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Hydrogen-bonded 1:1 adduct of 1,1′-(*p*-phenylene)dipyridin-4(1*H*)-one with terephthalic acid

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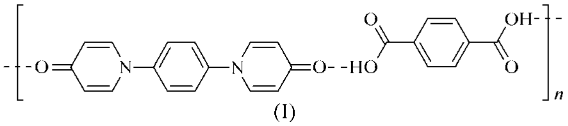
Cocrystallization of 1,1′-(*p*-phenylene)dipyridin-4(1*H*)-one (4,4′-dpy) and terephthalic acid (tpa) affords the hydrogen-bonded 1:1 title complex, $C_{16}H_{12}N_2O_2 \cdot C_8H_6O_4$. Both molecules are symmetrically disposed about independent symmetry centers. Strong O—H···O hydrogen bonds between tpa carboxyl groups and 4,4′-dpy carbonyl groups produce one-dimensional zigzag infinite chains. Each chain is linked to four surrounding chains *via* weak C—H···O interactions, resulting in a three-dimensional molecular framework.

Comment

Derivatives of 4,4′-bipyridine (hereafter, 4,4′-bpy) have been widely studied as versatile building blocks in various branches of chemistry, including coordination polymers (Würthner *et al.*, 2004), hydrogen-bonded adducts (Jayaraman *et al.*, 2006), and metal-organic frameworks (Yaghi *et al.*, 2003). Whenever 4,4′-bpy takes part in the formation of hydrogen-bonded adducts containing COOH groups, O—H···N hydrogen bonds are conventionally formed; this behavior is attributed to strong acid–base binary interactions (Du *et al.*, 2005*a*,*b*). However, the structure of the hydrogen-bonded adduct 1-(4-pyridyl)pyridin-4-one–acetic acid indicated that pyrid-4-one moiety can compete with pyridine to be a more effective hydrogen-bond acceptor (Goodgame *et al.*, 2001). Surprisingly, there is no report on 1,1′-(*p*-phenylene)dipyridin-4(1*H*)-one (hereafter, 4,4′-dpy), an analogue of 4,4′-bpy with an extended rigid aromatic core. Therefore, the present paper is the first report of the synthesis of 4,4′-dpy and its cocrystallization with terephthalic acid (hereafter, tpa) to form a hydrogen-bonded adduct, 4,4′-dpy·tpa, (I). This adduct may be useful in the field of crystal engineering and supramolecular chemistry.



(I)

X-ray crystal structure analysis shows that 4,4′-dpy cocrystallizes with tpa in a 1:1 molar ratio, consistent with the ratio of hydrogen-bond donor (OH) and acceptor (4,4′-dpy C═O) sites. The asymmetric unit contains one half-molecule of each of 4,4′-dpy and tpa. Inversion over centers of symmetry located at the center of the central 4,4′-dpy ring $(1, \frac{1}{2}, \frac{1}{2})$ and the center of the tpa ring $(-\frac{1}{2}, \frac{1}{2}, 0)$ generates the full molecule

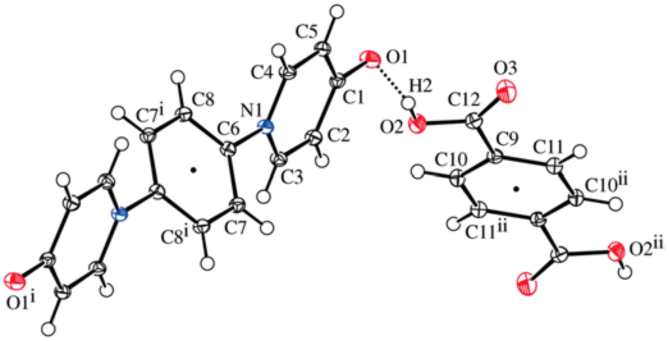


Figure 1
The molecular structure and atom-numbering scheme for (I), with displacement ellipsoids drawn at the 50% probability level. The dashed line represents a hydrogen bond and the black circles denote inversion centers. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x - 1, -y + 1, -z$.]

