# organic compounds

# 2,2′-Bipyridine–cyclopentane-1,2,3,4-tetracarboxylic acid (1/1)

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The asymmetric unit of the title compound, $C_{10}H_8N_2 \cdot C_9H_{10}O_8$, contains a half-molecule of 2,2′-bipyridine and a half-molecule of 1,2,3,4-cyclopentanetetracarboxylic acid, both components being completed by crystallographic inversion symmetry. In the crystal, the molecules are assembled into chains extending along [010] by O—H···N hydrogen bonds; adjacent chains are linked by O—H···O hydrogen bonds into a three-dimensional network.

## Related literature

For general background to coordination polymers, see: Bowers *et al.* (2005); Bowes *et al.* (2003). For related structures, see: Chen *et al.* (2005).
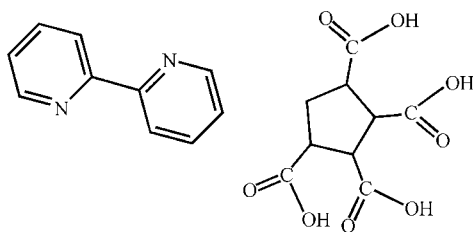


## Experimental

### Crystal data

$C_{10}H_8N_2 \cdot C_9H_{10}O_8$
$M_r = 402.35$
Orthorhombic, $Pnma$
$a = 12.942$ (3) Å
$b = 25.118$ (5) Å
$c = 5.4353$ (11) Å
$V = 1766.8$ (6) Å$^3$
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 0.12$ mm$^{-1}$
$T = 293$ K
$0.44 \times 0.36 \times 0.27$ mm

### Data collection

Rigaku R-AXIS RAPID diffractometer
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.949$, $T_{max} = 0.968$
15967 measured reflections
2054 independent reflections
1499 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.089$
$S = 1.02$
2054 reflections
141 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.19$ e Å$^{-3}$
$\Delta\rho_{min} = -0.16$ e Å$^{-3}$

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

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2B···O3$^i$ | 0.87 (2) | 1.80 (2) | 2.6520 (16) | 165 (2) |
| O4—H4A···N1$^{ii}$ | 0.94 (2) | 1.80 (2) | 2.7335 (18) | 169 (2) |

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

Data collection: *RAPID-AUTO* (Rigaku, 1998); cell refinement: *RAPID-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSC, 2004); 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: *SHELXL97*.

## References

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Chen, D.-M., Li, X.-H., Xiao, H.-P. & Hu, M.-L. (2005). *Acta Cryst.* E**61**, o317–o319.
Higashi, T. (1995). *ABSCOR.* Rigaku Corporation, Tokyo, Japan.
Rigaku (1998). *RAPID-AUTO.* Rigaku Corporation, Tokyo, Japan.
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Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

# supporting information

## 2,2′-Bipyridine–cyclopentane-1,2,3,4-tetracarboxylic acid (1/1)

### Jian-Li Lin, Xia-Xia Guo and Wen-Xiang Huang

### S1. Comment

In hydrogen-bonded adducts of simple di–, tri– and tetracarboxylic acids with tertiary diamines, the modes of hydrogen-bonded chains are often determined by hard and soft types. Our investigation builds on the associative behavior of carboxyl and pyridine functions. In this contribution, we report the title compound with bipyridine–cyclopentanetetra-carboxylic acid cocrystal.

The asymmetric unit contains one 2,2′-bipyridine molecule and one 1,2,3,4–cyclopentanetetracarboxylic acid molecule. Both bipyridine and cyclopentanetetracarboxylic acid molecules are generated *via* crystallographic 2–fold rotation axes (Fig. 1), and C3 atoms are located at the Wyckoff 4c sites. The carboxylic groups of cyclopentanetetracarboxylic acid connect with the corresponding bipyridine molecules through O4–H4A···N1[ii] hydrogen bonds generating a one-dimensional chain along [010] (Fig. 2). In this way, the adjacent one-dimensional chains are interconnected by O2–H2B···O3[i] hydrogen bonds to give three-dimensional network parallel to (001) (Fig. 3).

