

4-Pyridone–terephthalic acid–water  
(2/1/2) and bis(3-hydroxypyridinium)  
terephthalate

Selena L. Staun and Allen G. Oliver\*

Department of Chemistry and Biochemistry, University of Notre Dame, Notre Dame,  
IN 46556-5670, USA

Correspondence e-mail: aoliver2@nd.edu

Received 23 November 2011

Accepted 22 December 2011

Online 12 January 2012

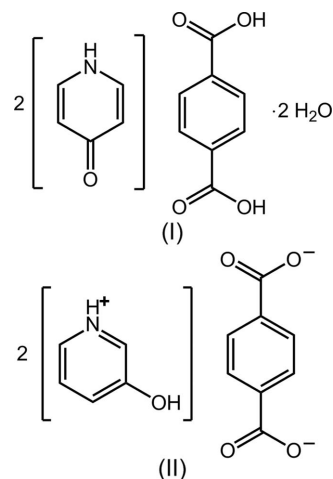
4-Hydroxypyridine and terephthalic acid cocrystallize as a hydrate, 4-pyridone–terephthalic acid–water (2/1/2),  $2C_5H_5NO \cdot C_8H_6O_4 \cdot 2H_2O$ , from a methanol–water solution. The molecules form a two-dimensional hydrogen-bonded network resulting in sheets of hydrogen-bonded molecules that lie parallel to the  $(10\bar{2})$  plane. In contrast, 3-hydroxypyridine and terephthalic acid form the salt bis(3-hydroxypyridinium) terephthalate,  $2C_5H_6NO^+ \cdot C_8H_4O_4^{2-}$ , giving rise to two-dimensional hydrogen-bonded sheets extending through the lattice parallel to the  $(10\bar{2})$  plane.

## Comment

Crystal engineering is a rapidly evolving field of chemistry that relies on intermolecular interactions such as hydrogen bonds to form new materials (Desiraju, 2003). The cocrystallization of two dissimilar compounds has led to an extensive body of work (see, for example, Bucar *et al.*, 2007; MacGillivray, 2008; Ugono *et al.*, 2011). Subtle differences in electronegativity and  $pK_a$  can influence the packing arrangement of these constituent molecules (Aakeröy *et al.*, 2009). Terephthalic acid has been used successfully as a cocrystallant in crystal engineering studies (Lemmerer, 2011). Both 3- and 4-hydroxypyridine and derivatives thereof have been incorporated as linker and spacer molecules in metal–organic frameworks (Castillo *et al.*, 2001; Gao *et al.*, 2006). Here, we present the structural study of the combination of terephthalic acid with 3- and 4-hydroxypyridine.

Terephthalic acid and 4-hydroxypyridine were found to cocrystallize with water to give the formulation 4-pyridone–terephthalic acid–water (2/1/2), (I) (Fig. 1). 4-Hydroxypyridine was found to rearrange to 4-pyridone, a rearrangement which has been previously reported (Tyl *et al.*, 2008). The 4-pyridone molecule presented here displays identical geometric parameters to those in Tyl's work. The terephthalic acid molecule crystallizes on a centre of inversion at  $(\frac{1}{2}, \frac{1}{2}, \frac{1}{2})$ .

The terephthalic acid molecule of (I) forms hydrogen-bonded chains incorporating the water molecule that extend parallel to the  $b$  axis. The 4-pyridone molecule also forms hydrogen-bonded chains, with hydrogen bonds from the N atom to the pyridone O atom of an adjacent pyridone molecule (Table 1 and Fig. 2a). The water H atom not involved in the carboxylic acid chain forms a hydrogen bond to the pyridone O atom, linking the two chains together. This results in two-dimensional sheets of hydrogen-bonded molecules extending through the lattice parallel to the  $(10\bar{2})$  plane (Fig. 2b).



