



# Redetermined structure of 4,4'-bipyridine–1,4-phenylenediacetic acid (1/1) co-crystal

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Received 14 September 2015; accepted 19 September 2015

Edited by W. T. A. Harrison, University of Aberdeen, Scotland

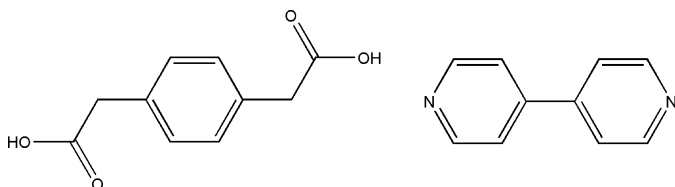
The asymmetric unit of the title 1:1 co-crystal,  $C_{10}H_8N_2 \cdot C_{10}H_{10}O_4$ , consists of one half-molecule each of 4,4'-bipyridine and 1,4-phenylenediacetic acid: the complete molecules are generated by crystallographic inversion centres. The dihedral angle between the  $-CO_2H$  group and the benzene ring in the diacid is  $73.02(7)^\circ$ . In the crystal, the components are linked by  $O-H \cdots N$  hydrogen bonds, generating  $[1\bar{2}1]$  chains of alternating amine and carboxylic acid molecules. The chains are cross-linked by  $C-H \cdots O$  interactions. This structure was previously incorrectly described as a  $(C_{10}H_{10}N_2)^{2+} \cdot (C_{10}H_8O_4)^{2-}$  molecular salt [Jia *et al.* (2009). *Acta Cryst.* **E65**, o2490–o2490].

**Keywords:** crystal structure; co-crystal; supramolecular interaction; hydrogen bonding.

**CCDC reference:** 1423417

## 1. Related literature

For the previous erroneous report of this structure as a molecular salt, see: Jia *et al.* (2009). For hydrogen-bonded co-crystals, see: Stahly (2009); Kavuru *et al.* (2010). For pharmaceutical co-crystals, see: Childs *et al.* (2009); Walsh *et al.* (2003). For a similar structure, see: Chinnakali *et al.* (1999).



## 2. Experimental

### 2.1. Crystal data

$C_{10}H_8N_2 \cdot C_{10}H_{10}O_4$	$\gamma = 97.643(7)^\circ$
$M_r = 350.36$	$V = 427.05(8) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 1$
$a = 4.5577(5) \text{ \AA}$	Mo $K\alpha$ radiation
$b = 6.9806(8) \text{ \AA}$	$\mu = 0.10 \text{ mm}^{-1}$
$c = 13.7995(15) \text{ \AA}$	$T = 296 \text{ K}$
$\alpha = 99.508(6)^\circ$	$0.20 \times 0.17 \times 0.13 \text{ mm}$
$\beta = 94.297(6)^\circ$	

### 2.2. Data collection

Bruker SMART CCD diffractometer	2405 independent reflections
8581 measured reflections	1876 reflections with $I > 2\sigma(I)$
	$R_{\text{int}} = 0.028$

### 2.3. Refinement

$R[F^2 > 2\sigma(F^2)] = 0.041$	155 parameters
$wR(F^2) = 0.123$	All H-atom parameters refined
$S = 1.05$	$\Delta\rho_{\text{max}} = 0.19 \text{ e \AA}^{-3}$
2405 reflections	$\Delta\rho_{\text{min}} = -0.16 \text{ e \AA}^{-3}$

Table 1

Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$O1-H9 \cdots N1^i$	1.02 (2)	1.62 (2)	2.6373 (13)	176 (2)
$C7-H6 \cdots O2^{ii}$	0.954 (16)	2.504 (16)	3.4196 (16)	160.8 (11)
$C9-H7 \cdots O2^{iii}$	1.00 (2)	2.45 (2)	3.4205 (18)	162.2 (16)

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

Data collection: *SMART* (Bruker, 2004); cell refinement: *SAINTE* (Bruker, 2004); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 2012); software used to prepare material for publication: *SHELXL97*.

