Hydrogen bonding and π–π interactions in a laminar structure: benzene-1,3-dicarboxylic acid–4-methylpyridine (1/2)

Zhi-Min Jin,[a]* **Hai Feng,**[a] **Bing Tu,**[a] **Mei-Chao Li**[b] **and Mao-Lin Hu**[c]

[a]College of Pharmaceutical Sciences, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, [b]College of Chemical Engineering, Zhejiang University of Technology, Hangzhou 310014, People's Republic of China, and [c]Department of Chemistry, Wenzhou Normal College, Wenzhou, Zhejiang 325003, People's Republic of China
Correspondence e-mail: zhimin-J@163.net

The title complex, $C_8H_6O_4 \cdot 2C_6H_7N$, consists of two crystallographically independent 1:2 clusters of benzene-1,3-dicarboxylic acid and 4-methylpyridine. Each cluster, the components of which are linked by O—H···N hydrogen bonds, is almost planar by alignment of C—H···O hydrogen bonds. Herring-bone ribbons of clusters are formed by other C—H···O hydrogen bonds, and these ribbons are further packed to form a laminar structure by π–π interactions.

Comment

Supramolecular aggregate design is an active field (Zaworotko, 2001; Bis & Zaworotko, 2005; Shattock et al., 2005; Turkington et al., 2005). Some cases have been reported using benzene-1,3-dicarboxylic acid (BDA) as a building block (Bielawski et al., 1998; Shan et al., 2002; Trivedi et al., 2003; Dale et al., 2004) to build supramolecular architectures. We have recently synthesized the title complex, (I), and describe

here the co-operation of O—H···N and C—H···O hydrogen bonds and π–π interactions in forming the novel laminar structure.
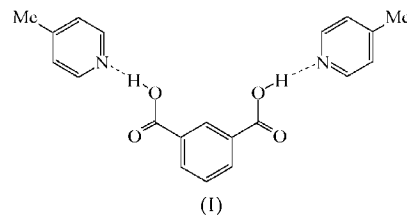
There are two crystallographically independent 1:2 clusters of benzene-1,3-dicarboxylic acid (BDA) and 4-methylpyridine (MP) in the asymmetric unit (Fig. 1); one cluster is labelled A for the three molecules with atoms O1, N1 and N2 and the other is labelled B for the three molecules with atoms O5, N3 and N4.

The A cluster is built up by two nearly linear O2—H2···N1 and O4—H4···N2 hydrogen bonds (Table 1). The dihedral angles between the aromatic ring and the carboxyl groups of the BDA molecule are 3.0 (3) and 2.4 (4)° for the carboxyl groups with atoms O1 and O3, repectively. This conformation differs from those observed in a nickel 1,3-benzene-dicarboxylate and a cobalt benzene-1,3-dicarboxylate (Bourne et al., 2001), where the benzene rings are skewed at large angles with respect to the carboxylate groups. The carboxylic acid groups are almost coplanar with the MP rings, allowing weak C17—H17···O1 and C23—H23···O3 hydrogen bonds (Steiner & Desiraju, 1998). Furthermore, there are short C1—H1···O2, C1—H1···O4, C3—H3···O1 and C5—H5···O3 contacts, with H···O distances in the range 2.44–2.50 Å. The coplanar arrangment is different from the situation in a BDA–pyridine (1/1) complex (Dale et al., 2004), where the dihedral angle between the carboxylic acid group and pyridine is large [28.6 (2)°] and allows no similar C—H···O hydrogen bonds. However, the coplanar arrangment in (I) resembles the situations observed in other BDA complexes, namely BDA and a pyridylamine derivative (Bielawski et al., 1998), and BDA–benzimidazole (1/1) (Trivedi et al., 2003). In a general view, therefore, the molecules in the A cluster of (I) are almost coplanar with one another, which is indicated by an r.m.s. deviation of 0.119 (6) Å for the atoms from the plane of the A cluster.

