organic compounds

Co-crystallization of hemimellitic acid with 4,4′-bipyridine forming a pillar-layered hydrogen-bonded network

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Co-crystallization of hemimellitic acid (benzene-1,2,3-tricarboxylic acid) dihydrate ($H_3HMA \cdot 2H_2O$) with 4,4′-bipyridine (4,4′-bpy) affords the 1:1 co-crystal benzene-1,2,3-tricarboxylic acid–4,4′-bipyridine (1/1), $H_3HMA \cdot 4,4′$-bpy or $C_9H_6O_6 \cdot C_{10}H_8N_2$. Strong O—H···O hydrogen bonds connect the acid molecules to form a one-dimensional zigzag chain, around which the 4,4′-bpy components are fixed as arms *via* O—H···N interactions, resulting in a ladder motif. Through weak C—H···O non-covalent forces, the resulting acid layers are extended into a three-dimensional pillar-layered architecture supported by rod-like 4,4′-bpy components. The influence on hydrogen-bonding models is also discussed, with the discovery of an unexpected interaction motif that does not follow the routine hydrogen-bonded hierarchical rule in the construction of an acid–base co-crystal.

Comment

One of the most important targets in crystal engineering is the rational design and preparation of molecular architectures with desired topologies and functions (Brammer, 2004; Steiner, 2002). Members of the aromatic carboxylic acid family are widely used as versatile building blocks in both coordination polymer synthesis (Yaghi *et al.*, 2003) and the generation of hydrogen-bonding arrays of organic co-crystals (Bowers *et al.*, 2005). Surprisingly, hemimellitic acid (H_3HMA, benzene-1,2,3-tricarboxylic acid) has received little attention from supramolecular scientists (Dale *et al.*, 2004) compared with its well known isomer H_3TMA (benzene-1,3,5-tricarboxylic acid). To the best of our knowledge, there is no example of H_3HMA being introduced in bimolecular co-crystal formation.

In contrast, 4,4′-bipyridine (hereafter 4,4′-bpy) has been investigated in all branches of crystal engineering, from coordination polymers (Hagraman *et al.*, 1999) to non-covalent hydrogen-bonding adducts (Ruiz-Perez *et al.*, 2004). Whenever 4,4′-bpy takes part in the formation of co-crystals with organic molecules containing carboxyl groups, O—H···N

hydrogen bonds are conventionally formed (Du *et al.*, 2005). We have used H_3HMA, which contains robust hydrogen-bonding sites, to co-crystallize with the rigid base 4,4′-bpy, affording a binary compound, $[(H_3HMA) \cdot (4,4′$-bpy$)]$, (I), which adopts a pillar-layered hydrogen-bonding architecture.