## Acknowledgements

Financial support from the Department of Science & Technology, India (under FASTRACK Grant No. SB/FT/CS-047/2013) is gratefully acknowledged. The authors also thank the USIC, Gauhati University, Guwahati (India), for providing the X-ray diffraction data.

Supporting information for this paper is available from the IUCr electronic archives (Reference: HB7506).

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## supporting information

*Acta Cryst.* (2015). E71, o799–o800 [doi:10.1107/S2056989015017569]

## Redetermined structure of 4,4'-bipyridine–1,4-phenylenediacetic acid (1/1) co-crystal

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### S1. Comment

Co-crystals represent a class of materials which contain two or more discrete molecular entities held together *via* non-covalent or supramolecular interactions in the crystal lattice (Stahly, 2009). Due to their robust and directional nature, hydrogen bonds are extensively used as a tool to shape the structure of co-crystals (Kavuru *et al.*, 2010). In this context, hydrogen bonds of varying strengths may be employed, ranging from strong O—H $\cdots$ O/N to weak C—H $\cdots$  $\pi$  interactions. The resulting crystal structures can generate diverse physical and chemical properties such as solubility and stability that differ from the properties of the individual components. Crystal engineering plays an important role in the formation of co-crystals of desired properties so that they can find their applications in pharmaceutical industries (Childs *et al.*, 2009 and Walsh *et al.*, 2003). Herein, we report the supramolecular architecture of 1,4-phenylenediacetic acid and 4,4'-bipyridine co-crystal formed *via* O—H $\cdots$ N hydrogen bridges and C—H $\cdots$  $\pi$  interactions.

The title compound can be prepared under hydrothermal condition using a mixture of 1,4-phenylenediacetic acid and 4,4'-bipyridine (1:1) in water. The acetic acid moiety involving C1, C2, O1 and O2 in 1,4-phenylenediacetic acid molecule makes dihedral angles of 73.04 (4) $^\circ$  and 2.06 (1) $^\circ$  with the phenyl and pyridyl ring planes respectively. These values are very close to those reported by Chinnakali *et al.* (1999). The dihedral angle between phenyl and planar pyridyl rings of 4,4'-bipyridine is found to be 73.21 (4) $^\circ$ . In the crystal lattice, the molecules are linked with one another through O1—H9 $\cdots$ N1 hydrogen bonds with O $\cdots$ N distance of 2.637 (1) Å that extends in one direction leading to a supramolecular chain like structure. These zig-zag 1D chains are further connected *via* C—H $\cdots$ O bridges (C7—H6 $\cdots$ O2 and C9—H7 $\cdots$ O2 with C $\cdots$ O distances of 2.50 (1) Å and 2.45 (2) Å respectively) giving rise to a 2D layered structure in the solid state. In graph set notations (Bernstain *et al.*, 1995), such 1D chains can be described as  $C_2^2(20)$  where the subscripts and superscripts are the number of hydrogen bond donors and acceptors respectively. There are certain hydrogen bonded rings of descriptors  $R_1^2(7)$ ,  $R_4^4(16)$  and  $R_4^4(30)$  which have periodic repetitions throughout the crystal lattice. The adjacent layers are stacked in nearly parallel fashion by means of weak C—H $\cdots$  $\pi$  interactions (C $\cdots$  $\pi$  distance = 3.838 Å) between the methylene C—H and phenyl ring- $\pi$  systems. These weak intermolecular forces together with the strong hydrogen bonds form the overall 3D supramolecular architecture.