Terephthalic acid and 3-hydroxypyridine were found to crystallize as the bis(3-hydroxypyridinium) terephthalate salt, (II) (Fig. 3). This mixture has been previously reported as a room-temperature analysis [Yao *et al.*, 2007; Cambridge Structural Database (CSD, Version 5.32; Allen, 2002) refcode DIWXOX]. The derived metrics reported here are similar to those found in Yao's work. As expected, upon cooling there is distortion of the unit cell, with  $a$  and  $c$  contracting [4.9245 (4) and 10.3256 (9) Å, respectively, compared with 4.978 (1) and

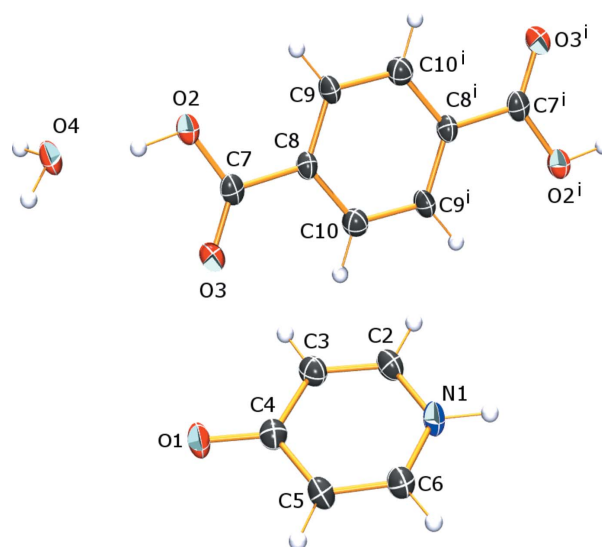
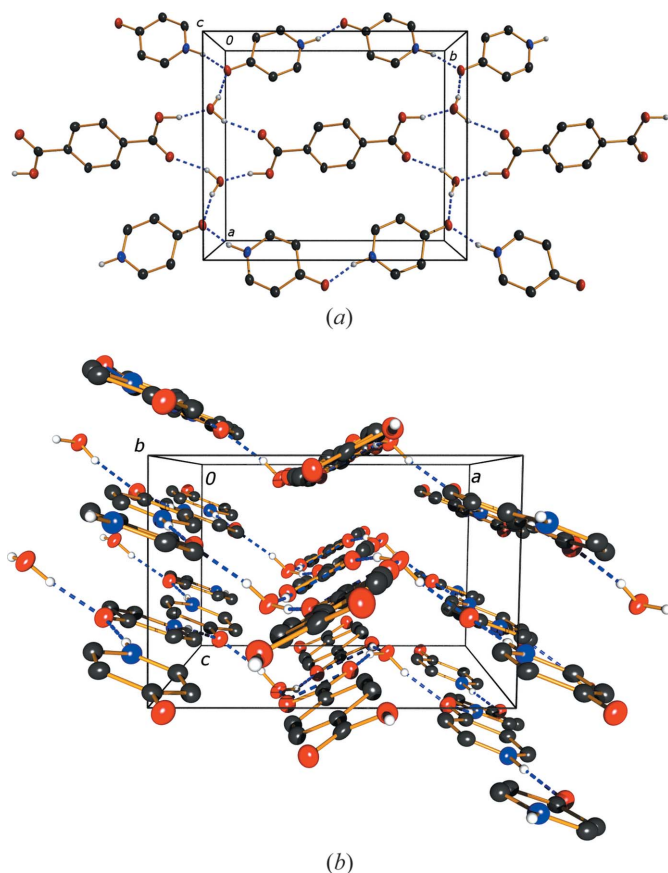


