al.*, 1998; Cho *et al.*, 2006; Ma *et al.*, 2008). Among these strategies, the choice and design of organic molecules as hydrogen-bond acceptors or donors are undoubtedly a key part of the construction of intriguing frameworks driven by hydrogen-bonding interactions (Albrecht, 2001; Telfer *et al.*, 2004; Burchell *et al.*, 2006). Imidazole or benzimidazole derivatives have been widely used in supramolecular chemistry and numerous coordination polymers with versatile structures and potential properties have been reported (Chen *et al.*, 2005; Zheng *et al.*, 2007). It is well known that imidazole-containing molecules can easily coordinate to metal ions as well as act as hydrogen-bond acceptors or donors in supramolecular assembly reactions. Although much effort has been put into the study of supramolecular chemistry based on imidazole-containing ligands, benzimidazole-functionalized imidazole ligands are less well studied (Li *et al.*, 2008). The inclusion of both benzimidazole and imidazole functional groups can lead to different coordination modes and may play a crucial role in the construction of supramolecular compounds driven by hydrogen-bonding interactions.



(I)

The study of lattice water molecules has also attracted much attention because of their fundamental importance in chemical and biological processes (Mascal *et al.*, 2006). Some hydrogen-bonded water molecules, such as water clusters (Ghosh *et al.*, 2005; Dai *et al.*, 2008), one-dimensional water chains (Sreenivasulu *et al.*, 2004) and two-dimensional water layers (Janiak *et al.*, 2002), have been found. However, infinite chains of hydrogen-bonded water molecules in biological molecules, especially in supramolecular compounds, are still rare (Wang *et al.*, 2007; Mukherjee *et al.*, 2004; Neogi *et al.*, 2005). We report here the synthesis and characterization of a novel three-dimensional hydrogen-bonded framework of 2-[(1*H*-imidazol-1-yl)methyl]-1*H*-benzimidazole dihydrate ($L \cdot 2H_2O$), (I), which contains infinite chains of hydrogen-bonded water molecules.

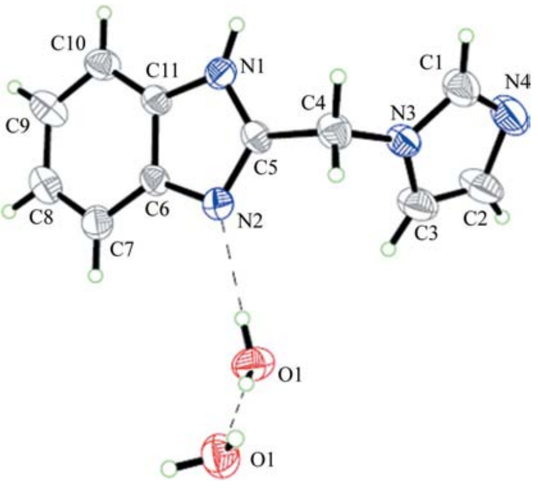


Figure 1
The molecular structure of (I) (displacement ellipsoids are drawn at the 30% probability level).

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(I) was found to crystallize in the noncentrosymmetric orthorhombic space group $Pna2_1$. The asymmetric unit contains one L molecule and two inequivalent water molecules (Fig. 1). The benzimidazole and imidazole rings of the L molecule are not coplanar but rather have a dihedral angle of 70.23 (9)°. The two types of water molecules are linked alternately into a one-dimensional zigzag water chain (Fig. 2) *via* O—H···O hydrogen bonds (Table 1) along the crystallographic *c* axis; as shown in Fig. 2, these hydrogen bonds are O2—H2*A*···O1 and O1—H1*A*···O2^{i} [symmetry code: (i) $x, y, z - 1$]. The water O atoms in the chain are coplanar, which corresponds with one literature report (Wang *et al.*, 2007) but contrasts with another (Neogi *et al.*, 2005), in which the O atoms of the water molecules in the chain are not coplanar. As shown in Fig. 2, atom O1 of the water molecule and atom N4^{iii} [symmetry code: (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$] of L are connected *via* an O—H···N hydrogen bond, while water atom O2 is linked by two N atoms [N1^{iv} and N2; symmetry code: (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z$] from two benzimidazole molecules *via* O—H···N and N—H···O hydrogen bonds (Table 1). Thus, in this water chain, atom O1 is in a three-coordinate configuration by coordinating to two water molecules and one benzimidazole molecule, while atom O2 is in a four-coordinate configuration resulting from two interactions with water molecules and two with benzimidazole molecules. This is different from the reported one-dimensional water chains (Wang *et al.*, 2007) in which all the O atoms are in a three-coordinate configuration with two bonds with water molecules and one bond with a ligand.