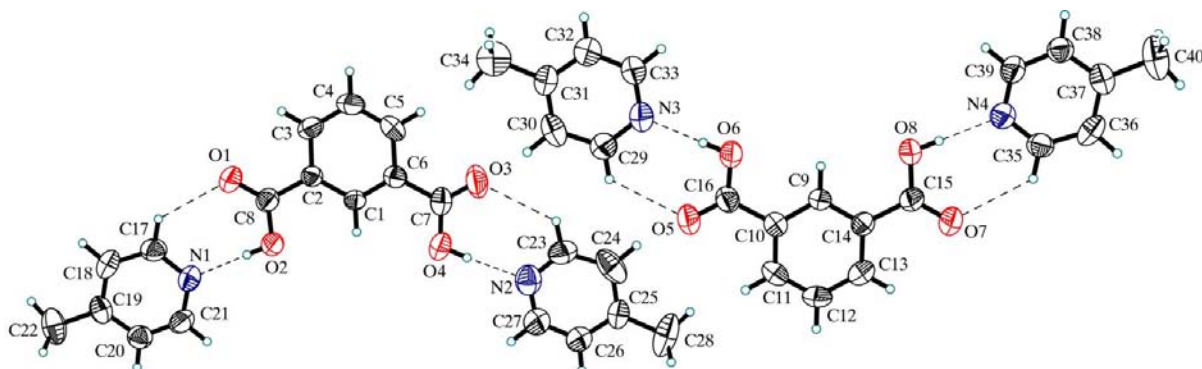

Figure 1
The formula unit of (I), with the atom-labelling scheme, showing 35% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are illustrated as dashed lines.
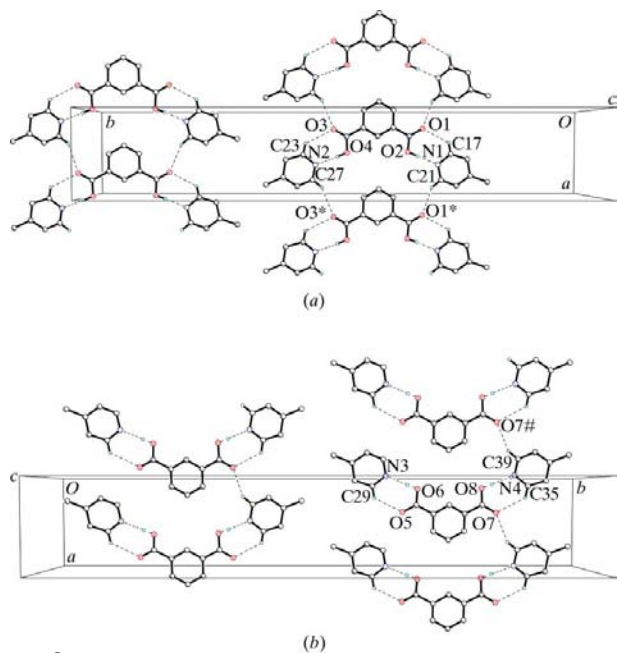
Figure 2
A view of the ribbons in (a) the A cluster and (b) the B cluster, extending along the a direction and viewed down the c axis. Intermolecular hydrogen bonds are shown as dashed lines. Atoms labelled with an asterisk (*) or hash (#) are at the symmetry positions $(x + 1, y, z)$ and $(x - 1, y, z)$, respectively.

The BDA molecule in the B cluster is less coplanar than that in the A cluster, as indicated by the dihedral angles between the aromatic ring and the carboxyl groups of 4.9 (4) and 10.4 (4)° for the carboxyl groups with atoms O5 and O7, repectively. However, similar to what was observed in the A cluster, due to O—H⋯N and C—H⋯O hydrogen bonds (Table 1), the molecules in the B cluster are also almost coplanar, as indicated by an r.m.s. deviation of 0.105 (7) Å for the atoms from the mean plane of the B cluster.

Viewed along the c axis (Fig. 2), the structure of (I) is characterized by layers of BDA and MP molecules, with a stratum equal to a quarter of the c axis. A ribbon of A-cluster molecules parallel to the (001) plane is formed by C21—H21⋯O1^i and C27—H27⋯O3^i hydrogen bonds [symmetry code: (i) $x + 1, y, z$]. The hydrogen-bonding patterns of this A-cluster ribbon can be described in graph-set terminolgy as $C_2^1(6)$, $C_2^2(7)$, $R_2^2(7)$, $R_4^4(22)$ and $R_4^4(24)$ (Etter, 1990; Grell et al., 2000). Another similar ribbon for the B cluster parallel to the (001) plane is created by the C39—H39⋯O7^{ii} hydrogen bond [symmetry code: (ii) $x - 1, y, z$].

The A- and B-cluster ribbons between neighbouring layers are associated by a number of π–π interactions (Sharma et al., 1993; Pedireddi et al., 1996), the shortest of which has a distance of 3.683 (4) Å between the centroids of the MP molecule with atom N2 in cluster A and the MP molecule with atom N3 in cluster B at $(1 + x, y, z)$; the angle between these two ring planes is 1.2°.

Experimental

BDA (0.01 mol) and MP (0.04 mol) were mixed and heated to a temperature of 353 K, producing a clear solution. Single crystals of

(I) were formed by gradual evaporation of excess MP in the resulting solution for a week at 293 K.