(I)
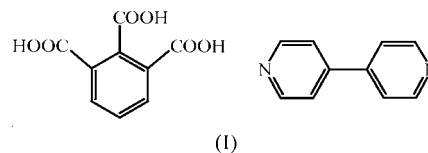
The structure analysis of (I) reveals a 1:1 stiochiometry, which is not consistent with the ratio of hydrogen-bonding donor and acceptor sites; the asymmetric unit of (I), which contains one formula unit, is depicted in Fig. 1. Bond lengths and angles (Table 1) agree with accepted values. Within each 4,4′-bpy subunit, the dihedral angle between the rings is 31.1 (1)°. For the H_3HMA component, the 2-carboxyl group (O3—C18—O4) presents an *anti*-planar conformation (Leiserowitz, 1976), in which the H atom is located in an *anti* orientation with respect to the –COO group; the 1- and 3-carboxyl groups (O1—C17—O2 and O5—C19—O6) adopt a *trans* arrangement in relation to the central benzene ring. The 2-carboxyl group lies approximately perpendicular to the benzene plane, making a dihedral angle of 100.3 (2)°, which is comparable to that in the structures of the dihydrate (Mo & Adman, 1975), the 2-methyl ester (Dale & Elsegood, 2003) and the dimethylformamide solvate (Dale & Elsegood, 2004) of H_3HMA.
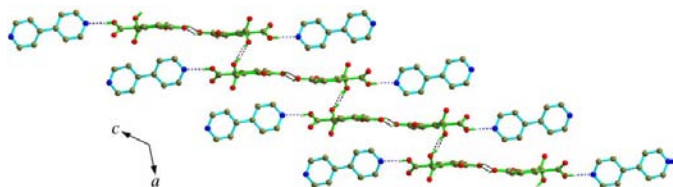
The hydrogen-bond geometries and symmetry codes are listed in Table 2. The three carboxyl groups in each H_3HMA molecule display different hydrogen-bonding modes. The terminal carboxyl group at atom C13 forms intermolecular interactions with the 4,4′-bpy molecule *via* strong O6—H6···N2[i] hydrogen bonds, while the carboxyl moiety at atom C11 (or C12) forms a unique 'double hydrogen-bonded bridge' [referring to the linkage of two related carboxyl groups by a pair of O—H···O hydrogen bonds, denoted as $R_2^2(4)$; see Fig. 2] *via* a pair of O1—H1···O1[ii] (or O4—H4···O4[iii])
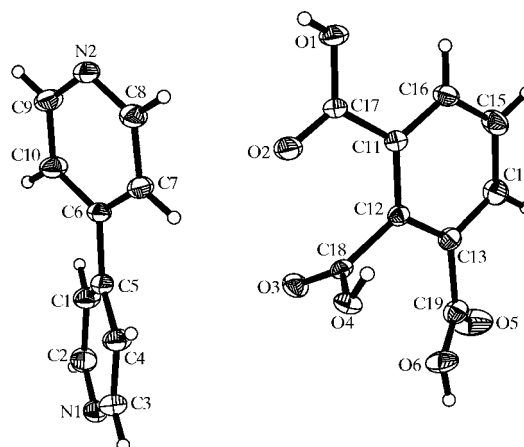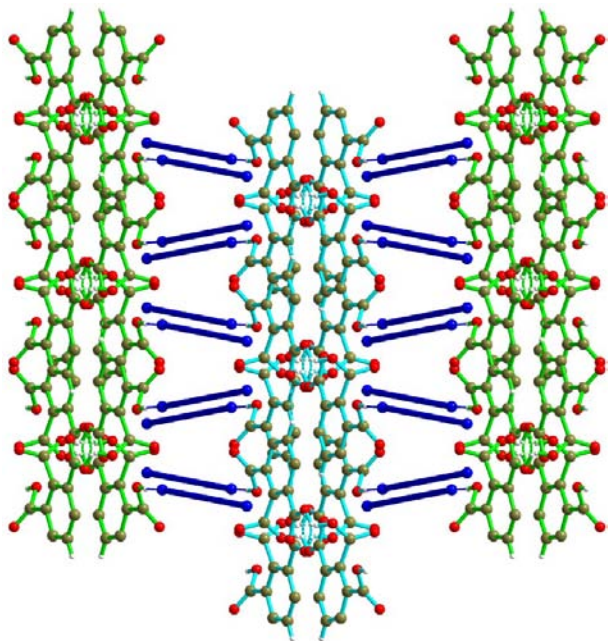

Figure 1
The molecular structure of (I), drawn with 30% probability displacement ellipsoids.

interactions, instead of engendering O—H···N bonds to N1 of the base subunit. Thus, the acid molecules are linked to afford a one-dimensional zigzag chain parallel to [001], and the 4,4′-bpy building blocks are located around this chain to produce a ladder-shaped motif (see Fig. 2). With respect to the acid molecules only, C15—H15···O2^{iv} interactions connect adjacent zigzag acid chains into a two-dimensional corrugated layer. By a combination of O—H···N bonds and additional weak C—H···O interactions, including C3—H3···O3^{v}, C8—H8···O2, C8—H8···O1^{ii} and C9—H9···O3^{vi}, between the base pillar and neighboring acid layer, a three-dimensional pillar-layered hydrogen-bonded architecture is generated (Fig. 3). Examination of this structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal structure.

Heteromeric intermolecular interactions are powerful synthetic tools for the formation of acid/base binary co-crystals. The hydrogen-bonding motifs in these compounds are always consistent with Etter's (1990) analysis of hierarchical rules, that is, the best hydrogen-bond donor and the best hydrogen-bond acceptor will preferentially form stable hydrogen bonds. The most common case occurs between a pyridyl N atom and a carboxyl group (Du *et al.*, 2005). However, in (I), pyridyl atom N1 does not form such a heteromeric bond with any carboxyl groups, nor is there even a possible C—H···N weak interaction. Instead, unusual 'double hydrogen-bonded bridges', as described above, are observed between the carboxyl groups. A Cambridge Structural Database search (Version 5.26 of November 2004, plus two updates) was carried out using *ConQuest* (Version 1.7; Allen, 2002) to investigate the general robustness of such double hydrogen-bonded bridges. 40 related examples were identified (those structures with $R1 > 0.1$, as well as organometallic entries, were discarded). More details for the target O—H···O interactions are as follows: (i) the H···O distances range between 1.55 and 1.98 Å, while the mean value is *ca* 1.77 Å; (ii) the O···O distances lie between 2.44 and 2.76 Å, and the mean value is *ca* 2.56 Å; (c) most of the O—H···O angles (37 cases among the 40 search results) lie in the range 154–178°, with a mean value of 168°. All related values in this structure are comparable to the above analysis.

