

Hydrogen-bonded sheets in the 1:1 cocrystal of biphenyl-4,4'-dicarboxylic acid with 2,5-di-4-pyridyl)-1,3,4-oxadiazole

Miao Du,* Yan-Ping You and Zhi-Hui Zhang

College of Chemistry and Life Science, Tianjin Normal University, Tianjin 300074, People's Republic of China

Correspondence e-mail: dumiao@public.tpt.tj.cn

Received 14 November 2005

Accepted 24 November 2005

Online 16 December 2005

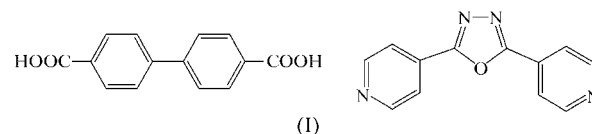
The combination of biphenyl-4,4'-dicarboxylic acid (H_2bpa) and the bent dipyridyl base 2,5-di-4-pyridyl-1,3,4-oxadiazole (4-bpo) in a 1:1 molar ratio leads to the formation of the molecular cocrystal $(H_2bpa) \cdot (4-bpo)$ or $C_{14}H_{10}O_4 \cdot C_{12}H_8N_4O$. The asymmetric unit contains one-half of an H_2bpa unit lying across a centre of inversion and one-half of a 4-bpo molecule lying across a twofold rotation axis. Intermolecular $O-H \cdots N$ interactions connect the acid and base molecules to form a one-dimensional zigzag chain. Through further weak $C-H \cdots O$ hydrogen bonds between adjacent chains, a two-dimensional sheet-like supramolecular network is afforded. As an extended analogue of terephthalic acid (H_2tp), the backbone geometry of H_2bpa has an evident influence on the hydrogen-bonding pattern of the title cocrystal compared with that of $(H_2tp) \cdot (4-bpo)$.

Comment

Organic crystal engineering of acid–base binary complexes assembled into predictable supramolecular architectures is a subject of continuing interest, which has focused on selective and directional hydrogen bonds in both natural and artificial systems (Desiraju, 1989; Steiner, 2002). One of the important approaches is to utilize the self-organization of small organic molecules with classical $O-H \cdots O$ and $O-H \cdots N$ hydrogen bonding and other weak hydrogen bonds, such as $C-H \cdots O$, to construct infinite one-, two- or three-dimensional networks in crystalline solids (Ma & Coppens, 2003; Aakeröy & Salmon, 2005). In this context, not only strong hydrogen-bonding interactions but also weak hydrogen bonds need to be considered carefully because they can affect the crystal packing in unpredictable ways (Desiraju, 2002).

2,5-Di-4-pyridyl-1,3,4-oxadiazole (4-bpo), a bent dipyridyl analogue, has abundant heteroatoms with free electron pairs that could be considered as multiple hydrogen-bonding sites. Recently, it has been successfully used to create a series of

hydrogen-bonded cocrystals displaying one-dimensional tape, two-dimensional layer, three-dimensional net and helical style frameworks, with aromatic di- or polycarboxylic acids (Du *et al.*, 2005*a,b*), such as terephthalic acid and trimesic acid. Biphenyl-4,4'-dicarboxylic acid (H_2bpa), as a long rod-shaped building block, has received considerable attention in the design of porous metal–organic frameworks (MOFs) with adsorption properties (Rosi *et al.*, 2005, and references therein). Such a building block attracts our interest for its similar geometry but different length compared with terephthalic acid, which can form strong and directional non-covalent interactions. Also, it is rarely utilized in cocrystallization with organic bases and always forms charge-transfer compounds and not molecular cocrystals (Felix *et al.*, 1997; Xue & Mak, 2000). Therefore, the combination of H_2bpa with 4-bpo may be expected to give diverse hydrogen-bonding modes and an interesting network. We report here the structure of the title cocrystal, $(H_2bpa) \cdot (4-bpo)$, (I), which has a two-dimensional sheet hydrogen-bonded network.



