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The cocrystal of 3-hydroxy-2-naphthoic acid and 4,4′-bipyridine

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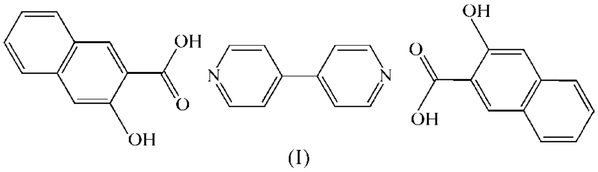
4,4′-Bipyridine cocrystallizes with 3-hydroxy-2-naphthoic acid in a 1:2 ratio to give a centrosymmetric three-component supramolecular adduct, namely 3-hydroxy-2-naphthoic acid–4,4′-bipyridine (2/1), $C_{11}H_8O_3{\cdot}0.5C_{10}H_8N_2$, in which 4,4′-bipyridine is located on an inversion center. The pyridine–carboxylic acid heterosynthon generates an infinite one-dimensional hydrogen-bonded chain *via* π–π interactions between naphthyl and 4,4′-bipyridine groups. The one-dimensional chains are further assembled into a three-dimensional network by weak C—H···π interactions between pyridyl and naphthyl rings, and C—H···O interactions between 3-hydroxy-2-naphthoic acid molecules.

Comment

Crystal engineering of organic molecules has been exploited in organic materials and in active pharmaceutical ingredients (Desiraju, 2003; Almarsson & Zaworotko, 2004). Supramolecular synthons provide an effective strategy for synthesizing specific organic supramolecular solids (Desiraju, 1997). In particular, supramolecular heterosynthons have great advantages in the design of cocrystals of two or more components. For example, Bailey Walsh *et al.* (2003) inserted 4,4′-bipyridine between carboxylic acid molecules and utilized the pyridine–carboxylic acid heterosynthon to obtain several pharmaceutical cocrystals. Weak C—H···O interactions play an important role in the heterosynthon. A pyridyl ring of 4,4′-bipyridine is also able to provide weak interactions, such as π–π and C—H···π interactions. We have treated 4,4′-bipyridine with 3-hydroxy-2-naphthoic acid and obtained the title crystalline supramolecular adduct, (I), in which the pyridine–carboxylic acid heterosynthon generates a molecular complex that is engineered into a three-dimensional assembly by π–π and C—H···π interactions between pyridyl and naphthyl rings.



(I)

X-ray diffraction shows that the centrosymmetric three-component adduct is formed between 3-hydroxy-2-naphthoic acid and 4,4′-bipyridine in a 2:1 ratio (Fig. 1). Selected geometric parameters are given in Table 1. The 4,4′-bipyridine molecule is located at the center of the adduct on an inversion center, and the two pyridine rings are coplanar. Moreover, the naphthoic acid rings are parallel to the 4,4′-bipyridine molecule. The pyridine–carboxylic acid heterosynthon contains hydrogen-bonding (O1—H1···N1; Table 2) and weak C—H···O (C12—H12···O2; Table 3) interactions between the pyridyl rings and the carboxylic acid groups. The hydroxy group is involved in intramolecular hydrogen bonding with the carbonyl O atom (O3—H3···O2; Table 2). The crystal packing of the adduct is controlled by two distinct weak interactions between the 4,4′-bipyridine and naphthoic acid rings. One naphthoic acid ring is involved in π–π interactions with a pyridine ring at $(x+1, y, z)$ (Table 3). Adjacent parallel adduct molecules are linked into an infinite one-dimensional chain, extending along the *a* axis, by face-to-face π–π stacking (Fig. 2). There also exists a point-to-face C15—H15···π interaction (Table 3) between the CH group of a pyridyl ring and an adjacent naphthoic acid ring. Moreover, the hydroxy O atom is involved in C9—H9···O3 interactions with naphthoic acid rings (Table 3). Thus, each adduct molecule interacts with ten adjacent molecules, and each one-dimensional chain resulting from π–π interactions connects four other chains through weak C—H···π and C—H···O interactions into a three-dimensional assembly (Fig. 3). Compound (I) exhibits intense photoluminescence at 534 nm upon photo-excitation at 365 nm. 3-Hydroxy-2-naphthoic acid exhibits luminescence at 524 nm upon excitation at 365 nm, which shows that the

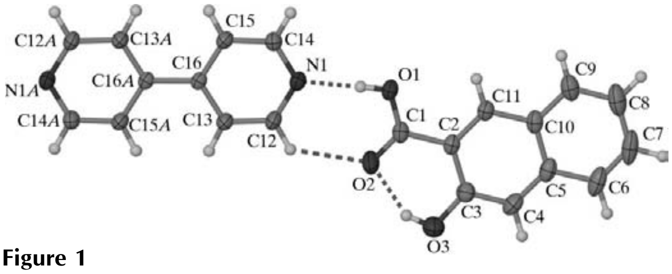


Figure 1
A plot of adduct (I) with 30% probability displacement ellipsoids. The dashed lines indicate hydrogen bonds.