Figure 1

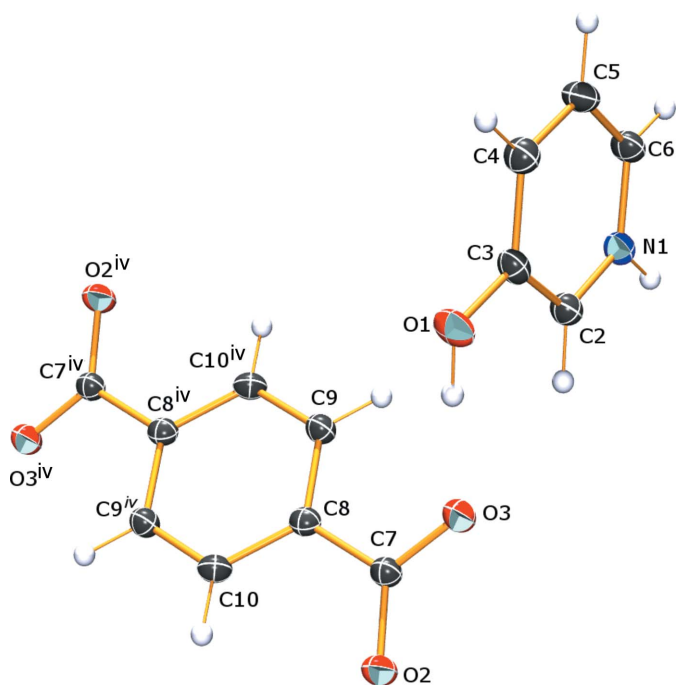
The atom-labelling scheme for (I). Displacement ellipsoids are depicted at the 50% probability level. [Symmetry code: (i)  $-x + 1, -y + 1, -z + 1$ ].

**Figure 2**

Packing diagrams for (I), viewed (a) along the *c* axis, depicting one layer of the two-dimensional network, and (b) along the *b* axis, depicting the two-dimensional sheets running parallel to the  $(10\bar{2})$  plane. Hydrogen bonds are represented by dashed lines.

10.623 (1) Å in Yao's work]. However, the *b* axis remains the same and  $\beta$  distorts significantly [ $b = 15.7128$  (14) Å and  $\beta = 98.386$  (5)° in this work, compared with  $b = 15.705$  (3) Å and  $\beta = 100.20$  (1)° in Yao's work]. Care should be taken when utilizing data-mining techniques; use of multiple search parameters may reveal information overlooked when only one parameter is used. The cocrystallization of (II) was also found to occur under milder conditions than those previously reported (see *Experimental* for details, cf. hydrothermal techniques for Yao's synthesis). Presumably, 3-hydroxypyridine is a strong enough Lewis base to abstract the H atom from the carboxylic acid under ambient conditions [ $pK_a(3\text{-hydroxypyridine}) = 4.80$  (Güven, 2005);  $pK_a(\text{terephthalic acid}) = 3.51$  and 4.82 (Braude & Nachod, 1955)].

Unlike (I), water is not incorporated into the lattice of (II) and it is purely a simple salt. Similar to (I), the terephthalate anion in (II) is found to crystallize about an inversion centre at  $(0, \frac{1}{2}, 0)$ . Presumably due to electronic constraints, the 3-hydroxypyridine molecule does not rearrange to form a pyridone. Instead, 3-hydroxypyridine abstracts the carboxyl H atom from terephthalic acid, forming a cation–anion pair. Unlike 4-hydroxypyridine, which can rearrange and localize its formal electronic structure to the pyridone, 3-hydroxypyridine cannot readily localize the aromatic bonds to incorporate a

