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N,*N*′-Bis(3-pyridylmethyl)benzene-1,4-dicarboxamide dihydrate

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The title compound, $C_{20}H_{18}N_4O_2 \cdot 2H_2O$, an amide-containing bipyridyl-type compound, crystallizes as a dihydrate. The organic molecule is centrosymmetric. Hydrogen-bonding and π–π stacking interactions in the crystal structure result in the formation of an infinite three-dimensional supramolecular network.

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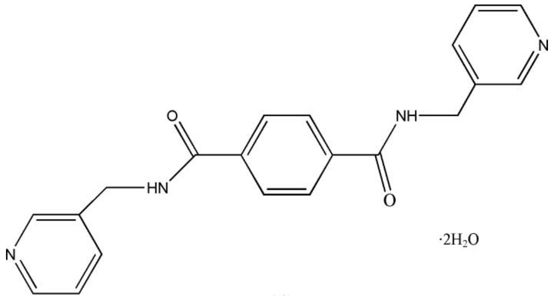
Key indicators

Single-crystal X-ray study
T = 295 K
Mean σ(C–C) = 0.003 Å
R factor = 0.039
wR factor = 0.129
Data-to-parameter ratio = 12.1

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

Comment

In the rapid developments of supramolecular chemistry, intermolecular interactions, such as hydrogen bonding and π–π stacking, can be utilized to control or direct the self-assembly process (Bushey *et al.*, 2004; Zhang *et al.*, 2005; Zhu *et al.*, 2004). The pyridine N atom can coordinate metals, the amide group can participate in hydrogen bonding and the pyridine pendant ring can perform π–π stacking. Pyridyl-type compounds that contain a carboxamide group have been used to produce a great number of novel supramolecular frameworks with interesting structural properties and potential applications for their multi-non-covalent interactions (Aakeröy *et al.*, 1999; Kamiyama *et al.*, 2000; Haycock *et al.*, 2000; Uemura *et al.*, 2004). Compared with the highly flexible 1,2-bis(4-pyridinecarboxamide)ethane (Ge, Zhang, Zhang, Guan *et al.*, 2003), *N*,*N*′-bipyridylmethylbenzenedicarboxamides are semi-rigid compounds, which have freely rotatable joints (methylenes) and rigid parts (benzene and pyridine groups) in the molecules. They exhibit a variety of conformations (Lü *et al.*, 2005) generating some quite different supramolecular structures. A macrotricyclic molecular cage with an ice-like arrangement of water as a decamer has been prepared *via* an amide derivative of 4-aminomethylpyridine (Barbour *et al.*, 1998). In this work, the title compound, (I), is reported.



(I)

The pyridyl rings of (I) adopt an *anti* orientation mode (Fig. 1). The average C—N bond length in the pyridyl rings (Table 1) is 1.334 Å, and the other bond lengths and angles are comparable with the values found in analogous compounds (Plater *et al.*, 2001). The dihedral angle between the benzene

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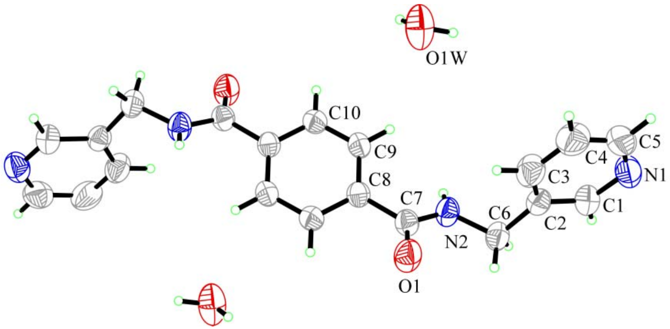

Figure 1
A view of the molecule, with the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are represented by circles of arbitrary size. Unlabelled atoms are related to labelled atoms by the symmetry operator $(1 - x, 1 - y, 1 - z)$.

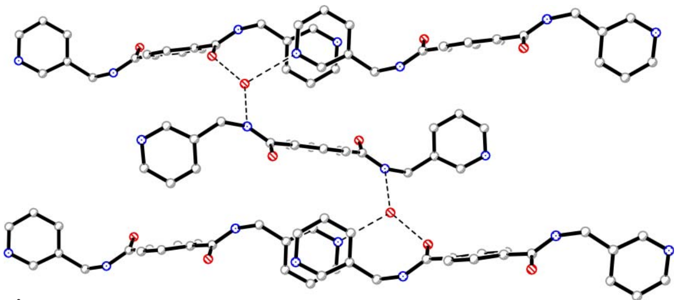

Figure 2
Hydrogen-bonding interactions (indicated as dashed lines) and π–π stacking (between the overlapped pyridyl rings) among the molecules, viewed along the *a* axis. H atoms have been omitted for clarity.