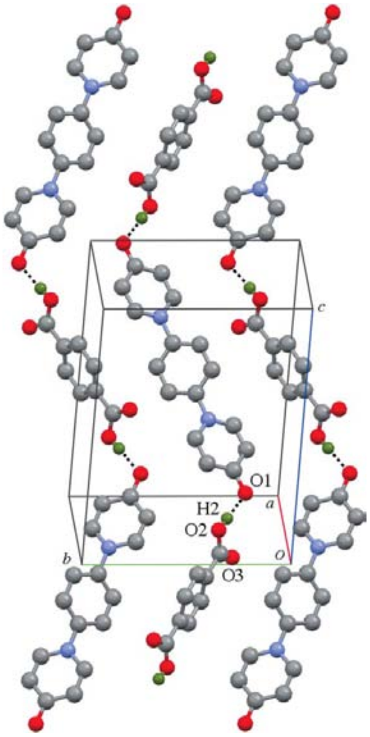


Figure 2
Rows of hydrogen-bonded chains in (I), as viewed in the $(\bar{1}04)$ plane; dashed lines represent hydrogen bonds. Within this plane, no C—H···O interactions occur.

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in both cases. The resulting structure is shown in Fig. 1, along with the atom-numbering scheme. The dihedral angle between the planes of the pyridone ring of 4,4′-dpy and the central tpa ring is 118.88 (4)°. The crystallographically equivalent terminal pyridone rings form dihedral angles of 46.73 (4)° with the plane of the central benzene ring, and atom O1 is essentially in the pyridone ring plane. For the tpa component, the two COOH groups adopt a *trans*-coplanar conformation in relation to the benzene ring, and the O2/O3/C12 plane is at an angle of 15.04 (10)° to the C9/C10/C11 plane, primarily as a result of rotation around the C9—C12 vector, since atom C12 lies only 0.043 (1) Å out of the C9/C10/C11 plane. No bond distances or angles of interest were noted.

As can be seen in Figs. 1 and 2, the 4,4′-dpy and tpa components are connected through strong O2—H2···O1 interactions, generating infinite one-dimensional zigzag chains parallel to the ($\overline{1}04$) plane. Within this plane, the chains are not interconnected, evidently because the tpa molecules are oriented nearly normal to ($\overline{1}04$), making their O3 acceptor atoms inaccessible to donors within the plane, as can be seen in Figs. 2 and 3; however, each chain is surrounded by, and hydrogen bonded to, four additional chains [two in front of and two behind ($\overline{1}04$)] *via* weak C8—H8···O3 interactions, as illustrated in Fig. 3. (Note that each of the four individual molecules shown in Fig. 3 represents a small section of a separate and distinct chain.) These four chains are symmetrically disposed about the central chain and C—H···O interactions link the chains into a three-dimensional framework. Shan *et al.* (2002) conducted a Cambridge Structural Database (Allen, 2002) survey of hydrogen-bond geometry in 4,4′-bpy–carboxylic acid adducts and reported an average H···*A* distance of 1.65 Å, *D*—*A* distances ranging between 2.60 and 2.65 Å, and *D*—H···*A* angles in the range 165–180°. These values are similar to the hydrogen-bond geometry found in (I), as reported in Table 1.

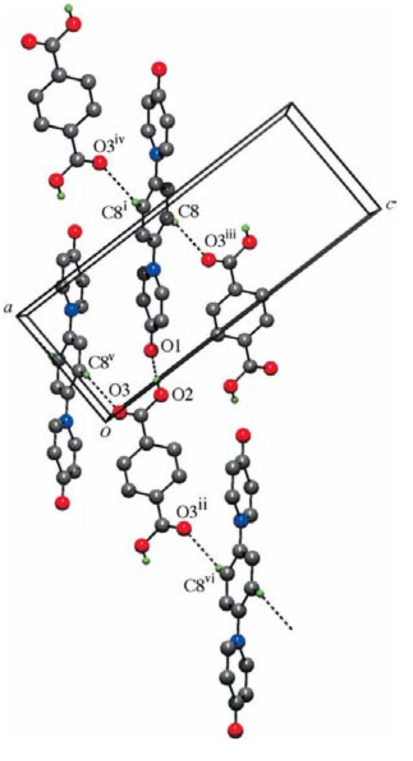

Figure 3
C—H···O hydrogen bonding in (I), as viewed down [010]. The central chain interacts with four surrounding chains through C8—H8···O3 interactions at O3^{iii}, O3^{iv}, C8^{v} and C8^{vi}. The trace of the ($\overline{1}04$) plane is vertical and only one molecule from each surrounding chain is shown for clarity. H atoms not involved in hydrogen bonding have also been omitted. [Symmetry codes: (i) $-x + 2, -y + 1, -z + 1$; (ii) $-x - 1, -y + 1, -z$; (iii) $x + \frac{1}{2}, -y + \frac{1}{2}, z + \frac{1}{2}$; (iv) $-x + \frac{3}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$; (v) $x - \frac{1}{2}, -y + \frac{1}{2}, z - \frac{1}{2}$; (vi) $-x - \frac{1}{2}, y + \frac{1}{2}, -z + \frac{1}{2}$.]