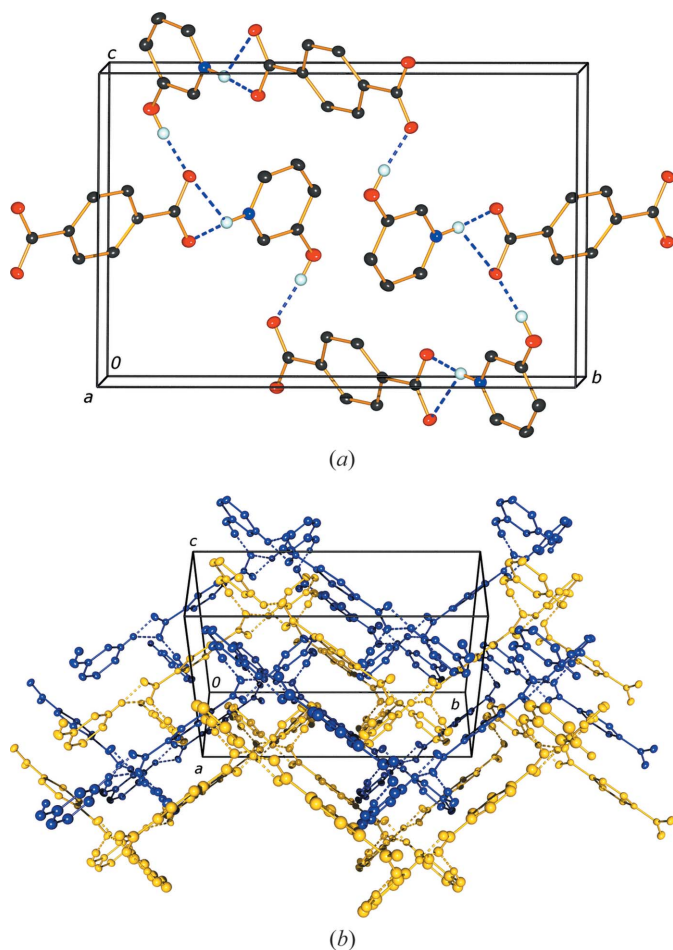
**Figure 3**

The atom-abelling scheme for (II). Displacement ellipsoids are depicted at the 50% probability level. [Symmetry code: (iv)  $-x + 1, -y + 1, -z$ .]

carbonyl group at the 3-position. Hence, it retains the 3-hydroxy substituent and forms a cation. A similar hydrogen abstraction was observed by Lemmerer (2011), wherein a series of primary amines were cocrystallized with terephthalic acid yielding similar cation–anion pairs.

One carboxylate O atom of (II) (O2) accepts a hydrogen bond from the pyridinium N atom related by the *c*-glide plane. Atom O3 accepts a hydrogen bond from the hydroxy O atom (O1) of the 3-hydroxypyridinium cation. This generates a two-dimensional sheet of hydrogen-bonded molecules (Fig. 4a). Formally, the framework is a 2,4-connected square net, with the pyridinium forming the edges of the square and the terephthalate the corners (analysis using *TOPOS*; Blatov, 2006). The sheets lie in a plane parallel to the  $(10\bar{2})$  crystallographic plane. The topology viewed approximately parallel to the  $(10\bar{2})$  plane is depicted in Fig. 4(b).

In the previous characterization (Yao *et al.*, 2007), the dihedral angle formed by the pyridinium and benzene rings was reported to be 2.2°. Yao *et al.* appear to have overlooked the extended packing of (II) in their report. The compounds form a two-dimensional network (described above), yielding additional information about the intermolecular geometry. For example, the dihedral angle between the planes of the terephthalate and the pyridinium ions is dependent upon the choice of location of pyridinium and terephthalate within the lattice. We found that the plane of one pyridinium cation within the network is almost perpendicular to the plane of the benzene ring of the terephthalate [dihedral angle formed by the planes of the pyridinium and benzene rings = 78.79 (7)°] and another cation that is closer to coplanar with the benzene ring [interplanar angle = 9.61 (16)°]. This choice depends on



**Figure 4**  
Packing diagrams for (II), viewed (a) along the *a* axis of the square net subunit within the layers and (b) approximately parallel to the (102) plane, showing the overall packing of the sheets (in the electronic version of the paper, alternate sheets are coloured blue and gold for clarity). Hydrogen bonds are represented by dashed lines.

which hydrogen-bonding group (amide or hydroxy) is selected as the orienting group.