X-ray single-crystal diffraction analysis shows that H_2bpa cocrystallizes with 4-bpo in a 1:1 molar ratio, producing a binary molecular crystal, $(H_2bpa) \cdot (4-bpo)$, (I), as depicted in Fig. 1. Bond lengths and angles agree with accepted values (Du *et al.*, 2005*a,b*). The asymmetric unit of (I) contains half of a centrosymmetric H_2bpa subunit with the inversion centre $(\frac{1}{2}, 1, 0)$ at the mid-point of the C11–C11A bond [symmetry code: (A) $1-x, 2-y, -z$], and half of a crystallographic twofold symmetric 4-bpo molecule, in which the twofold rotation axis passes through atom O1 and the centre of the N2–N2B bond along $(0, y, \frac{1}{2})$ [symmetry code: (B) $-x, y, -z + \frac{1}{2}$]. The mean planes of the two components including all non-H atoms are inclined to each other with a dihedral angle of $9.4(3)^\circ$. The terminal pyridyl rings in 4-bpo form dihedral angles of $1.0(2)^\circ$ with the central oxadiazole plane, and a dihedral angle of $1.9(2)^\circ$ with each other. For the H_2bpa component, the two terminal carboxylic acid groups adopt a *trans*-coplanar conformation in relation to the central biphenyl moiety, due to its symmetry.

The hydrogen-bond geometries and symmetry codes are listed in Table 1. From Fig. 2, we can clearly see that the base and acid components are connected through $O2-H2A \cdots N1$

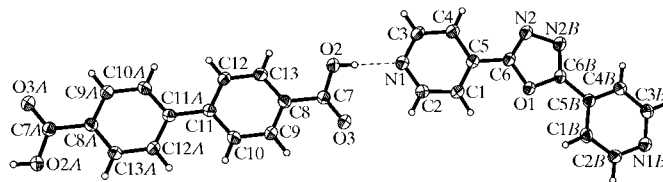


Figure 1

The molecular structure of (I), drawn with 30% probability ellipsoids. [Symmetry codes: (A) $1-x, 2-y, -z$; (B) $-x, y, \frac{1}{2}-z$.]

