Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

N,*N*′-Bis(pyridin-4-ylmethyl)terephthalamide dihydrate: a self-interpenetrating hydrogen-bonding network

Hong-Tao Zhang* and Xiao-Zeng You

Coordination Chemistry Institute, State Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China

Correspondence e-mail:
hongtaozhang2000@yahoo.com

Received 10 May 2005
Accepted 3 June 2005
Online 10 June 2005

Key indicators

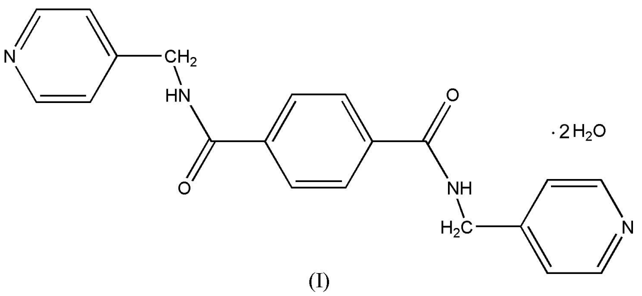
Single-crystal X-ray study
T = 298 K
Mean σ(C–C) = 0.004 Å
R factor = 0.050
wR factor = 0.113
Data-to-parameter ratio = 11.9

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

The title compound, $C_{20}H_{18}N_4O_2\cdot2H_2O$, has an inversion center at the mid-point of the central benzene ring. The asymmetric unit consists of one-half of an N^1,N^4-bis(pyridin-4-ylmethyl)terephthalamide molecule and one water molecule. The intermolecular hydrogen bonds connect the amide molecules and water molecules to produce a self-interpenetrating hydrogen-bonding network. The crystal packing is also governed by intermolecular π–π stacking and a weak C—H$\cdots\pi$ interaction.

Comment

Non-covalent interactions, such as hydrogen bonding, π–π stacking and C—H$\cdots\pi$ interactions, play a dominant role in supramolecular self-assembly (Casnati *et al.*, 2003; Ghosh & Bharadwaj, 2004; Glidewell *et al.*, 2005; Jennings *et al.*, 2001). Moreover, the conformations of molecular building blocks have an important influence on the supramolecular structure. Generally, rigidity of molecule is helpful in the construction of a framework structure, while flexibility in a molecule can induce an interpenetrating structure (Batten & Robson, 1998). Accordingly, *N*-substituted aromatic amides should be useful molecular building blocks for assembling and investigating supramolecular architectures, because the amide C═O and the amide N—H groups could serve as a hydrogen bond acceptor and donor, respectively. Rigid aromatic rings, such as benzene or pyridine, could also be helpful for π–π stacking, while the σ-rotation of the amide N—C bond could induce flexibility in the molecule. In order to further understand supramolecular self-assembly through non-covalent interactions, we have designed and synthesized an *N*-substituted aromatic amide, the title compound, (I).



(I)

The asymmetric unit of the title compound consists of one-half of an N^1,N^4-bis(pyridin-4-ylmethyl)terephthalamide molecule arranged around an inversion center and an uncoordinated water molecule, as shown in Fig. 1. The amide group CO—N lies out of the benzene ring plane, with a dihedral angle of 22.4 (3)° between the benzene plane N2/C7/O1 and C8–C10/C8^{i}–C10^{i} [symmetry code: (i) $-x$, $1-y$, $-z$]. The

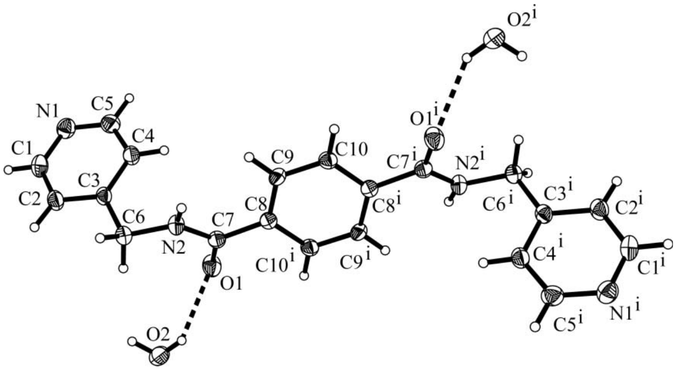


Figure 1
The molecular structure of (I), with displacement ellipsoids at the 30% probability level. Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, 1-y, -z$.]

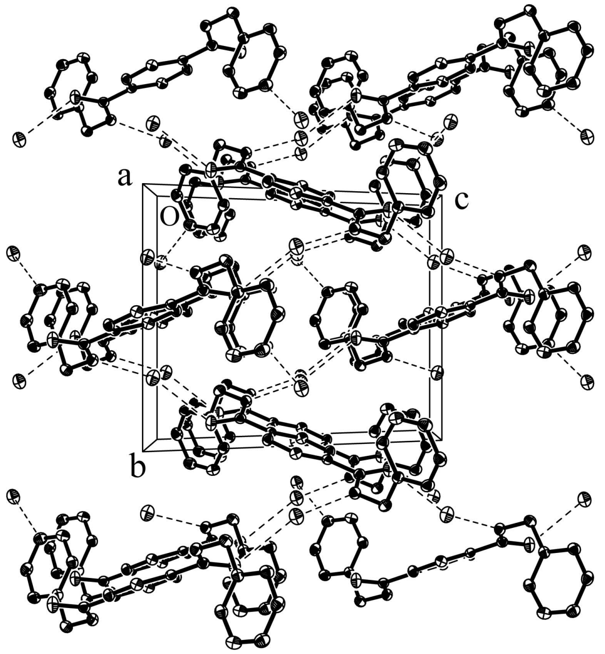


Figure 2
A packing diagram of (I), showing intermolecular hydrogen bonding (dashed lines). H atoms have been omitted.

amide plane is almost perpendicular to the pyridyl plane, with a dihedral angle of 89.85 (15)°. It is interesting that the N2—C6 σ-bond is almost in the plane of the pyridyl ring [C4—C3—C6—N2 = 0.7 (4)°], while the dihedral angle between phenyl plane and the pyridyl plane is 67.80 (24)°. The C3—C6—N2—C7 torsion angle of −86.2 (3)° indicates the flexibility arising from the amide N—C σ-rotation in the molecule. An intramolecular C4—H4$\cdots$N2 hydrogen bond stabilizes the molecular conformation.