In conclusion, this work indicates that 4,4′-dpy is potentially an excellent hydrogen-bond acceptor; notably, (I) is the first utilization of these types of molecules in crystal engineering and supramolecular chemistry.

Experimental

4,4′-Dpy was prepared by a modified literature procedure (You & Twieg, 1999). 1, 4-Difluorobenzene (0.57 g, 5.0 mmol) and 4-hydroxypyridine (1.90 g, 20.0 mmol) were dissolved in *N*-methylpyrrolidone (NMP, 6 ml). Anhydrous K_2CO_3 (2.76 g, 20.0 mmol) was added, and the resulting mixture was heated at 423 K under argon overnight. After cooling to room temperature, the mixture was diluted with water and the precipitate was collected by vacuum filtration. Recrystallization from methanol/water gave 0.22 g of colorless 4,4′-dpy (m.p. 480.3 K, yield 17%). R_F = 0.24 (90/10, CH_2Cl_2/MeOH); ^{1}H NMR (300 MHz, CD_3OD): δ 8.15 (*d*, *J* = 7.2 Hz, 4H), 7.80 (*s*, 4H), 6.61 (*d*, *J* = 7.2 Hz, 4H); ^{13}C NMR (75 MHz, CD_3OD): δ 180.21, 141.08, 124.83, 117.80. Dilute solutions of 4,4′-dpy and tpa, both in CH_3OH, were mixed and allowed to stand at room temperature until solvent evaporation produced colorless plate-shaped crystals of (I). ^{1}H NMR (400 MHz, DMSO): δ 13.27 (broad, COOH), 8.02 (*d*, *J* = 7.6 Hz, 4H), 8.01 (*s*, 4H), 7.73 (*s*, 4H), 6.23 (*d*, *J* = 7.6 Hz, 4H); ^{13}C NMR (100 MHz, DMSO): δ 178.1 (C=O), 167.3 (COOH), 142.4, 140.3, 130.1, 124.6, 118.7; IR (KBr, cm^{-1}): 1700, 1676, 1636, 1633.

Crystal data

$C_{16}H_{12}N_2O_2 \cdot C_8H_6O_4$
$M_r = 430.40$
Monoclinic, $P2_1/n$
$a = 6.0931$ (2) Å
$b = 10.2759$ (3) Å
$c = 15.2973$ (5) Å
$\beta = 92.148$ (1)°
$V = 957.12$ (5) Å^3
$Z = 2$
$D_x = 1.493$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.11$ mm^{-1}
$T = 100$ (2) K
Prism cut from plate, colorless
0.37 × 0.27 × 0.22 mm

Data collection

Bruker Kappa-APEX-II CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
$T_{min} = 0.916$, $T_{max} = 0.976$
17765 measured reflections
3717 independent reflections
3183 reflections with $I > 2\sigma(I)$
$R_{int} = 0.026$
$\theta_{max} = 33.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.041$
$wR(F^2) = 0.121$
$S = 1.05$
3717 reflections
146 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0683P)^2 + 0.2721P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.26$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O2—H2···O1	0.82	1.71	2.5228 (10)	175
C8—H8···O3^{iii}	0.93	2.47	3.1628 (11)	132

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

The location of the hydroxy H atom was optimized by the circular Fourier method available in *SHELXL97* (Sheldrick, 1997). All H atoms were treated as riding, with O—H and C—H distances of 0.82 and 0.93 Å, respectively, and U_{iso}(H) values equal to 1.5 (hydroxy) or 1.2 times (all other H atoms) U_{eq} of the parent atom.

Data collection: *APEXII* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT* and *SADABS* (Bruker, 2005); program(s) used to solve structure: *SIR92* (Burla *et al.*, 1989); program(s) used to refine structure: *LS* in *TEXSAN* (Molecular Structure Corporation, 1997) and *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003) and *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: GZ3009). Services for accessing these data are described at the back of the journal.

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