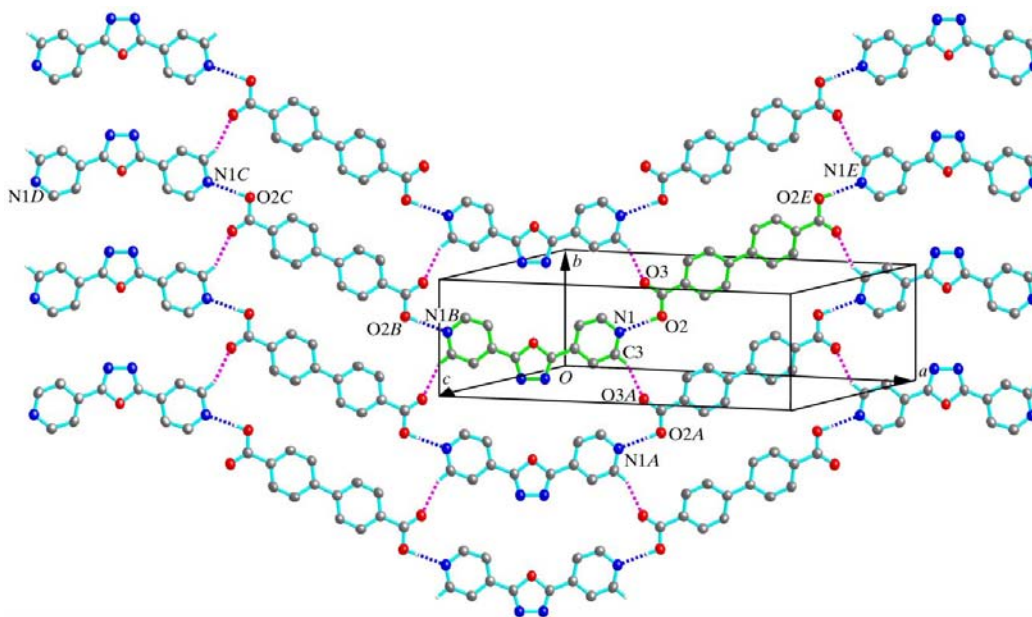


Figure 2

A perspective view of the two-dimensional hydrogen-bonded sheet along (102). Hydrogen bonds are indicated by dashed lines. The base molecules are indicated by the unit cell. H atoms not involved in the hydrogen bonds shown have been omitted. [Symmetry codes: (A) $x, -1 + y, z$; (B) $-x, y, \frac{1}{2} - z$; (C) $-1 + x, 2 - y, \frac{1}{2} + z$; (D) $-1 - x, 2 - y, 1 - z$; (E) $1 - x, 2 - y, -z$.]

interactions, producing a one-dimensional zigzag chain running along the $[\bar{2}01]$ direction. Adjacent chains arrayed in a parallel mode along the crystallographic $[0\bar{1}0]$ direction are further linked by weak $C3-H3 \cdots O3$ hydrogen bonds to form a two-dimensional planar network. These (102) sheets are packed in a parallel and somewhat offset manner. There are no further hydrogen-bonding interactions or aromatic stacking between adjacent layers and five such sheets pass through the unit cell. Examination of this structure with *PLATON* (Spek, 2003) showed that there were no solvent-accessible voids in the crystal lattice.

H_2bpa has a similar carboxylate geometry compared with terephthalic acid (H_2tp) and could act as a longer rod-like building block with a separation of *ca* 12 Å (the corresponding value for H_2tp is *ca* 8 Å). In contrast with the structure of the cocrystal based on 4-bpo and H_2tp (Du *et al.*, 2005*a*), the characteristic hydrogen-bonding motif and further crystal packing of compound (I) are as follows. The length of the acid component H_2bpa , as the only variable factor compared with H_2tp , may adjust the crystal structure into a two-dimensional planar network in which the acid–base chains are arranged in a parallel fashion, while for (H_2tp)·(4-bpo), H_2tp and 4-bpo are arrayed alternately on either side of the two-dimensional acid–base plane. The low slope between the acid and base molecules and the large separation between the adjacent layers in (I) result in an absence of interlayer hydrogen-bonding interactions or aromatic stacking, while for (H_2tp)·(4-bpo)], the two-dimensional layers are further extended to form a three-dimensional net *via* interlayer $C-H \cdots O$ interactions.

In conclusion, this work indicates that H_2bpa is also a good participant in hydrogen-bonding networks for the formation

of acid–base molecular cocrystals and, notably, compound (I) represents the first example of H_2bpa as a neutral component in acid–base adducts.

Experimental

A dimethylformamide solution (10 ml) of H_2bpa (24.2 mg, 0.1 mmol) was carefully layered on to a solution of 4-bpo (22.4 mg, 0.1 mmol) in $CHCl_3$ (6 ml) in a straight glass tube. Colourless block-shaped crystals of (I) formed on the tube wall over a period of three weeks in 85% yield. Analysis calculated for $C_{26}H_{18}N_4O_5$: C 66.95, H 3.89, N 12.01%; found: C 66.91, H 3.74, N 12.31%. IR (KBr pellet, ν , cm^{-1}): 3434 (*b*), 2973 (*s*), 2938 (*s*), 2802 (*m*), 2739 (*s*), 2677 (*vs*), 2601 (*m*), 2569 (*m*), 2528 (*m*), 2396 (*w*), 2354 (*w*), 1763 (*w*), 1606 (*w*), 1562 (*w*), 1474 (*s*), 1393 (*vs*), 1170 (*m*), 1075 (*w*), 1036 (*m*), 847 (*w*), 827 (*m*), 804 (*w*), 714 (*w*), 460 (*w*).

