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4,4′-Bipyridine-3,3′-dicarboxylic acid dihydrate

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Key indicators

Single-crystal X-ray study
T = 130 K
Mean σ(C–C) = 0.004 Å
R factor = 0.055
wR factor = 0.108
Data-to-parameter ratio = 10.6

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

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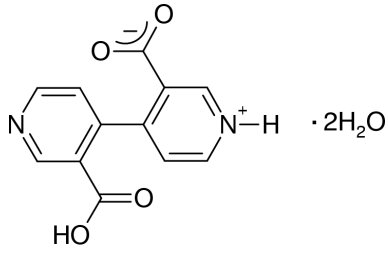
The crystal structure of 4,4′-bipyridine-3,3′-dicarboxylic acid dihydrate, $C_{12}H_8N_2O_4\cdot 2H_2O$, has been determined at 130 (1) K. The molecule exists in a zwitterionic form in the crystal and forms an extensive network of hydrogen bonds *via* the incorporated water molecules.

Comment

4,4′-Bipyridine-3,3′-dicarboxylic acid, (I), crystallizes from aqueous solution as a dihydrate. The location in a difference Fourier map of H4 bound to N4 indicates that (I) is present in the crystal in a zwitterionic form. The bipyridine unit adopts a twisted conformation with the least-squares planes through the two pyridine rings forming an angle of 49.8 (1)° (Fig. 1).



(I)

Molecules of (I) are linked into infinite linear chains along [001] *via* hydrogen bonds between the pyridinium H4 atom and N4*A* in an adjacent bipyridine molecule (Table 1), with adjacent chains running in opposite directions. In addition, an extensive hydrogen-bond network lying roughly parallel to the (110) plane links molecules of (I) into a catemer arrangement (Fig. 2). A direct hydrogen bond exists between two carboxylic acid groups in adjacent molecules, and these groups are also hydrogen bonded *via* the two water molecules (Table 1). An equivalent catemer arrangement is adopted roughly parallel to the $(1\bar{1}0)$ plane, giving rise to two-dimensional 'crinkled' sheets parallel to the (010) plane. These sheets are interdigitated, stacking along the [010] direction (Fig. 3). Between the sheets, several C—H···O contacts exist with geometries indicative of directional hydrogen-bond interactions (Table 1) (Desiraju & Steiner, 1999).

The observation that (I) crystallizes as a dihydrate may be rationalized by considering that the ratio of conventional hydrogen-bond donors (2) to hydrogen-bond acceptors (4) in (I) is mismatched (Desiraju, 1991). Incorporation of water molecules, with an inherent donor–acceptor ratio of 1:2, facilitates overall equalization of hydrogen-bond donor and acceptor functionality.

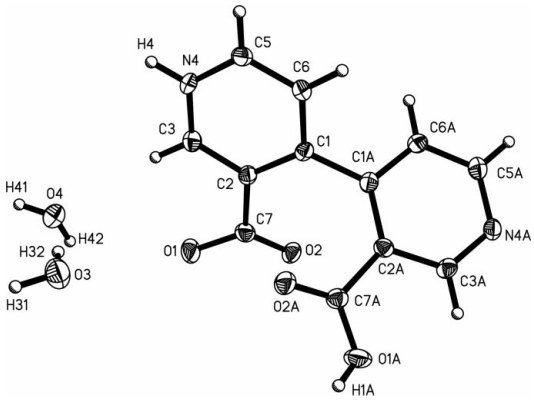


Figure 1
The asymmetric unit in (I) showing displacement ellipsoids at the 50% probability level (*XP*; Sheldrick, 1993).

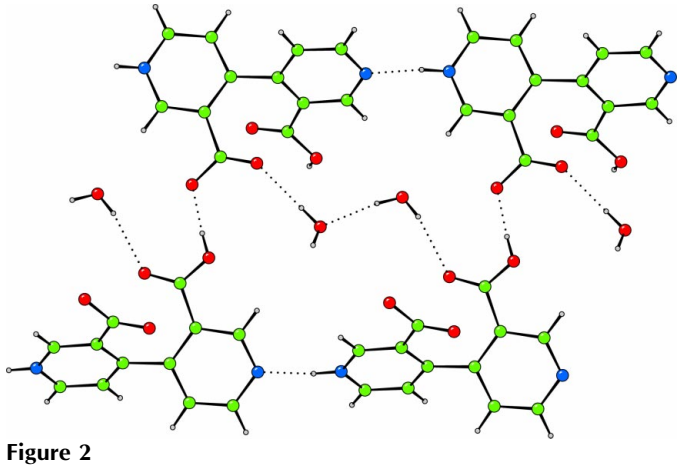


Figure 2
The molecules of (I) linked by hydrogen bonds *via* water molecules into a catemer arrangement, projected onto (110). An equivalent arrangement is formed parallel to (1$\bar{1}$0) (*CAMERON*; Watkin *et al.*, 1996).

Experimental

4,4′-Bipyridine-2,2′-dicarboxylic acid was prepared according to literature procedures (Becker & Neumann, 1972; Rebek *et al.*, 1985). Crystals were grown by slow evaporation of an aqueous solution at room temperature.