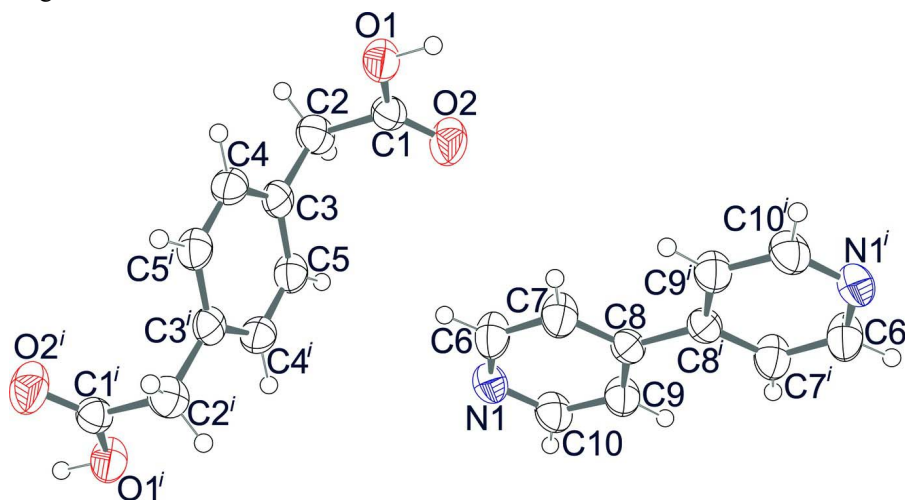
?

### S2. Synthesis and crystallization

A mixture of 1,4-phenylenediacetic acid (1 mmol, 0.194 g) and 4,4'-bipyridine (1 mmol, 0.156 g) in water (10 ml) were placed in a 23 ml Teflon lined stainless steel reaction vessel. It was then heated to 393K for 24 hours at a heating rate of 5K min $^{-1}$ . On overnight standing, rectangular block shaped colourless crystals were obtained. The crystals were then filtered off, washed with water and dried in a vacuum desiccator over fused CaCl $_2$ . Yield: 71%.

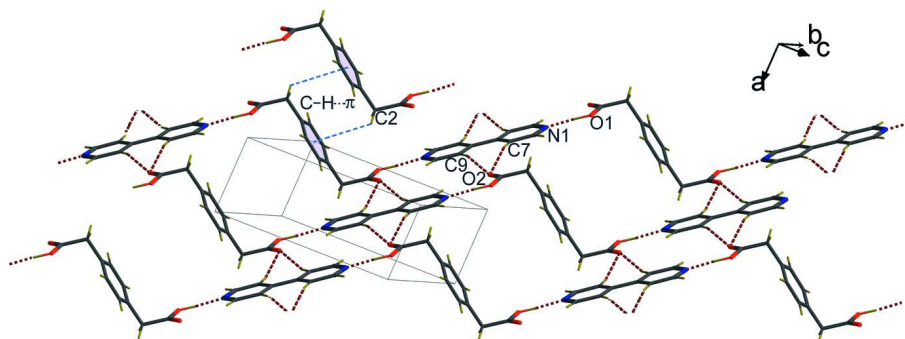
### S3. Refinement

Structure determination work was done using the *WinGX* platform (Farrugia, 2012). All the hydrogen atoms were located in difference Fourier maps and refined with isotropic atomic displacement parameters. No restraints were applied for any other parameter during structure refinement.



**Figure 1**

The molecular structure of (I) showing 50% probability displacement ellipsoids.



**Figure 2**

A view of the O—H...N, C—H...O and C—H... $\pi$  interactions observed in the crystal structure of the title compound.

#### 4,4'-Bipyridine-1,4-phenylenediacetic acid (1/1)

##### Crystal data

$C_{10}H_8N_2 \cdot C_{10}H_{10}O_4$

$M_r = 350.36$

Triclinic,  $P\bar{1}$

$a = 4.5577$  (5) Å

$b = 6.9806$  (8) Å

$c = 13.7995$  (15) Å

$\alpha = 99.508$  (6)°

$\beta = 94.297$  (6)°

$\gamma = 97.643$  (7)°

$V = 427.05$  (8) Å<sup>3</sup>

$Z = 1$

$F(000) = 184$

$D_x = 1.362$  Mg m<sup>-3</sup>

Mo  $K\alpha$  radiation,  $\lambda = 0.71073$  Å

$\mu = 0.10$  mm<sup>-1</sup>

$T = 296$  K

Rectangular block, colourless

$0.20 \times 0.17 \times 0.13$  mm

*Data collection*

Bruker SMART CCD  
diffractometer

Radiation source: fine-focus sealed tube

Graphite monochromator

phi and  $\omega$  scans

8581 measured reflections

2405 independent reflections

1876 reflections with  $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\text{max}} = 29.8^\circ$ ,  $\theta_{\text{min}} = 3.0^\circ$