Crystal data

$C_{14}H_{10}O_4 \cdot C_{12}H_8N_4O$
 $M_r = 466.44$
 Monoclinic, $C2/c$
 $a = 21.131$ (4) Å
 $b = 6.8459$ (11) Å
 $c = 15.376$ (3) Å
 $\beta = 103.135$ (2)°
 $V = 2166.1$ (7) Å³
 $Z = 4$
 $D_x = 1.430$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 978 reflections
 $\theta = 3.1$ – 21.9°
 $\mu = 0.10$ mm⁻¹
 $T = 293$ (2) K
 Block, colourless
 $0.28 \times 0.18 \times 0.10$ mm

Data collection

Bruker SMART APEX-II CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
 $T_{min} = 0.795$, $T_{max} = 0.990$
 5668 measured reflections

1906 independent reflections
 1256 reflections with $I > 2\sigma(I)$
 $R_{int} = 0.025$
 $\theta_{max} = 25.0^\circ$
 $h = -24 \rightarrow 24$
 $k = -7 \rightarrow 8$
 $l = -17 \rightarrow 18$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.111$
 $S = 0.98$
 1906 reflections
 161 parameters
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0658P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} < 0.001$
 $\Delta\rho_{\max} = 0.17 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.16 \text{ e } \text{Å}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.0014 (4)

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$O2-H2A\cdots N1$	0.82	1.83	2.654 (2)	179
$C3-H3\cdots O3^i$	0.93	2.29	3.153 (2)	155

Symmetry code: (i) $x, y - 1, z$.

There was no evidence of crystal decay during data collection. The space group $C2/c$ was uniquely assigned from the systematic absences. All H atoms were visible in difference maps. C-bound H atoms were placed in calculated positions, with C–H distances of 0.93 Å, and refined as riding atoms, with $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$. O-bound carboxyl H atoms were refined as rigid groups, with O–H distances of 0.82 Å, and allowed to rotate but not tip, with $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{O})$.

Data collection: *APEX2* (Bruker, 2003); cell refinement: *APEX2* 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*.

The authors gratefully acknowledge financial support from the National Natural Science Foundation of China (grant No. 20401012), the Key Project of Tianjin Natural Science Foundation (grant No. 043804111) and Tianjin Normal University (to MD).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: GD1421). Services for accessing these data are described at the back of the journal.

References

- Aakeröy, C. B. & Salmon, D. J. (2005). *CrystEngComm*, **7**, 439–448.
 Brandenburg, K. & Berndt, M. (1999). *DIAMOND*. Version 2.1c. Crystal Impact GbR, Bonn, Germany.
 Bruker (2001). *SAINT* (Version 6.02) and *SHELXTL* (Version 6.12). Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2003). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Desiraju, G. R. (1989). *Crystal Engineering: The Design of Organic Solids*. New York: Elsevier.
 Desiraju, G. R. (2002). *Acc. Chem. Res.* **35**, 565–573.
 Du, M., Zhang, Z.-H. & Zhao, X.-J. (2005a). *Cryst. Growth Des.* **5**, 1199–1208.
 Du, M., Zhang, Z.-H. & Zhao, X.-J. (2005b). *Cryst. Growth Des.* **5**, 1247–1254.
 Felix, O., Hosseini, M. W., De Cian, A. & Fischer, J. (1997). *Tetrahedron Lett.* **38**, 1755–1758.
 Ma, B.-Q. & Coppens, P. (2003). *Chem. Commun.* pp. 2290–2291.
 Rosi, N. L., Kim, J., Eddaoudi, M., Chen, B., O'Keeffe, M. & Yaghi, O. M. (2005). *J. Am. Chem. Soc.* **127**, 1504–1518.
 Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
 Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.
 Steiner, T. (2002). *Angew. Chem. Int. Ed.* **41**, 48–76.
 Xue, F. & Mak, T. C. W. (2000). *J. Phys. Org. Chem.* **13**, 405–414.