### S2. Experimental

Under continuous stirring, a solution of 2,2′-bipyridine (0.1560 g, 1.00 mmol) in 10 ml $CH_3OH$ was added dropwise to an aqueous solution of 1,2,3,4–cyclopentanetetracarboxylic acid (0.1230 g, 0.50 mmol) in 10 ml $H_2O$. The resulting mixture was further stirred for *ca* 30 min. After slow evaporation of the solution for one week at 35°C, colorless pillar sized crystals were obtained.

### S3. Refinement

H atoms bonded to C atoms were palced in geometrically calculated position and were refined using a riding model, with $U_{iso}(H) = 1.2\ U_{eq}(C)$. H atoms attached to O atoms were found in a difference Fourier synthesis and were refined using a riding model, with the O—H distances fixed as initially found and with $U_{iso}(H)$ values set at 1.2 $U$eq(O).
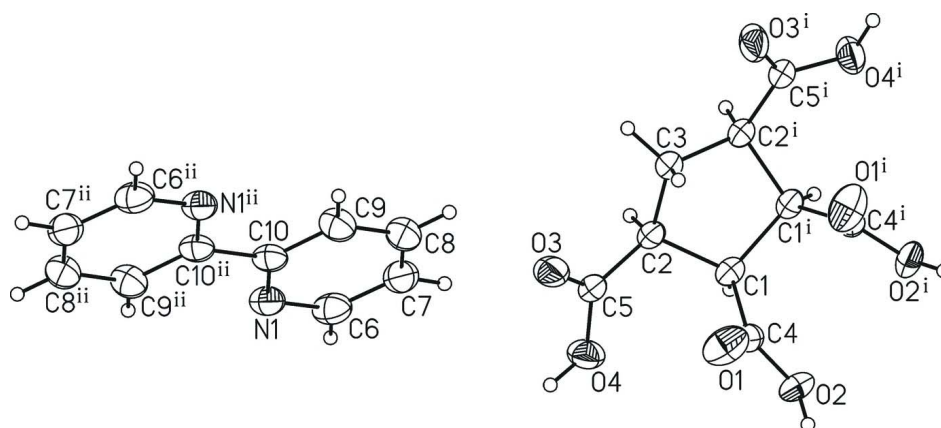
**Figure 1**

*ORTEP* view of the title compound, The dispalcement ellipsoids are drawn at 45% probability dispalcement ellipsoids. [Symmetry codes: (i)$x$, $-y+1/2$, $z$;(ii)$-x$, $y + 1$, $-z$.]
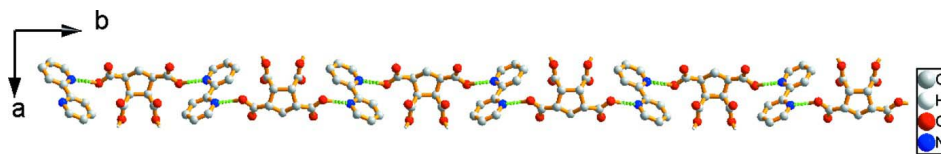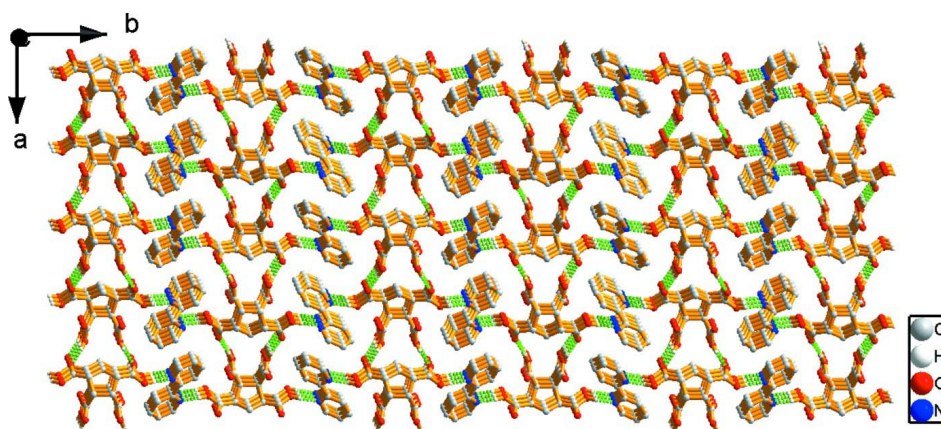


**Figure 2**

one-dimensional chain of the title cocrystal viewed along the $b$ axis. O–H⋯N hydrogen bonds are shown as dashed lines.



