

Short N···O hydrogen bonds in the 1:1  
adduct of 4,4'-bipyridyl and oxalic acidJohn A. Cowan,<sup>a\*</sup> Judith A. K.  
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## Key indicators

Single-crystal X-ray study

T = 100 K

Mean  $\sigma(\text{C}-\text{C}) = 0.004 \text{ \AA}$ 

R factor = 0.070

wR factor = 0.193

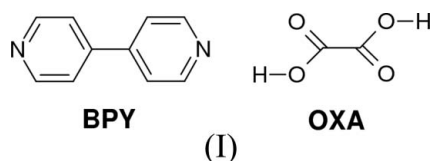
Data-to-parameter ratio = 13.9

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

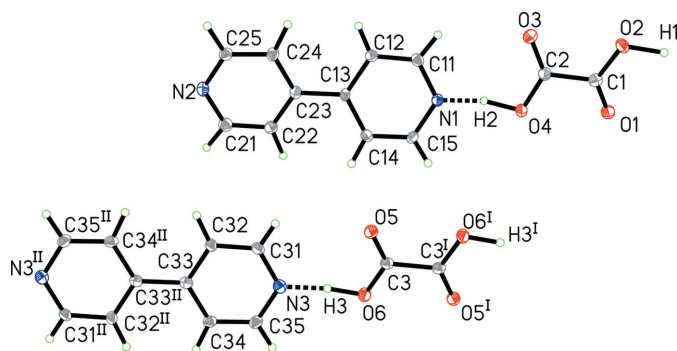
Oxalic acid,  $\text{C}_2\text{O}_4\text{H}_2$ , and 4,4'-bipyridyl,  $\text{C}_{10}\text{H}_8\text{N}_2$ , crystallize in a 1:1 ratio. The asymmetric unit consists of one oxalic acid (OXA) molecule and one 4,4'-bipyridyl (BPY) molecule in general positions, together with one half-OXA molecule and one half-BPY molecule; the latter two molecules are centrosymmetric. The molecules are linked in two parallel independent chains by strong  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds. In one chain there is one independent  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bond [ $\text{N}\cdots\text{O} = 2.557(3) \text{ \AA}$ ] and the molecules lie on centres of symmetry and are therefore constrained to have planar central portions. The second chain contains two independent  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds [ $\text{O}\cdots\text{N} = 2.549(3)$  and  $2.581(3) \text{ \AA}$ ] and both molecules are twisted about their central bonds.

## Comment

Temperature-dependent proton migration has recently been observed in short  $\text{N}\cdots\text{O}$  hydrogen bonds between carboxylic acid and pyridyl groups (Cowan *et al.*, 2003, 2005). It occurred to us that 4,4'-bipyridyl (BPY) and oxalic acid (OXA) would be likely to co-crystallize in the same intermolecular configuration, but hopefully with only one independent  $\text{N}-\text{H}\cdots\text{O}$  hydrogen bond in the asymmetric unit. We present here the crystal structure of the title 1:1 adduct of BPY and OXA, (I).

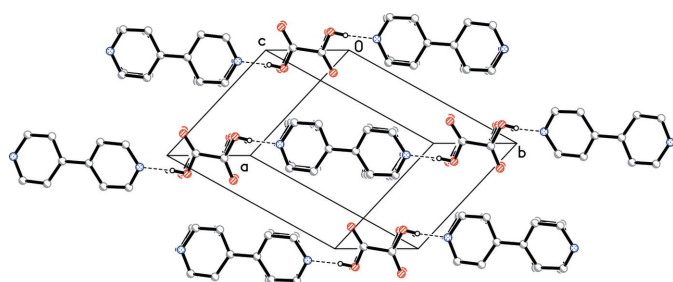


The asymmetric unit of (I) consists of one oxalic acid (OXA) molecule and one 4,4'-bipyridyl (BPY) molecule in general positions, together with one half-OXA molecule and one half-BPY molecule; the latter two molecules are centrosymmetric. BPY and OXA crystallize to form two similar independent one-dimensional chains. In both chains the OXA and BPY molecules are linked together by strong  $\text{O}-\text{H}\cdots\text{N}$  hydrogen bonds in concert with  $\text{C}-\text{H}\cdots\text{O}$  hydrogen bonds (Table 1). A similar configuration is often observed in co-crystals of BPY and carboxylic acids, for example in the co-crystals of BPY with fumaric acid (Chatterjee *et al.*, 1998), phosphonoacetic acid (Bowes *et al.*, 2003) and malonic acid (Pedireddi *et al.*, 1998). That one-dimensional tapes are formed is unsurprising considering the co-crystals of BPY with 2,5-dihydroxybenzoquinone (Cowan *et al.*, 2001), squaric acid (Reetz *et al.*, 1994) and 2,5-dichloro-3,6-dihydroxybenzoquinone (Zaman *et al.*, 1999), which all have a similar



**Figure 1**

The structures of segments of both independent chain, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds and H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (I)  $2 - x, 2 - y, 1 - z$ ; (II)  $3 - x, 1 - y, 1 - z$ .]