Crystal data

$C_{12}H_8N_2O_4{\cdot}2H_2O$
M_r = 280.24
Monoclinic, $P2_1/n$
a = 8.520 (1) Å
b = 15.970 (2) Å
c = 9.670 (1) Å
β = 110.77 (1)°
V = 1230.2 (2) Å^3
Z = 4
D_x = 1.513 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 3856 reflections
θ = 2.6–25.2°
μ = 0.12 mm^{-1}
T = 130 (2) K
Block, colourless
0.15 × 0.15 × 0.10 mm

Data collection

Rigaku R-AXIS IIc diffractometer
Thin-slice φ scans
3856 measured reflections
2126 independent reflections
1270 reflections with $I > 2\sigma(I)$
R_{int} = 0.043
θ_{max} = 25.2°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 19$
$l = -11 \rightarrow 10$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.108
S = 0.94
2126 reflections
200 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0246P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max}$ = 0.003
$\Delta\rho_{max}$ = 0.22 e Å^{-3}
$\Delta\rho_{min}$ = −0.30 e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.037 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N4—H4···N4A^{i}	0.88 (1)	1.78 (1)	2.650 (4)	172 (3)
O1A—H1A···O1^{ii}	0.85 (1)	1.59 (1)	2.433 (3)	168 (3)
O3—H32···O4	0.84 (1)	2.04 (1)	2.875 (3)	172 (3)
O3—H31···O2^{iii}	0.85 (1)	2.01 (1)	2.854 (3)	174 (3)
O4—H41···O3^{iv}	0.84 (1)	2.09 (1)	2.916 (3)	165 (3)
O4—H42···O2A^{iv}	0.84 (1)	2.15 (2)	2.942 (3)	156 (3)
C3—H3···O4	0.95	2.58	3.491 (4)	161
C5A—H5A···O3^{v}	0.95	2.66	3.569 (4)	161

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

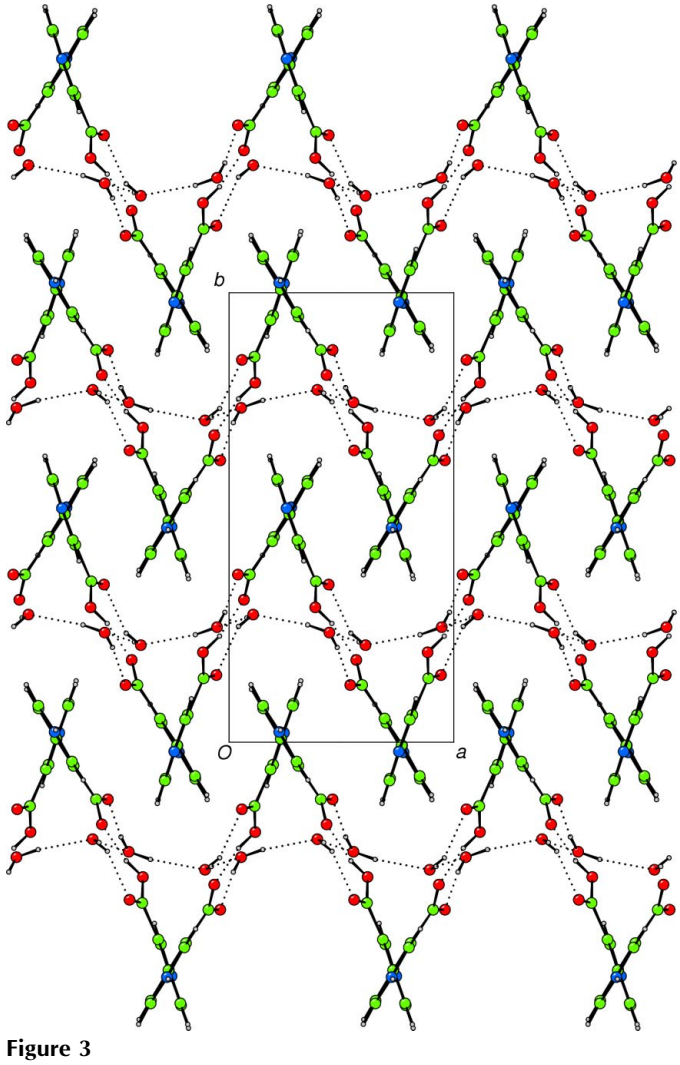


Figure 3
Projection on to the (001) plane showing the hydrogen-bonded sheets of (I) stacked along the [010] direction (*CAMERON*; Watkin *et al.*, 1996).

H atoms bound to C atoms were placed geometrically and refined using a riding model with an isotropic displacement parameter fixed

at 1.2 times U_{eq} of the C atom to which they are attached. H atoms on O1*A*, N4 and the water molecules were located in difference Fourier maps and refined with an isotropic displacement parameter fixed at 1.2 times the atom to which they are bound and O—H and N—H distances restrained to be 0.88 (1) and 0.84 (1) Å, respectively. The H···H distances in the water molecules were also restrained to be 1.37 (2) Å to ensure a chemically reasonable H—O—H bond angle.

Data collection: *R-AXIS PROCESS* (Molecular Structure Corporation, 1995); cell refinement: *R-AXIS PROCESS*; data reduction: *R-AXIS PROCESS*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Sheldrick, 1993); software used to prepare material for publication: *SHELXL*97.

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