**Figure 3**

Packing diagram of the title co-crystal viewed down the $c$ axis. O–H⋯N and O–H⋯O hydrogen bonds are shown as dashed lines.

**2,2′-Bipyridine–cyclopentane-1,2,3,4-tetracarboxylic acid (1/1)**

*Crystal data*

| | |
|---|---|
| $C_{10}H_8N_2 \cdot C_9H_{10}O_8$ | $c = 5.4353\ (11)$ Å |
| $M_r = 402.35$ | $V = 1766.8\ (6)$ Å$^3$ |
| Orthorhombic, *Pnma* | $Z = 4$ |
| Hall symbol: -P 2ac 2n | $F(000) = 840$ |
| $a = 12.942\ (3)$ Å | $D_x = 1.513$ Mg m$^{-3}$ |
| $b = 25.118\ (5)$ Å | Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å |

Cell parameters from 8201 reflections
$\theta = 3.2–27.5°$
$\mu = 0.12$ mm$^{-1}$

$T = 293$ K
Block, white
$0.44 \times 0.36 \times 0.27$ mm

*Data collection*

Rigaku R-AXIS RAPID diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
Detector resolution: 0 pixels mm$^{-1}$
$\omega$ scans
Absorption correction: multi-scan (*ABSCOR*; Higashi, 1995)
$T_{min} = 0.949$, $T_{max} = 0.968$

15967 measured reflections
2054 independent reflections
1499 reflections with $I > 2\sigma(I)$
$R_{int} = 0.055$
$\theta_{max} = 27.4°$, $\theta_{min} = 3.2°$
$h = -16\rightarrow16$
$k = -32\rightarrow32$
$l = -7\rightarrow7$

*Refinement*

Refinement on $F^2$
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.089$
$S = 1.02$
2054 reflections
141 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.034P)^2 + 0.4998P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.19$ e Å$^{-3}$
$\Delta\rho_{min} = -0.16$ e Å$^{-3}$

*Special details*

**Geometry**. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

**Refinement**. Refinement of $F^2$ against ALL reflections. The weighted $R$-factor $wR$ and goodness of fit $S$ are based on $F^2$, conventional $R$-factors $R$ are based on $F$, with $F$ set to zero for negative $F^2$. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating $R$-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. $R$-factors based on $F^2$ are statistically about twice as large as those based on $F$, and $R$- factors based on ALL data will be even larger.

*Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)*

|  | *x* | *y* | *z* | $U_{iso}$*/$U_{eq}$ |
|---|---|---|---|---|
| C1 | 0.51833 (9) | 0.28149 (5) | 0.1032 (3) | 0.0282 (3) |
| H1A | 0.5337 | 0.2944 | 0.2694 | 0.034* |
| C2 | 0.40596 (10) | 0.29744 (5) | 0.0333 (3) | 0.0311 (3) |
| H2A | 0.3672 | 0.3004 | 0.1875 | 0.037* |
| C3 | 0.36186 (15) | 0.2500 | −0.1051 (4) | 0.0354 (5) |
| H3A | 0.3842 | 0.2500 | −0.2754 | 0.043* |
| H3B | 0.2869 | 0.2500 | −0.0997 | 0.043* |
| O1 | 0.58022 (9) | 0.31419 (5) | −0.2864 (2) | 0.0560 (4) |
| O2 | 0.68873 (8) | 0.30931 (4) | 0.0286 (2) | 0.0429 (3) |
| C4 | 0.59708 (10) | 0.30368 (5) | −0.0745 (3) | 0.0313 (3) |
| O3 | 0.33802 (8) | 0.35651 (4) | −0.2754 (3) | 0.0535 (4) |
| O4 | 0.44673 (9) | 0.38926 (4) | 0.0007 (2) | 0.0438 (3) |