## Experimental

To 4-hydroxypyridine (12 mg) and terephthalic acid (15 mg) were added methanol (5 ml) and water (5 ml) in a 20 ml vial. This solution was allowed to evaporate and colourless blade-like crystals of (I) were harvested. In the same manner, 3-hydroxypyridine (27 mg) and terephthalic acid (33 mg) were dissolved in methanol (5 ml) and water (5 ml) in a 20 ml vial and the solvents allowed to evaporate. Colourless columnar crystals of (II) were harvested.

## Compound (I)

### Crystal data

$2C_5H_5NO \cdot C_8H_6O_4 \cdot 2H_2O$   $V = 887.6 (4) \text{ \AA}^3$   
 $M_r = 392.36$   $Z = 2$   
 Monoclinic,  $P2_1/c$  Mo  $K\alpha$  radiation  
 $a = 10.412 (2) \text{ \AA}$   $\mu = 0.12 \text{ mm}^{-1}$   
 $b = 11.994 (3) \text{ \AA}$   $T = 120 \text{ K}$   
 $c = 7.1077 (17) \text{ \AA}$   $0.23 \times 0.05 \times 0.02 \text{ mm}$   
 $\beta = 90.743 (4)^\circ$

**Table 1**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (I).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O2—H2...O4	0.84	1.75	2.5753 (17)	167
O4—H4Y...O3 <sup>i</sup>	0.85 (1)	2.05 (1)	2.8379 (18)	155 (2)
O4—H4Z...O1 <sup>i</sup>	0.85 (1)	1.85 (1)	2.6951 (18)	176 (2)
N1—H1N...O1 <sup>ii</sup>	0.88	1.80	2.6628 (19)	168

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

### Data collection

Bruker APEXII Kappa X8 area-detector diffractometer 15289 measured reflections  
 2214 independent reflections  
 Absorption correction: numerical (SADABS; Sheldrick, 2008) 1589 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.070$   
 $T_{min} = 0.907, T_{max} = 1.000$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$  H atoms treated by a mixture of independent and constrained refinement  
 $wR(F^2) = 0.104$   
 $S = 1.04$   
 2214 reflections  
 134 parameters  
 2 restraints  
 $\Delta\rho_{max} = 0.26 \text{ e \AA}^{-3}$   
 $\Delta\rho_{min} = -0.27 \text{ e \AA}^{-3}$

## Compound (II)

### Crystal data

$2C_5H_6NO^+ \cdot C_8H_4O_4^{2-}$   $V = 790.43 (12) \text{ \AA}^3$   
 $M_r = 356.33$   $Z = 2$   
 Monoclinic,  $P2_1/c$  Mo  $K\alpha$  radiation  
 $a = 4.9245 (4) \text{ \AA}$   $\mu = 0.11 \text{ mm}^{-1}$   
 $b = 15.7128 (14) \text{ \AA}$   $T = 120 \text{ K}$   
 $c = 10.3256 (9) \text{ \AA}$   $0.25 \times 0.23 \times 0.15 \text{ mm}$   
 $\beta = 98.386 (5)^\circ$

### Data collection

Bruker APEXII Kappa X8 area-detector diffractometer 16777 measured reflections  
 1979 independent reflections  
 Absorption correction: numerical (SADABS; Sheldrick, 2008) 1735 reflections with  $I > 2\sigma(I)$   
 $R_{int} = 0.024$   
 $T_{min} = 0.927, T_{max} = 1.000$

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$  119 parameters  
 $wR(F^2) = 0.094$  H-atom parameters constrained  
 $S = 1.02$   $\Delta\rho_{max} = 0.37 \text{ e \AA}^{-3}$   
 1979 reflections  $\Delta\rho_{min} = -0.22 \text{ e \AA}^{-3}$

All C-bound H atoms were included in geometrically calculated positions, with C—H = 0.95  $\text{\AA}$ . The pyridone, carboxylic acid, water and hydroxy H atoms were initially located from a difference Fourier map in positions that form good hydrogen bonds to nearby acceptors. Water O—H distances were restrained to 0.84 (1)  $\text{\AA}$ , carboxylic acid and hydroxy O—H distances were constrained to 0.84  $\text{\AA}$ , and amine N—H distances were constrained to 0.88  $\text{\AA}$ . All O-bound H atoms