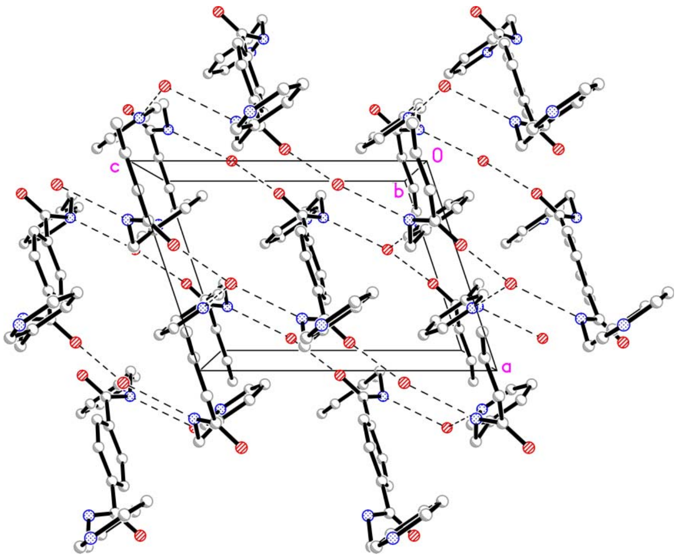

Figure 3
The three-dimensional network of the title compound, viewed along the *b* axis. Hydrogen-bonding interactions are indicated as dashed lines and H atoms have been omitted for clarity.

ring plane and the plane defined by the amide group (O1/C7/N2) is 31.4 (2)°, and that between the benzene ring plane and the pyridyl ring plane is 73.3 (2)°. These values differ from those in the ligand-containing complex (12.6 and 93.0°, respectively; Ge, Zhang, Zhang, Guo & Liu, 2003), indicating that the ligand is somewhat flexible.

The water molecules are found to be strongly hydrogen bonded to the organic molecules in the crystal structure. Each water molecule acts as a three-connector, with hydrogen bonds linking the organic molecules into a three-dimensional network (Table 2). Besides hydrogen bonding, adjacent organic molecules are also involved in face-to-face π–π interactions with a centroid-to-centroid distance of 3.804 Å (between pyridyl rings; Fig. 2). The intricate intermolecular synergetic interactions create a three-dimensional network (Fig. 3).

Experimental

N,*N*′-Bis(3-pyridylmethyl)benzene-1,4-dicarboxamide was prepared according to the procedure for the synthesis of the pyridyl–amide compound (Noveron *et al.*, 2002). Slow evaporation of an ethanol–water mixed solution (1:1, *v*/*v*) of the organic compound at room temperature yielded colourless crystals suitable for single-crystal diffraction analysis.

Crystal data

$C_{20}H_{18}N_4O_2\cdot 2H_2O$
$M_r = 382.42$
Monoclinic, $P2_1/n$
$a = 7.3871$ (7) Å
$b = 13.8981$ (16) Å
$c = 9.8971$ (12) Å
$\beta = 108.441$ (8)°
$V = 963.92$ (19) Å^3
$Z = 2$

$D_x = 1.318$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 49 reflections
$\theta = 2.9$–17.9°
$\mu = 0.09$ mm^{-1}
$T = 295$ (2) K
Block, colourless
0.4 × 0.4 × 0.3 mm

Data collection

Bruker *P*4 diffractometer
ω scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.972$, $T_{\max} = 0.973$
2294 measured reflections
1694 independent reflections
1125 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.022$
$\theta_{\max} = 25.0°$
$h = -1 \rightarrow 8$
$k = -1 \rightarrow 16$
$l = -11 \rightarrow 11$
3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.039$
$wR(F^2) = 0.129$
$S = 1.09$
1694 reflections
140 parameters
H atoms treated by a mixture of independent and constrained refinementt

$w = 1/[\sigma^2(F_o^2) + (0.0524P)^2 + 0.1416P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.14$ e Å^{-3}
$\Delta\rho_{\min} = -0.15$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.237 (2)	C2—C6	1.506 (3)
N2—C7	1.331 (2)	C10—C8$^{\rm i}$	1.385 (3)
N2—C6	1.454 (3)	C8—C7	1.498 (3)
C9—C10	1.381 (3)	N1—C5	1.331 (3)
C9—C8	1.395 (3)	N1—C1	1.337 (3)
C2—C1	1.376 (3)	C5—C4	1.366 (4)
C2—C3	1.380 (3)	C4—C3	1.373 (3)
C7—N2—C6	123.57 (18)	C5—N1—C1	116.7 (2)
O1—C7—N2	123.06 (19)	N2—C6—C2	113.43 (17)
O1—C7—C8	120.09 (18)	N1—C5—C4	123.3 (2)
N2—C7—C8	116.85 (17)	C5—C4—C3	119.0 (2)

Symmetry code: (i) $1 - x, 1 - y, 1 - z$.

Table 2
Hydrogen-bonding geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
$\text{N2}-\text{H7}\cdots\text{O1}W^{\text{ii}}$	0.84	2.01	2.817 (3)	161
$\text{O1}W-\text{H1}W\cdots\text{O1}^{\text{iii}}$	0.89	1.95	2.837 (2)	176
$\text{O1}W-\text{H2}W\cdots\text{N1}^{\text{iv}}$	0.93	1.88	2.809 (3)	179

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

The H atoms of the water molecules were located in difference Fourier maps. H atoms bound to C and N atoms were also visible in difference maps. All H atoms were treated as riding atoms, constrained to ride on their parent atoms with C—H = 0.93–0.97 Å and N—H = 0.84 Å, and with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{iso}}(\text{C})$].

Data collection: *XSCANS* (Bruker, 1997); cell refinement: *XSCANS*; data reduction: *SHELXTL* (Siemens, 1996); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXL97*.

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