$h = -6 \rightarrow 6$

$k = -9 \rightarrow 9$

$l = -19 \rightarrow 19$

*Refinement*

Refinement on  $F^2$

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.041$

$wR(F^2) = 0.123$

$S = 1.05$

2405 reflections

155 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

All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0605P)^2 + 0.0515P]$

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

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

$\Delta\rho_{\text{max}} = 0.19 \text{ e } \text{\AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.16 \text{ e } \text{\AA}^{-3}$

Extinction correction: *SHELXL*,

$F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.061 (11)

*Special details*

**Geometry.** All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.8197 (2)	0.45294 (13)	-0.18830 (6)	0.0541 (3)
C1	0.7209 (2)	0.60720 (15)	-0.21279 (8)	0.0408 (3)
C2	0.5619 (3)	0.71533 (19)	-0.13310 (10)	0.0490 (3)
C3	0.7850 (2)	0.86342 (15)	-0.06291 (8)	0.0400 (3)
C4	0.9459 (3)	0.80852 (16)	0.01476 (9)	0.0454 (3)
C5	0.8422 (3)	1.05717 (17)	-0.07687 (8)	0.0446 (3)
O2	0.7616 (3)	0.66207 (15)	-0.28973 (7)	0.0675 (3)
N1	0.8832 (2)	0.73182 (15)	0.32203 (7)	0.0476 (3)
C6	0.8316 (3)	0.67172 (18)	0.40629 (9)	0.0517 (3)
C7	0.6844 (3)	0.77149 (18)	0.47798 (9)	0.0487 (3)
C8	0.5796 (2)	0.94340 (15)	0.46266 (7)	0.0376 (2)
C10	0.7840 (3)	0.8964 (2)	0.30711 (10)	0.0566 (3)
C9	0.6326 (3)	1.00451 (19)	0.37423 (9)	0.0532 (3)
H9	0.927 (5)	0.382 (3)	-0.2421 (15)	0.104 (7)*
H3	0.908 (3)	0.676 (2)	0.0263 (11)	0.061 (4)*

H4	0.731 (3)	1.100 (2)	-0.1302 (11)	0.055 (4)*
H6	0.660 (3)	0.722 (2)	0.5378 (12)	0.067 (4)*
H1	0.462 (4)	0.621 (2)	-0.0977 (12)	0.065 (4)*
H8	0.822 (4)	0.935 (2)	0.2459 (13)	0.073 (5)*
H7	0.560 (4)	1.122 (3)	0.3533 (13)	0.081 (5)*
H2	0.412 (4)	0.787 (3)	-0.1669 (12)	0.071 (5)*
H5	0.902 (4)	0.551 (3)	0.4159 (12)	0.071 (4)*

*Atomic displacement parameters (Å<sup>2</sup>)*

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
O1	0.0764 (6)	0.0483 (5)	0.0463 (5)	0.0272 (4)	0.0173 (4)	0.0141 (4)
C1	0.0449 (6)	0.0370 (5)	0.0403 (5)	0.0071 (4)	0.0035 (4)	0.0055 (4)
C2	0.0434 (6)	0.0489 (6)	0.0549 (7)	0.0115 (5)	0.0119 (5)	0.0025 (5)
C3	0.0431 (5)	0.0405 (5)	0.0396 (5)	0.0148 (4)	0.0163 (4)	0.0046 (4)
C4	0.0580 (7)	0.0363 (5)	0.0467 (6)	0.0141 (5)	0.0146 (5)	0.0116 (4)
C5	0.0545 (7)	0.0452 (6)	0.0394 (5)	0.0184 (5)	0.0097 (5)	0.0116 (4)
O2	0.1023 (8)	0.0630 (6)	0.0502 (5)	0.0351 (6)	0.0215 (5)	0.0232 (4)
N1	0.0507 (6)	0.0478 (5)	0.0450 (5)	0.0158 (4)	0.0075 (4)	0.0023 (4)
C6	0.0643 (8)	0.0439 (6)	0.0511 (7)	0.0221 (6)	0.0096 (6)	0.0075 (5)
C7	0.0631 (7)	0.0441 (6)	0.0443 (6)	0.0189 (5)	0.0116 (5)	0.0117 (5)
C8	0.0370 (5)	0.0374 (5)	0.0379 (5)	0.0073 (4)	0.0026 (4)	0.0045 (4)
C10	0.0714 (9)	0.0614 (8)	0.0466 (7)	0.0285 (6)	0.0200 (6)	0.0159 (6)
C9	0.0691 (8)	0.0515 (7)	0.0490 (6)	0.0284 (6)	0.0181 (6)	0.0166 (5)