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ) for (II).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
O1—H1O...O3	0.84	1.74	2.5767 (12)	174
N1—H1N...O2 <sup>i</sup>	0.88	1.73	2.6072 (12)	173
N1—H1N...O3 <sup>i</sup>	0.88	2.47	3.0651 (12)	125

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

were refined with  $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$ . All other H atoms were refined with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{parent atom})$ .

For both compounds, data collection: *APEX2* (Bruker, 2008); cell refinement: *SAINT* (Bruker, 2008); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* (Sheldrick, 2008), *POV-RAY* (Cason, 2003) and *DIAMOND* (Brandenburg, 2009). Software used to prepare material for publication: *XCIF* (Sheldrick, 2008), *enCIFer* (Allen *et al.*, 2004) and *pubCIF* (Westrip, 2010) for (I); *XCIF*, *enCIFer*, *pubCIF* and *TOPOS* (Blatov, 2006) for (II).

SLS thanks the Indiana Academy of Science for a Junior Research Grant. We also thank Jeffery Bertke for the donation of compounds and insightful discussions.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: MX3062). Services for accessing these data are described at the back of the journal.

## References

- Aakeröy, C. B., Forbes, S. & Desper, J. (2009). *J. Am. Chem. Soc.* **131**, 17048–17049.
- Allen, F. H. (2002). *Acta Cryst.* **B58**, 380–388.
- Allen, F. H., Johnson, O., Shields, G. P., Smith, B. R. & Towler, M. (2004). - *J. Appl. Cryst.* **37**, 335–338.
- Blatov, V. A. (2006). *IUCr Comput. Comm. Newsl.* **7**, 4–38.
- Brandenburg, K. (2009). *DIAMOND*. Crystal Impact GbR, Bonn, Germany.
- Braude, E. A. & Nachod, F. C. (1955). In *Determination of Organic Structures by Physical Methods*. New York: Academic Press.
- Bruker (2008). *APEX2* and *SAINT*. Bruker–Nonius AXS Inc., Madison, Wisconsin, USA.
- Bucar, D.-K., Henry, R. F., Lou, X., Borchardt, T. B., MacGillivray, L. R. & Zhang, G. G. Z. (2007). *Mol. Pharm.* **4**, 339–346.
- Cason, C. J. (2003). *POV-RAY*. Persistence of Vision Raytracer Pty. Ltd, Victoria, Australia.
- Castillo, O., Luque, A., Julve, M., Lloret, F. & Román, P. (2001). *Inorg. Chim. Acta*, **315**, 9–17.
- Desiraju, G. R. (2003). *J. Mol. Struct.* **656**, 5–15.
- Gao, H.-L., Yi, L., Zhao, B., Zhao, X.-Q., Cheng, P., Liao, D.-Z. & Yan, S.-P. (2006). *Inorg. Chem.* **45**, 5980–5988.
- Güven, A. (2005). *Int. J. Mol. Sci.* **6**, 257–275.
- Lemmerer, A. (2011). *Cryst. Growth Des.* **11**, 583–593.
- MacGillivray, L. R. (2008). *J. Org. Chem.* **73**, 3311–3317.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Tyl, A., Nowak, M. & Kusz, J. (2008). *Acta Cryst.* **C64**, o661–o664.
- Ugono, O., Rath, N. P. & Beatty, A. M. (2011). *CrystEngComm*, **13**, 753–758.
- Westrip, S. P. (2010). *J. Appl. Cryst.* **43**, 920–925.
- Yao, J.-C., Qin, J.-H., Sun, Q.-B., Qu, L. & Li, Y.-G. (2007). *Z. Kristallogr. New Cryst. Struct.* **222**, 371–372.