| | | | |
|---|---|---|---|
| C5 | 0.39410 (10) | 0.34981 (6) | −0.0985 (3) | 0.0341 (3) |
| N1 | 0.07695 (9) | 0.51473 (5) | 0.2707 (2) | 0.0392 (3) |
| C6 | 0.14948 (12) | 0.49161 (7) | 0.4103 (3) | 0.0456 (4) |
| H6A | 0.1737 | 0.5103 | 0.5463 | 0.055* |
| C7 | 0.19052 (12) | 0.44202 (7) | 0.3654 (3) | 0.0453 (4) |
| H7A | 0.2406 | 0.4276 | 0.4683 | 0.054* |
| C8 | 0.15516 (13) | 0.41452 (7) | 0.1634 (3) | 0.0448 (4) |
| H8A | 0.1816 | 0.3811 | 0.1258 | 0.054* |
| C9 | 0.08006 (13) | 0.43719 (6) | 0.0176 (3) | 0.0430 (4) |
| H9A | 0.0553 | 0.4190 | −0.1193 | 0.052* |
| C10 | 0.04132 (11) | 0.48714 (6) | 0.0747 (3) | 0.0357 (3) |
| H2B | 0.7334 (16) | 0.3216 (8) | −0.077 (4) | 0.074 (7)* |
| H4A | 0.4380 (18) | 0.4198 (10) | −0.098 (5) | 0.095 (8)* |

*Atomic displacement parameters (Å²)*

| | $U^{11}$ | $U^{22}$ | $U^{33}$ | $U^{12}$ | $U^{13}$ | $U^{23}$ |
|---|---|---|---|---|---|---|
| C1 | 0.0233 (6) | 0.0356 (7) | 0.0258 (7) | −0.0014 (5) | 0.0007 (6) | −0.0040 (6) |
| C2 | 0.0225 (6) | 0.0321 (7) | 0.0389 (8) | −0.0010 (5) | 0.0033 (6) | −0.0016 (6) |
| C3 | 0.0260 (9) | 0.0286 (10) | 0.0517 (14) | 0.000 | −0.0046 (10) | 0.000 |
| O1 | 0.0469 (7) | 0.0863 (10) | 0.0350 (7) | −0.0119 (6) | 0.0054 (5) | 0.0090 (6) |
| O2 | 0.0249 (5) | 0.0494 (7) | 0.0544 (8) | −0.0087 (5) | 0.0019 (5) | 0.0014 (6) |
| C4 | 0.0279 (7) | 0.0290 (7) | 0.0371 (9) | −0.0010 (6) | 0.0046 (6) | −0.0054 (6) |
| O3 | 0.0430 (6) | 0.0380 (6) | 0.0796 (9) | −0.0087 (5) | −0.0285 (6) | 0.0102 (6) |
| O4 | 0.0467 (6) | 0.0340 (6) | 0.0508 (7) | −0.0104 (5) | −0.0073 (5) | −0.0026 (5) |
| C5 | 0.0236 (6) | 0.0311 (7) | 0.0475 (9) | −0.0015 (6) | 0.0004 (7) | −0.0026 (7) |
| N1 | 0.0387 (7) | 0.0378 (7) | 0.0411 (8) | −0.0084 (6) | −0.0029 (6) | 0.0029 (6) |
| C6 | 0.0430 (8) | 0.0494 (9) | 0.0443 (10) | −0.0126 (8) | −0.0101 (8) | 0.0036 (8) |
| C7 | 0.0390 (8) | 0.0458 (9) | 0.0510 (11) | −0.0051 (7) | −0.0069 (8) | 0.0125 (8) |
| C8 | 0.0467 (9) | 0.0394 (9) | 0.0483 (10) | −0.0018 (7) | 0.0023 (8) | 0.0083 (8) |
| C9 | 0.0507 (9) | 0.0386 (8) | 0.0396 (9) | −0.0046 (7) | −0.0054 (8) | 0.0021 (7) |
| C10 | 0.0375 (7) | 0.0353 (8) | 0.0343 (8) | −0.0093 (6) | 0.0013 (7) | 0.0057 (7) |

