

Diphenic acid–4,4'-bipyridine (2/1)

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Key indicators

Single-crystal X-ray study

T = 298 K

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

R factor = 0.036

wR factor = 0.054

Data-to-parameter ratio = 12.6

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

In the title co-crystal, $2\text{C}_{14}\text{H}_{10}\text{O}_4 \cdot \text{C}_{10}\text{H}_8\text{N}_2$, the diphenic acid molecules form a centrosymmetric dimeric pair, through strong $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds involving a carboxylic acid group from each molecule. In the crystal structure, the dimers are linked by $\text{C}-\text{H} \cdots \text{O}$ interactions to form layers parallel to the (001) plane. The adjacent layers are interlinked by bipyridine molecules, $\text{C}_{10}\text{H}_8\text{N}_2$, through $\text{O}-\text{H} \cdots \text{N}$ hydrogen bonds. The bipyridine molecule lies on a centre of symmetry.

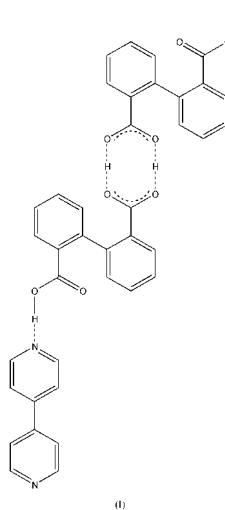
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Comment

The binding properties of the carboxyl groups of benzoic acid and its derivatives are interesting themes of structural chemistry (Lam *et al.*, 2003). Diphenic acid (biphenyl-2,2'-dicarboxylic acid) is an extremely versatile building block for the purposes of crystal engineering. In the crystal structure of this compound, molecules form infinite chains, *via* $R_2^2(8)$ carboxylic acid pairs (Fronczek *et al.*, 1987). A co-crystal structure of diphenic acid, diphenic acid–acridine (1/1), has been reported (Shaameri *et al.*, 2001). Here we report the co-crystal structure of diphenic acid–4,4'-bipyridine (2/1), (I), which comprises two acid and one base molecule.



The asymmetric unit of (I) consists of one molecule of diphenic acid and a half molecule of 4,4'-bipyridine. The other diphenic acid molecule and the other half of the bipyridine molecule are generated by the inversion symmetry $(2-x, 1-y, -z)$ and $(1-x, 2-y, 1-z)$, respectively. In the diphenic acid, one of the carboxylic acid groups shows normal $\text{C}-\text{O}$ distances [$\text{O1}-\text{C1} = 1.321(3)$ and $\text{O2}-\text{C1} = 1.197(3) \text{ \AA}$], while in the other these distances are nearly equal [$\text{C14}-\text{O3} = 1.272(2)$ and $\text{C14}-\text{O4} = 1.256(2) \text{ \AA}$], indicating that it exists as a COO^- ion. However, no proton transfer from this carboxylic acid group to an N atom of the

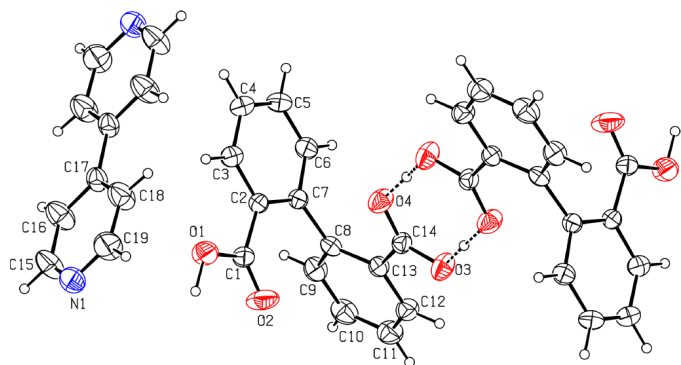


Figure 1

The structure of (I), showing 50% probability displacement ellipsoids and the atom-numbering scheme for one asymmetric unit. The other diphenic acid molecule and the other half of the bipyridine molecule are generated by the crystallographic inversion centres.