Figure 2
The one-dimensional ladder structure formed *via* O—H···O and O—H···N interactions (H atoms not involved in these hydrogen bonds, which are represented by dashed lines here and in Fig. 3, have been omitted).

Figure 3
The three-dimensional pillar-layered supramolecular network, viewed in the crystallographic [001] direction (4,4′-bpy molecules are simplified to rods, and weak C—H···O interactions between the base pillar and acid layer have been omitted for clarity).

Experimental

Crystal data

C$_9$H$_6$O$_6$·C$_{10}$H$_8$N$_2$	$D_x = 1.502$ Mg m^{-3}
$M_r = 366.32$	Mo $K\alpha$ radiation
Monoclinic, $C2/c$	Cell parameters from 2052
$a = 26.118$ (3) Å	reflections
$b = 7.8131$ (9) Å	$\theta = 2.6$–23.1°
$c = 19.881$ (2) Å	$\mu = 0.11$ mm^{-1}
$\beta = 127.005$ (1)°	$T = 293$ (2) K
$V = 3239.8$ (6) Å^3	Block, colorless
$Z = 8$	$0.42 \times 0.26 \times 0.20$ mm

Data collection

Bruker APEX-II CCD area-detector diffractometer	2845 independent reflections
	2212 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.024$
Absorption correction: multi-scan	$\theta_{max} = 25.0°$
(*SADABS*; Sheldrick, 1996)	$h = -29 \rightarrow 30$
$T_{min} = 0.829$, $T_{max} = 1.000$	$k = -7 \rightarrow 9$
8469 measured reflections	$l = -23 \rightarrow 22$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0824P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.041$	$+ 0.8334P]$
$wR(F^2) = 0.133$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
2845 reflections	$\Delta\rho_{max} = 0.56$ e Å^{-3}
247 parameters	$\Delta\rho_{min} = -0.33$ e Å^{-3}
H-atom parameters constrained	

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Table 1
Selected geometric parameters (Å, °).

O1—C17	1.283 (2)	O6—C19	1.304 (2)
O2—C17	1.215 (2)	N1—C2	1.324 (3)
O3—C18	1.216 (2)	N1—C3	1.329 (3)
O4—C18	1.293 (2)	N2—C9	1.328 (3)
O5—C19	1.207 (2)	N2—C8	1.332 (3)
C2—N1—C3	121.52 (17)	O3—C18—O4	121.32 (16)
C9—N2—C8	117.55 (16)	O5—C19—O6	123.64 (18)
O2—C17—O1	124.27 (17)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O6—H6$\cdots$N2^{i}	0.82	1.79	2.612 (2)	175
O1—H1$\cdots$O1^{ii}	0.82	1.72	2.464 (2)	150
O4—H4$\cdots$O4^{iii}	0.82	1.67	2.454 (2)	159
C15—H15$\cdots$O2^{iv}	0.93	2.30	3.194 (3)	160
C3—H3$\cdots$O3^{v}	0.93	2.50	3.129 (3)	125
C8—H8$\cdots$O2	0.93	2.56	3.250 (4)	131
C8—H8$\cdots$O1^{ii}	0.93	2.57	3.410 (3)	151
C9—H9$\cdots$O3^{vi}	0.93	2.47	3.120 (4)	127

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

All H atoms were visible in difference maps. C-bound H atoms were placed at calculated positions, with C—H distances of 0.93 Å, and refined as riding atoms. O-bound H atoms were refined as rigid groups, allowed to rotate but not tip. Isotropic displacement parameters were derived from the parent atoms [U_{iso}(H) = 1.2U_{eq}(C) and 1.5U_{eq}(O)].

Data collection: *APEX-II* (Bruker, 2003); cell refinement: *APEX-II* and *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Bruker, 2001) and *DIAMOND* (Brandenburg & Berndt, 1999); software used to prepare material for publication: *SHELXTL*.

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