*Geometric parameters (Å, º)*

| | | | |
|---|---|---|---|
| C1—C4 | 1.5105 (19) | O4—C5 | 1.3177 (17) |
| C1—C2 | 1.5555 (18) | O4—H4A | 0.94 (2) |
| C1—C1ⁱ | 1.582 (3) | N1—C6 | 1.339 (2) |
| C1—H1A | 0.9800 | N1—C10 | 1.352 (2) |
| C2—C5 | 1.506 (2) | C6—C7 | 1.376 (2) |
| C2—C3 | 1.5202 (19) | C6—H6A | 0.9300 |
| C2—H2A | 0.9800 | C7—C8 | 1.375 (2) |
| C3—C2ⁱ | 1.5202 (19) | C7—H7A | 0.9300 |
| C3—H3A | 0.9700 | C8—C9 | 1.377 (2) |
| C3—H3B | 0.9700 | C8—H8A | 0.9300 |
| O1—C4 | 1.2015 (19) | C9—C10 | 1.386 (2) |
| O2—C4 | 1.3194 (17) | C9—H9A | 0.9300 |
| O2—H2B | 0.87 (2) | C10—C10ⁱⁱ | 1.490 (3) |

| | | | |
|---|---|---|---|
| O3—C5 | 1.2166 (19) | | |
| | | | |
| C4—C1—C2 | 112.31 (12) | O2—C4—C1 | 111.99 (13) |
| C4—C1—C1ⁱ | 111.65 (7) | C5—O4—H4A | 108.6 (14) |
| C2—C1—C1ⁱ | 104.92 (7) | O3—C5—O4 | 121.84 (14) |
| C4—C1—H1A | 109.3 | O3—C5—C2 | 123.90 (13) |
| C2—C1—H1A | 109.3 | O4—C5—C2 | 114.19 (13) |
| C1ⁱ—C1—H1A | 109.3 | C6—N1—C10 | 117.60 (14) |
| C5—C2—C3 | 114.28 (13) | N1—C6—C7 | 124.23 (16) |
| C5—C2—C1 | 115.88 (11) | N1—C6—H6A | 117.9 |
| C3—C2—C1 | 105.67 (12) | C7—C6—H6A | 117.9 |
| C5—C2—H2A | 106.8 | C8—C7—C6 | 117.89 (16) |
| C3—C2—H2A | 106.8 | C8—C7—H7A | 121.1 |
| C1—C2—H2A | 106.8 | C6—C7—H7A | 121.1 |
| C2—C3—C2ⁱ | 103.21 (17) | C7—C8—C9 | 119.11 (16) |
| C2—C3—H3A | 111.1 | C7—C8—H8A | 120.4 |
| C2ⁱ—C3—H3A | 111.1 | C9—C8—H8A | 120.4 |
| C2—C3—H3B | 111.1 | C8—C9—C10 | 120.02 (16) |
| C2ⁱ—C3—H3B | 111.1 | C8—C9—H9A | 120.0 |
| H3A—C3—H3B | 109.1 | C10—C9—H9A | 120.0 |
| C4—O2—H2B | 110.7 (14) | N1—C10—C9 | 121.14 (14) |
| O1—C4—O2 | 123.15 (14) | N1—C10—C10ⁱⁱ | 116.88 (17) |
| O1—C4—C1 | 124.84 (13) | C9—C10—C10ⁱⁱ | 121.98 (18) |

Symmetry codes: (i) $x$, $-y+1/2$, $z$; (ii) $-x$, $-y+1$, $-z$.

*Hydrogen-bond geometry (Å, º)*

| $D$—H···$A$ | $D$—H | H···$A$ | $D$···$A$ | $D$—H···$A$ |
|---|---|---|---|---|
| O2—H2$B$···O3ⁱⁱⁱ | 0.87 (2) | 1.80 (2) | 2.6520 (16) | 165 (2) |
| O4—H4$A$···N1ⁱᵛ | 0.94 (2) | 1.80 (2) | 2.7335 (18) | 169 (2) |

Symmetry codes: (iii) $x+1/2$, $y$, $-z-1/2$; (iv) $-x+1/2$, $-y+1$, $z-1/2$.