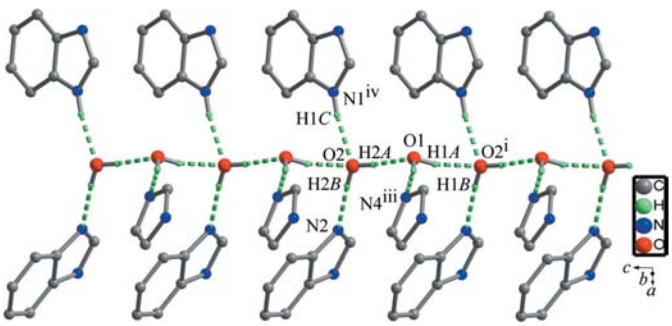

Figure 2
The one-dimensional water chain in (I). For clarity, only the portions of L interacting directly with the shown water chain are depicted. [Symmetry codes: (i) $x, y, z - 1$; (iii) $-x + \frac{1}{2}, y + \frac{1}{2}, z - \frac{1}{2}$; (iv) $x - \frac{1}{2}, -y + \frac{3}{2}, z$.]

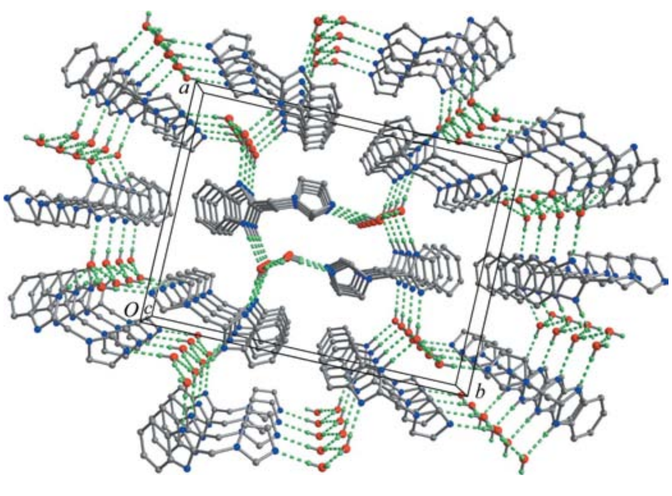

Figure 3
Perspective view of the three-dimensional hydrogen-bonded framework in (I). (Hydrogen-bonding interactions are shown as dashed lines.)

As discussed above, L acts as both hydrogen-bond acceptor and donor and is connected to the water chains. Each benzimidazole molecule is linked by three water molecules from three water chains. The infinite chains of hydrogen-bonded water molecules further extend into a three-dimensional framework *via* the connection of ligands and water chains (Fig. 3). As a result, all the organic molecules in the framework are surrounded by one-dimensional water chains along the crystallographic *c* axis. It is the first example of one-dimensional water chains located in a three-dimensional framework based on an imidazole-rich organic ligand.