**Figure 2**

A packing diagram for (I), illustrating the molecular chains. All H atoms, except those involved in strong hydrogen bonds, have been omitted for clarity.

arrangement of O atoms to OXA and which all form one-dimensional tapes.

The two types of chains are distinguished by the twists within the molecules. In one chain, the planes of the pyridyl rings of the BPY molecule are twisted by  $23.75(6)^\circ$  with respect to each other and there is a twist of  $5.35(11)^\circ$  between the carboxylic acid groups of the OXA molecule, while in the other chain, the OXA and BPY molecules lie on centres of symmetry and are consequently both have planar central portions. Both chains lie in the  $ab$  plane and propagate in the  $[1\bar{1}0]$  direction (Fig. 2). The chains are linked by  $C-H\cdots O$  hydrogen bonds into parallel planes. One set of planes consists of only flat molecules and the other consists of only twisted molecules. The only significant interaction linking the planes is a  $C-H\cdots O$  hydrogen bond ( $C11\cdots O3$ ) between adjacent planes of twisted molecules.

There are three similar  $O-H\cdots N$  hydrogen bonds in the structure of (I). Although the H-atom positions were constrained in the final refinement,  $O-H$  distances between 1.15 and 1.25 Å in earlier free refinements hint that the true H-atom positions may be close to the centres of the hydrogen bonds. The graph produced by Steiner (2002) from neutron diffraction data of  $N\cdots O$  hydrogen bonds suggests that the  $O-H$  distance becomes significantly elongated when the  $N-O$  distance is below  $\sim 2.6$  Å. Although not as short as the

hydrogen bonds in which temperature-dependent proton migration has been observed, the  $N\cdots O$  distances in the three hydrogen bonds in (I) are all below  $\sim 2.6$  Å. Therefore, a large elongation of the  $O-H$  bond is expected and the H-atom position may be temperature-dependent. Neutron diffraction is required for accurate H-atom positions.

## Experimental

Equimolar quantities of BPY and OXA were dissolved in methanol. Crystals of (I) suitable for X-ray structure determination were prepared by slow evaporation of the solvent at room temperature.

### Crystal data

$C_{10}H_8N_2 \cdot C_2H_2O_4$

$M_r = 246.22$

Triclinic,  $P\bar{1}$

$a = 8.7365(18)$  Å

$b = 9.9154(19)$  Å

$c = 10.380(2)$  Å

$\alpha = 100.253(10)^\circ$

$\beta = 105.349(11)^\circ$

$\gamma = 107.569(10)^\circ$

$V = 793.5(3)$  Å<sup>3</sup>

$Z = 3$

$D_x = 1.546$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation

$\mu = 0.12$  mm<sup>-1</sup>

$T = 100(2)$  K

Block, brown

$0.3 \times 0.2 \times 0.15$  mm

### Data collection

Bruker SMART CCD area-detector diffractometer

$\omega$  scans

Absorption correction: none

8434 measured reflections

3601 independent reflections

2523 reflections with  $I > 2\sigma(I)$

$R_{int} = 0.058$

$\theta_{max} = 27.5^\circ$

### Refinement

Refinement on  $F^2$

$R[F^2 > 2\sigma(F^2)] = 0.070$

$wR(F^2) = 0.193$

$S = 1.09$

3601 reflections

259 parameters

Only H-atom displacement parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0821P)^2 + 0.9233P]$

where  $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.53$  e Å<sup>-3</sup>

$\Delta\rho_{min} = -0.34$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H1\cdots N2^i$	0.82	1.77	2.586 (3)	174
$O4-H2\cdots N1$	0.82	1.74	2.553 (3)	174
$O6-H3\cdots N3$	0.82	1.74	2.560 (3)	174
$C11-H11\cdots O3^{ii}$	0.93	2.59	3.270 (4)	130
$C22-H22\cdots O3^{iii}$	0.93	2.45	3.375 (3)	172
$C24-H24\cdots O1^{iv}$	0.93	2.40	3.326 (4)	171
$C25-H25\cdots O4^{iv}$	0.93	2.48	3.216 (3)	136
$C32-H32\cdots O5^v$	0.93	2.56	3.418 (3)	153
$C34-H34\cdots O5^{iii}$	0.93	2.52	3.373 (3)	153
$C35-H35\cdots O6^{vi}$	0.93	2.57	3.207 (3)	126

Symmetry codes: (i)  $x - 1, y + 1, z$ ; (ii)  $-x, -y + 1, -z$ ; (iii)  $x + 1, y, z$ ; (iv)  $x, y - 1, z$ ; (v)  $-x + 2, -y + 1, -z + 1$ ; (vi)  $-x + 3, -y + 2, -z + 1$ .

All H atoms were located in a difference Fourier map and then repositioned in idealized locations, with  $O-H = 0.82$  Å and  $C-H = 0.93$  Å. They were refined with their coordinates, but not their isotropic displacement parameters, riding on their parent atoms.

Data collection: *SMART* (Bruker, 1998); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1998); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL/PC* (Sheldrick, 1999); software used to prepare material for publication: *SHELXL97*.

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