In the crystal structure, the hydrogen-bonding interactions between the uncoordinated water molecule and the amide group, as well as the pyridyl N atom, connect the amide and water molecules to form a three-dimensional self-interpenetrating network. The geometries of the hydrogen bonds are listed in Table 2. Moreover, the shortest intermolecular pyridine–pyridine separation of 3.845 (6) Å indicates the presence of π–π interactions, while the shortest phenyl–phenyl separations of about 8.11 Å indicate no significant π–π interaction. A weak intermolecular C—H$\cdots\pi$ [C10—H10$\cdots$*Cg*1^{ii}; *Cg*1 is the centroid of the N1/C1–C5 pyridyl ring; symmetry code: (ii) $1-x, 1-y, -z$] interaction also contributes to stabilizing the solid-state structure.

Experimental

The title compound was synthesized by reaction of 4-(aminomethyl)pyridine and terephthaloyl dichloride according to the reported method (Buchan *et al.*, 2002). Colorless block single crystals were obtained by slow evaporation of an aqueous solution. Analysis found: C 62.75, H 5.92, N 14.54%; calculated for $C_{20}H_{22}N_4O_4$: C 62.82, H 5.80, N 14.65%.

Crystal data

$C_{20}H_{18}N_4O_2 \cdot 2H_2O$
$M_r = 382.42$
Monoclinic, $P2_1/c$
$a = 8.1173$ (13) Å
$b = 9.8449$ (15) Å
$c = 13.6802$ (17) Å
$\beta = 122.944$ (7)°
$V = 917.4$ (2) Å^3
$Z = 2$
$D_x = 1.384$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 573 reflections
$\theta = 3.0$–19.2°
$\mu = 0.10$ mm^{-1}
$T = 298$ (2) K
Block, colorless
0.20 × 0.10 × 0.10 mm

Data collection

Bruker SMART CCD area-detector diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min} = 0.980$, $T_{\max} = 0.988$
4470 measured reflections
1614 independent reflections
969 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.048$
$\theta_{\max} = 25.0$°
$h = -8 \rightarrow 9$
$k = -7 \rightarrow 11$
$l = -16 \rightarrow 15$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.113$
$S = 0.91$
1614 reflections
136 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0437P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.23$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

C6—N2	1.446 (3)	C7—N2	1.340 (3)
C7—O1	1.228 (3)		
O1—C7—N2	122.1 (2)	C7—N2—C6	122.6 (2)
O1—C7—C8	121.0 (2)		
C3—C6—N2—C7	−86.2 (3)		

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

D—H$\cdots$*A*	*D*—H	H$\cdots$*A*	*D*$\cdots$*A*	*D*—H$\cdots$*A*
O2—H7*A*$\cdots$O1	0.85	2.17	2.879 (3)	140
O2—H7*B*$\cdots$N1^{iii}	0.85	2.35	2.834 (3)	116
N2—H3$\cdots$O2^{iv}	0.86	2.07	2.856 (3)	151
C4—H4$\cdots$N2	0.93	2.52	2.849 (3)	101

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

H atoms attached to C and N atoms were placed in calculated positions and refined using a riding model, with Csp^2—H = 0.93 Å, Csp^3—H = 0.97 Å and Nsp^2—H = 0.86 Å. All H atoms of the water molecules were located in difference maps at an intermediate stage of the refinement and were then treated as riding, with O—H = 0.85 Å.. In all cases, $U_{\rm iso}$(H) is 1.2$U_{\rm eq}$ of the parent atom.

Data collection: *SMART* (Bruker, 1997); cell refinement: *SAINT-Plus* (Bruker, 1997); data reduction: *SAINT-Plus* and *SHELXS97* (Sheldrick, 1997); program(s) used to solve structure: *SHELXS97*; program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* (Sheldrick, 2000).

This work was supported by the Postdoctoral Research Foundation of Nanjing University (No. 2003022).

References

Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.

Bruker (1997). *SMART* (version 5.625) and *SAINT-Plus* (version 6.02a). Bruker AXS Inc., Madison, Wisconsin, USA.

Buchan, S., Plater, M. J., Foreman, M. R. St J., De Silva, B. M., Skakle, J. M. S. & Slawin, A. M. Z. (2002). *J. Chem. Crystallogr.* **32**, 5–10.

Casnati, A., Sansone, F. & Ungaro, R. (2003). *Acc. Chem. Res.* **36**, 246–254.

Ghosh, S. K. & Bharadwaj, P. K. (2004). *Inorg. Chem.* **43**, 5180–5182.

Glidewell, C., Low, J. N., Skakle, J. M. S., Wardell, S. M. S. V. & Wardell, J. L. (2005). *Acta Cryst.* B**61**, 227–237.

Jennings, W. B., Farell, B. M. & Malone, J. F. (2001). *Acc. Chem. Res.* **34**, 885–894.

Sheldrick, G. M. (1996). *SADABS*. Version 2.01. University of Göttingen, Germany.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sheldrick, G. M. (2000). *SHELXTL*. Version 6.1. Bruker AXS Inc., Madison, Wisconsin, USA.