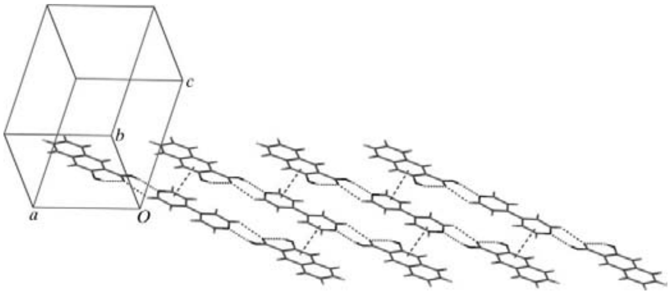


Figure 2
The one-dimensional structure of (I) along the *a* axis. The dashed lines indicate hydrogen bonds and π–π interactions

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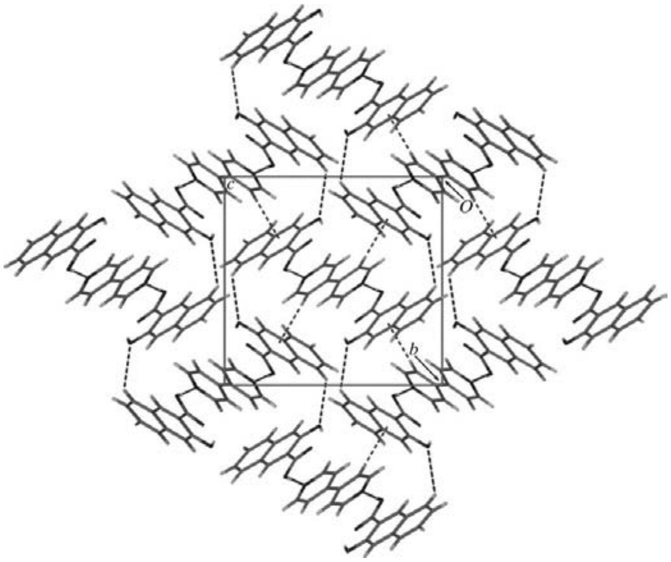

Figure 3
The three-dimensional structure of (I), viewed along the *a* axis. The dashed lines indicate C—H$\cdots$O/π interactions

interactions between 3-hydroxy-2-naphthoic acid and 4,4′-bipyridine slightly affect the luminescence. This study also demonstrates the fact that the pyridyl ring is an excellent former of cocrystals.

Experimental

A mixture of 3-hydroxy-2-naphthoic acid (0.075 g, 0.4 mmol) and 4,4′-bipyridine (0.032 g, 0.2 mmol) was stirred in ethanol (10 ml). The solution was kept in air and after several days yellow crystals were obtained in 70% yield.

Crystal data

$C_{11}H_8O_3\cdot0.5C_{10}H_8N_2$
$M_r = 266.27$
Monoclinic, $P2_1/c$
$a = 8.999$ (5) Å
$b = 11.735$ (7) Å
$c = 12.393$ (7) Å
$\beta = 98.799$ (12)°
$V = 1293.4$ (13) Å^3
$Z = 4$
$D_x = 1.367$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.10$ mm^{-1}
$T = 293$ (2) K
Prism, yellow
0.44 × 0.38 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
ω scans
Absorption correction: multi-scan (*CrystalClear*; Rigaku, 2000)
$T_{\min} = 0.821$, $T_{\max} = 1.000$
9720 measured reflections
2934 independent reflections
1768 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.042$
$\theta_{\max} = 27.4°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.158$
$S = 0.96$
2934 reflections
182 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0944P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max} = 0.27$ e Å^{-3}
$\Delta\rho_{\min} = -0.19$ e Å^{-3}
Extinction correction: *SHELXL97*
Extinction coefficient: 0.29 (2)

Table 1
Selected geometric parameters (Å, °).

O1—C1	1.286 (2)	N1—C12	1.324 (2)
O2—C1	1.240 (2)	N1—C14	1.330 (2)
O3—C3	1.355 (2)		
C12—N1—C14	117.34 (14)	O1—C1—C2	117.01 (16)
O2—C1—O1	123.16 (16)	O3—C3—C4	118.45 (18)
O2—C1—C2	119.81 (17)		

Table 2
Hydrogen-bond geometry (Å, °).

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O1—H1$\cdots$N1	0.84	1.79	2.625 (2)	172
O3—H3$\cdots$O2	0.84	1.81	2.557 (2)	147

Table 3
Parameters (Å, °) for weak hydrogen bonds and π–π interactions.

*Cg*1 is the centroid of the C2–C5/C10/C11 ring and *Cg*2 is the centroid of the N1/C12–C16 ring.

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
C12—H12$\cdots$O2	0.95	2.38	3.074 (7)	130
C9—H9$\cdots$O3$^{\rm i}$	0.95	2.70	3.342 (1)	126
C15—H15$\cdots$*Cg*1$^{\rm ii}$	0.95	2.86	3.755 (2)	158
*Cg*1$\cdots$*Cg*2$^{\rm iii}$		3.480[a]	3.629 (6)[b]	16[c]

Notes: (*a*) the perpendicular distance between *Cg*1 and the N1/C12–C16 plane; (*b*) the distance between ring centroids; (*c*) the angle between the *Cg*1$\cdots$*Cg*2 vector and the normal to the N1/C12–C16 plane. Symmetry codes: (i) $-x+1, y-\frac{1}{2}, -z+\frac{1}{2}$; (ii) $-x, y-\frac{1}{2}, -z+\frac{1}{2}$; (iii) $x+1, y, z$.

All H atoms were constrained to ride on their parent atoms, with $U_{\rm iso}({\rm H}) = 1.2U_{\rm eq}$(parent atom) and C—H = 0.95 Å.

Data collection: *CrystalClear* (Rigaku, 2000); cell refinement: *CrystalClear*; data reduction: *CrystalClear*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: AV3011). Services for accessing these data are described at the back of the journal.

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