bipyridine is observed. Instead, the H^+ ion is located at a distance of 1.33 (4) Å from O3 and 1.29 (4) Å from O4ⁱ, indicating the formation of a centrosymmetric diphenic acid dimer through strong O—H...O hydrogen bonds (Table 2). The dimers are linked through C4—H4...O2ⁱⁱⁱ and C6—H6...O3^{iv} interactions to form molecular layers parallel to the (001) plane. The adjacent layers are interlinked by the bipyridine molecules through O1—H1...N1ⁱⁱ hydrogen bonds. (Symmetry codes are given in Table 2.)

Experimental

Diphenic acid and 4,4'-bipyridine were obtained from Aldrich. Equimolar quantities of diphenic acid (27 mg) and 4,4'-bipyridine (15 mg) were dissolved in 15 ml of ethanol. The resulting solution was then set aside to crystallize at room temperature.

Crystal data

$2\text{C}_{14}\text{H}_{10}\text{O}_4 \cdot \text{C}_{10}\text{H}_8\text{N}_2$	$Z = 1$
$M_r = 640.62$	$D_x = 1.326 \text{ Mg m}^{-3}$
Triclinic, $P\bar{1}$	Mo $K\alpha$ radiation
$a = 6.498 (2) \text{ \AA}$	Cell parameters from 25 reflections
$b = 8.002 (7) \text{ \AA}$	$\theta = 13.2\text{--}16.3^\circ$
$c = 16.208 (6) \text{ \AA}$	$\mu = 0.09 \text{ mm}^{-1}$
$\alpha = 99.45 (5)^\circ$	$T = 298 (2) \text{ K}$
$\beta = 100.93 (3)^\circ$	Block, colourless
$\gamma = 98.42 (5)^\circ$	$0.44 \times 0.32 \times 0.28 \text{ mm}$
$V = 802.4 (8) \text{ \AA}^3$	

Data collection

AFC-7R diffractometer	$R_{\text{int}} = 0.016$
$\omega/2\theta$ scans	$\theta_{\text{max}} = 25.0^\circ$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$h = -7 \rightarrow 7$
$T_{\text{min}} = 0.957$, $T_{\text{max}} = 0.996$	$k = 0 \rightarrow 9$
3049 measured reflections	$l = -19 \rightarrow 18$
2830 independent reflections	3 standard reflections every 250 reflections
1448 reflections with $I > 2\sigma(I)$	intensity decay: 0.9%

Refinement

Refinement on F	H atoms treated by a mixture of independent and constrained refinement
$R = 0.036$	$w = 1/[(\sigma)^2(F_o) + 0.00016(F_o)^2]$
$wR = 0.054$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.31$	$\Delta\rho_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
2830 reflections	$\Delta\rho_{\text{min}} = -0.27 \text{ e \AA}^{-3}$
225 parameters	