Crystal data

$C_8H_6O_4 \cdot 2C_6H_7N$	$D_x = 1.269$ Mg m^{-3}
$M_r = 352.38$	Mo $K\alpha$ radiation
Monoclinic, Cc	Cell parameters from 239
$a = 6.863$ (6) Å	reflections
$b = 39.81$ (3) Å	$\theta = 2.8$–24.9°
$c = 13.527$ (11) Å	$\mu = 0.09$ mm^{-1}
$\beta = 93.276$ (15)°	$T = 273$ (2) K
$V = 3690$ (5) Å^3	Sheet, colourless
$Z = 8$	$0.30 \times 0.25 \times 0.20$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer	3370 independent reflections
	2692 reflections with $I > 2\sigma(I)$
φ and ω scans	$R_{int} = 0.021$
Absorption correction: multi-scan	$\theta_{max} = 25.4°$
(*SADABS*; Bruker, 2000)	$h = -8 \rightarrow 8$
$T_{min} = 0.974$, $T_{max} = 0.982$	$k = -48 \rightarrow 22$
9779 measured reflections	$l = -16 \rightarrow 16$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0929P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.065$	$+ 1.2415P]$
$wR(F^2) = 0.173$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} < 0.001$
3370 reflections	$\Delta\rho_{max} = 0.17$ e Å^{-3}
476 parameters	$\Delta\rho_{min} = -0.30$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected bond lengths (Å).

O1—C8	1.192 (6)	C5—C6	1.381 (7)
O2—C8	1.292 (6)	C6—C7	1.466 (7)
O3—C7	1.197 (6)	N1—C17	1.306 (6)
O4—C7	1.294 (7)	N1—C21	1.308 (7)
C1—C6	1.372 (6)	C17—C18	1.402 (8)
C1—C2	1.387 (6)	C18—C19	1.387 (9)
C2—C3	1.387 (7)	C19—C20	1.356 (9)
C2—C8	1.482 (7)	C19—C22	1.481 (8)
C3—C4	1.362 (7)	C20—C21	1.322 (8)
C4—C5	1.354 (7)		

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

D—H⋯A	D—H	H⋯A	D⋯A	D—H⋯A
O2—H2O⋯N1	0.82	1.83	2.652 (6)	177
O4—H4O⋯N2	0.82	1.84	2.657 (6)	172
O6—H6O⋯N3	0.82	1.83	2.648 (6)	175
O8—H8O⋯N4	0.82	1.82	2.642 (6)	176
C17—H17⋯O1	0.93	2.41	3.093 (7)	130
C21—H21⋯O1^i	0.93	2.48	3.258 (7)	141
C23—H23⋯O3	0.93	2.48	3.139 (8)	128
C27—H27⋯O3^i	0.93	2.59	3.375 (9)	142
C29—H29⋯O5	0.93	2.50	3.171 (8)	129
C35—H35⋯O7	0.93	2.47	3.138 (7)	129
C39—H39⋯O7^{ii}	0.93	2.41	3.221 (8)	146

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

H atoms were placed in calculated positions and allowed to ride on their parent atoms at distances of 0.82 (hydroxy), 0.93 (C—H aromatic) and 0.96 Å (methyl), with isotropic displacement parameters 1.2–1.5 times the U_{eq} values of their parent atoms. As the compound contains no heavy atoms, Friedel reflections were merged before the final refinement.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 2000); program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1861). Services for accessing these data are described at the back of the journal.

References

Bielawski, C., Chen, Y. S., Zhang, P., Prest, P. J. & Moore, J. S. (1998). *J. Chem. Soc. Chem. Commun.* pp. 1313–1314.

Bis, J. A. & Zaworotko, M. J. (2005). *Cryst. Growth Des.* **5**, 1169–1179.

Bourne, S. A., Mondal, A. & Zaworotko, M. J. (2001). *Cryst. Eng.* **4**, 25–36.

Bruker (2000). *SADABS* (Version 2.05), *SMART* (Version 5.618), *SAINT* (Version 6.02a) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Dale, S. H., Elsegood, M. R. J., Hemmings, M. & Wilkinson, A. L. (2004). *CrystEngComm*, **6**, 207–214.

Etter, M. C. (1990). *Acc. Chem. Res.* **23**, 120–126.

Grell, J., Bernstein, J. & Timhofer, G. (2000). *Acta Cryst.* B**56**, 166–179.

Pedireddi, V. R., Jones, W., Choriton, A. P. & Docherty, R. (1996). *Chem. Commun.* pp. 997–998.

Shan, N., Bond, A. D. & Jones, W. (2002). *Cryst. Eng.* **5**, 9–24.

Sharma, C. V. K. M., Panneerselvam, K., Pilati, T. & Desiraju, G. R. (1993). *J. Chem. Soc. Perkin Trans. 2*, pp. 2209–2216.

Shattock, T. R., Vishweshwar, P., Wang, Z. Q. & Zaworotko, M. J. (2005). *Cryst. Growth Des.* **5**. In the press. (DOI: 10.1021/cg0501985.)

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Steiner, T. & Desiraju, G. R. (1998). *J. Chem. Soc. Chem. Commun.* pp. 891–892.

Trivedi, D. R., Ballabh, A. & Dastidar, P. (2003). *CrystEngComm*, **5**, 358–367.

Turkington, D. E., MacLean, E. J., Lough, A. J., Ferguson, G. & Glidewell, C. (2005). *Acta Cryst.* B**61**, 103–114.

Zaworotko, M. J. (2001). *Chem. Commun.* pp. 1–9.