In summary, a novel three-dimensional hydrogen-bonded supramolecular framework has been synthesized. The benzimidazole-functionalized imidazole organic molecule 2-[(1*H*-imidazol-1-yl)methyl]-1*H*-benzimidazole plays a crucial role in the construction of the framework by acting as both hydrogen-bond acceptor and donor. More importantly, one-dimensional water chains are found in this framework. As water molecules play an important role in contributing to the conformation, stability, function and dynamics of biomacromolecules (Luan *et al.*, 2006), the new one-dimensional water chain may provide new insight into the hydrogen-bonding motif of the aqueous environment in living systems.

Experimental

All solvents and reagents used for the synthesis were commercially available and were used as received. Under a nitrogen atmosphere, 2-(1*H*-imidazol-1-yl)acetic acid (0.80 g, 6.3 mmol), benzene-1,2-diamine (0.68 g, 6.3 mmol) and polyphosphoric acid (10 ml) were combined and stirred at 443 K for 3 h. After cooling to room temperature, the reaction mixture was poured into ice water and aqueous ammonia was added until the pH of the system was adjusted to about 7. The system was filtered and subsequently washed by water to provide a white precipitate of $L\cdot2H_2O$, (I) (yield: 82.6%). ^{1}H NMR (300 MHz, DMSO-d_6): δ 12.44 (*s*, 1H, NH), 7.76 (*s*, 1H, CH), 7.52 (*d*, 2H, *o*-C_6H_4), 7.22 (*d*, 1H, CH), 7.16 (*d*, 2H, *o*-C_6H_4), 6.91 (*d*, 1H, CH), 5.43 (*s*, 2H, CH_2). IR (KBr, cm^{-1}): ν 3371, 3325, 3130, 2977, 2836, 2674, 1787, 1616, 1439, 1324, 1291, 1270, 1079, 917, 833, 754, 655, 615. (I) was dissolved in methanol and colourless crystals were obtained after slow evaporation of the solvent.

Crystal data

$C_{11}H_{10}N_4\cdot2H_2O$
$M_r = 234.26$
Orthorhombic, $Pna2_1$
$a = 14.030$ (2) Å
$b = 19.121$ (3) Å
$c = 4.6240$ (8) Å
$V = 1240.5$ (4) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.09$ mm^{-1}
$T = 298$ (2) K
0.30 × 0.27 × 0.25 mm

Data collection

Bruker SMART CCD area-detector diffractometer
6623 measured reflections
1313 independent reflections
1117 reflections with $I > 2\sigma(I)$
$R_{\text{int}} = 0.055$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.079$
$S = 1.03$
1313 reflections
154 parameters
5 restraints
H-atom parameters constrained
$\Delta\rho_{\text{max}} = 0.10$ e Å^{-3}
$\Delta\rho_{\text{min}} = -0.11$ e Å^{-3}

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O1—H1A⋯O2$^{\text{i}}$	0.84	2.02	2.836 (3)	162
N1—H1C⋯O2$^{\text{ii}}$	0.86	1.94	2.794 (2)	172
O1—H1B⋯N4$^{\text{iii}}$	0.84	1.93	2.772 (2)	173
O2—H2A⋯O1	0.84	1.87	2.696 (3)	169
O2—H2B⋯N2	0.84	1.93	2.764 (2)	176

Symmetry codes: (i) $x, y, z-1$; (ii) $x+\frac{1}{2}, -y+\frac{3}{2}, z$; (iii) $-x+\frac{1}{2}, y+\frac{1}{2}, z-\frac{1}{2}$.

The Friedel pairs were merged prior to the final refinement and the absolute configuration was not determined. The absolute structure was chosen randomly. Water H atoms were located in a difference map and their positions were initially refined subject to an O—H distance restraint of 0.84 (2) Å. Subsequently, these H atoms were treated as riding, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{O2})$. Other H atoms were placed in idealized positions and treated as riding, with C—H = 0.97 (CH_2) or 0.93 Å (CH), N—H = 0.86 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C,N})$.

Data collection: *SMART* (Bruker, 2003); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2003); 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*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ3184). Services for accessing these data are described at the back of the journal.

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