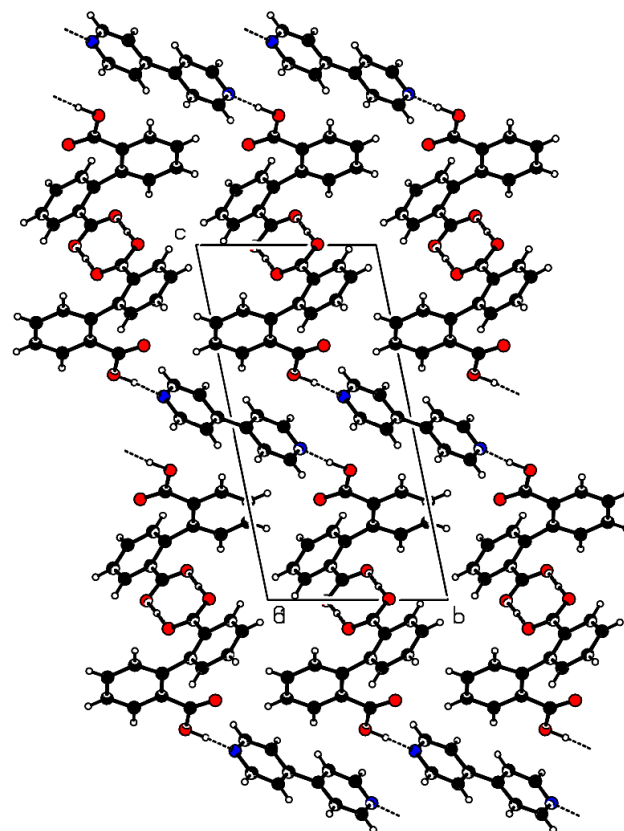


Figure 2

Molecular packing of (I), viewed down the a axis.

Table 1

Selected geometric parameters (Å).

O1—C1	1.321 (3)	C7—C8	1.498 (3)
O2—C1	1.197 (3)	C13—C14	1.486 (3)
O3—C14	1.272 (2)	C15—C16	1.375 (4)
O4—C14	1.256 (2)	C16—C17	1.370 (3)
N1—C15	1.309 (3)	C17—C17 ^v	1.497 (4)
N1—C19	1.313 (3)	C17—C18	1.368 (3)
C1—C2	1.489 (3)	C18—C19	1.382 (4)

Symmetry code: (v) $1 - x, 2 - y, 1 - z$.

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H \cdots A$	$D\text{—}H$	$H \cdots A$	$D \cdots A$	$D\text{—}H \cdots A$
O3—H2...O4 ⁱ	1.33 (4)	1.29 (4)	2.618 (3)	171 (3)
O1—H1...N1 ⁱⁱ	1.04 (3)	1.65 (3)	2.691 (4)	172 (3)
C4—H4...O2 ⁱⁱⁱ	0.95	2.56	3.235 (4)	128
C6—H6...O3 ^{iv}	0.95	2.57	3.472 (4)	158
C3—H3...O1	0.95	2.33	2.683 (4)	101
C12—H10...O3	0.95	2.39	2.730 (4)	100

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

The C-bound H atoms were placed at their geometrically calculated positions, with C—H = 0.95 Å and refined in the riding model with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. Attempts to place H2 at the calculated position resulted in a non-planar $R_2^2(8)$ ring formation, with an O—H...O angle of 133° . Hence, H1 and H2 were located in a difference Fourier map and both positional and isotropic displacement para-

meters were refined. H2 is involved in nearly symmetrical O—H···O hydrogen bonds with O···H distances of 1.33 (4) and 1.29 (4) Å, respectively.

Data collection: *AFC Diffractometer Control Software* (Molecular Structure Corporation, 1992); cell refinement: *AFC Diffractometer Control Software*; data reduction: *TEXSAN* (Molecular Structure Corporation, 1992); program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *TEXSAN*; molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *TEXSAN*.

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References

- Altomare, A., Cascarano, G., Giacovazzo, G., Guagliardi, A., Burla, M. C., Polidori, G. & Camalli, M. (1994). *J. Appl. Cryst.* **27**, 435.
- Fronczek, F. R., Davis, S. T., Gehrig, L. M. B. & Gandour, R. D. (1987). *Acta Cryst.* **C43**, 1615–1618.
- Lam, A. W.-H., Wong, W.-T., Gao, S., Wen, G. & Zhang, X.-X. (2003). *Eur. J. Inorg. Chem.* pp. 149–163.
- Molecular Structure Corporation (1992). *AFC Diffractometer Control Software*. Molecular Structure Corporation, The Woodlands, TX, USA.
- Molecular Structure Corporation (1992). *TEXSAN*. Molecular Structure Corporation, The Woodlands, TX, USA.
- North, A. C. T., Philips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Shaameri, Z., Shan, N. & Jones, W. (2001). *Acta Cryst.* **E57**, o1075–o1077.
- Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.