*Geometric parameters (Å, °)*

O1—C1	1.3051 (13)	C5—H4	0.972 (14)
O1—H9	1.02 (2)	N1—C6	1.3264 (16)
C1—O2	1.2056 (14)	N1—C10	1.3301 (16)
C1—C2	1.5147 (16)	C6—C7	1.3820 (17)
C2—C3	1.5108 (17)	C6—H5	0.964 (17)
C2—H1	0.970 (16)	C7—C8	1.3906 (15)
C2—H2	1.027 (17)	C7—H6	0.955 (16)
C3—C4	1.3877 (16)	C8—C9	1.3850 (16)
C3—C5	1.3908 (15)	C8—C8 <sup>ii</sup>	1.486 (2)
C4—C5 <sup>i</sup>	1.3844 (18)	C10—C9	1.3810 (17)
C4—H3	0.961 (15)	C10—H8	0.950 (18)
C5—C4 <sup>i</sup>	1.3844 (18)	C9—H7	0.998 (19)
C1—O1—H9	112.6 (12)	C3—C5—H4	120.1 (8)
O2—C1—O1	123.26 (10)	C6—N1—C10	117.10 (10)
O2—C1—C2	123.39 (11)	N1—C6—C7	123.47 (11)
O1—C1—C2	113.30 (10)	N1—C6—H5	116.3 (10)
C3—C2—C1	109.58 (9)	C7—C6—H5	120.2 (10)
C3—C2—H1	110.0 (9)	C6—C7—C8	119.66 (11)
C1—C2—H1	108.9 (10)	C6—C7—H6	119.0 (10)
C3—C2—H2	109.4 (9)	C8—C7—H6	121.4 (10)

C1—C2—H2	107.7 (9)	C9—C8—C7	116.53 (10)
H1—C2—H2	111.2 (13)	C9—C8—C8 <sup>ii</sup>	121.59 (12)
C4—C3—C5	118.28 (11)	C7—C8—C8 <sup>ii</sup>	121.88 (12)
C4—C3—C2	121.06 (10)	N1—C10—C9	123.35 (12)
C5—C3—C2	120.61 (10)	N1—C10—H8	115.3 (10)
C5 <sup>i</sup> —C4—C3	120.99 (10)	C9—C10—H8	121.3 (10)
C5 <sup>i</sup> —C4—H3	119.3 (9)	C10—C9—C8	119.89 (11)
C3—C4—H3	119.7 (9)	C10—C9—H7	116.0 (11)
C4 <sup>i</sup> —C5—C3	120.73 (11)	C8—C9—H7	124.1 (11)
C4 <sup>i</sup> —C5—H4	119.2 (8)		

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

*Hydrogen-bond geometry (Å, °)*

<i>D—H...A</i>	<i>D—H</i>	<i>H...A</i>	<i>D...A</i>	<i>D—H...A</i>
O1—H9...N1 <sup>iii</sup>	1.02 (2)	1.62 (2)	2.6373 (13)	176 (2)
C7—H6...O2 <sup>iv</sup>	0.954 (16)	2.504 (16)	3.4196 (16)	160.8 (11)
C9—H7...O2 <sup>v</sup>	1.00 (2)	2.45 (2)	3.4205 (18)	162.2 (16)

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