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The 2:1 cocrystal of benzamide and pentafluorobenzoic acid

Wojciech Jankowski,[a] Maria Gdaniec[a]* and Tadeusz Połoński[b]

[a]Faculty of Chemistry, Adam Mickiewicz University, 60-780 Poznań, Poland, and [b]Department of Chemistry, Technical University of Gdańsk, 80-952 Gdańsk, Poland
Correspondence e-mail: magdan@amu.edu.pl

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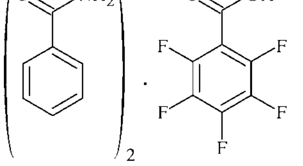
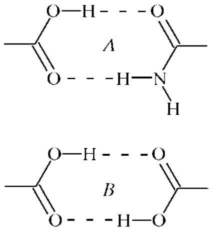
The crystal structure of the title compound, benzamide–2,3,4,5,6-pentafluorobenzoic acid (2/1), $2C_7H_7NO{\cdot}C_7HF_5O_2$, consists of centrosymmetric hexameric supermolecules composed of four amide and two carboxylic acid molecules connected *via* O—H···O and N—H···O hydrogen bonds. No phenyl–perfluorophenyl π–π stacking interactions are observed in this cocrystal.

Comment

Aryl–perfluoroaryl stacking interactions have attracted increasing attention in crystal engineering (Reichenbächer *et al.*, 2005) and have become a powerful tool in rational supramolecular synthesis (Coates *et al.*, 1997; Collings *et al.*, 2002; Shu *et al.*, 2006; Watt *et al.*, 2004; Xu *et al.*, 2006). Recently, we have shown that, when used in cooperation with hydrogen bonding, these specific intermolecular interactions can be employed to control an aggregation mode of carboxylic acid dimers (Gdaniec *et al.*, 2003). Shortly thereafter, Reddy *et al.* (2004) reported that phenyl–perfluorophenyl stacking interactions play an important role in the cocrystallization process of benzamide with pentafluorobenzamide, or of benzamide with pentafluorobenzoic acid. In the latter case, the 1:1 adduct was obtained from an equimolar mixture of the acid and the amide dissolved in ethyl acetate/hexane. The crystal consisted of acid–amide heterodimers arranged into centrosymmetric pairs *via* phenyl–perfluorophenyl stacking interactions. At that time we were also examining cocrystallization of benzamides or benzoic acids with pentafluorobenzamide, and cocrystallization of benzamide with pentafluorobenzoic acid using an acetone/water mixture as the solvent. The outcome of these experiments was rather poor, showing that the structure-directing role of the phenyl–pentafluorophenyl synthon in cocrystallization of aromatic amides, or aromatic amides with aromatic acids, was significantly limited when compared with that found in cocrystallization of aromatic acids. The only cocrystals isolated from these experiments were the benzamide–pentafluorobenzamide (1/1) adduct reported by Reddy *et al.* (2004) and a new form of pentafluorobenzoic acid–benzamide cocrystal with a 1:2 stoichiometry, (I). The melting point of (I) (361–363 K) is slightly higher than that reported for the 1:1 adduct (359 K).



(I)



The asymmetric unit of (I) (Fig. 1 and Table 1) comprises two amide molecules and one molecule of the carboxylic acid. The molecules are assembled *via* hydrogen bonds into centrosymmetric hexameric supermolecules consisting of the amide homodimer *A* and two amide–acid heterodimers *B* (see scheme above and Fig. 1). The amide molecule forming the dimer *B* is essentially planar and is coplanar with the carboxylic acid group. The very strong O—H···O hydrogen bond (Table 2) within the heterodimer strongly influences the geometry of the amide group. The C=O and C—N bond lengths for amide molecule *B*, not involved in strong hydrogen

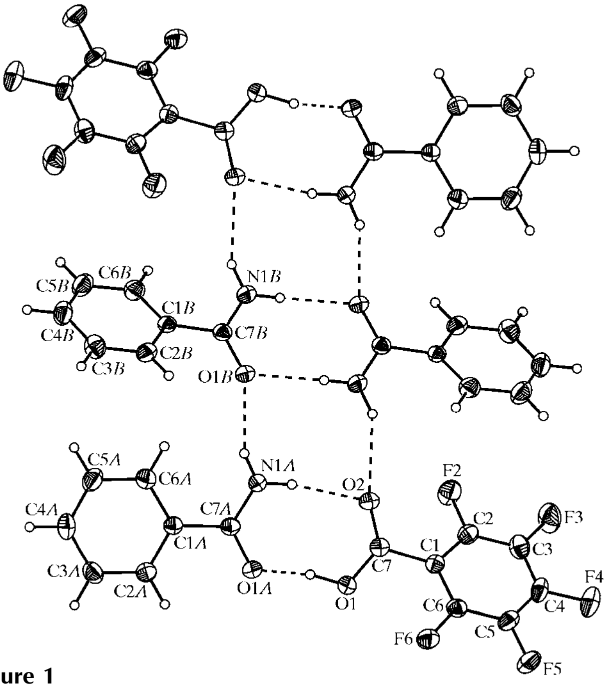


Figure 1
The centrosymmetric hexameric supermolecule in (I), with displacement ellipsoids drawn at the 50% probability level and hydrogen bonds shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry operation ($-x$, $-y + 1$, $-z + 1$).

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bonding, are 1.244 (2) and 1.335 (2) Å, respectively, whereas in molecule *A* the corresponding bond lengths are 1.292 (2) and 1.320 (2) Å.

Interestingly, it is quite unusual for the two motifs *A* and *B* to co-exist in one crystal structure. Our search of the Cambridge Structural Database (CSD; Version 5.27 plus January 1 update; Allen & Motherwell, 2002) did not reveal any crystal structure with a similar carboxylic acid–primary amide aggregation mode. Only in two structures [CSD refcodes MIHWUV (Ito *et al.*, 2000) and XAXQAO (Hosomi *et al.*, 2000)] among 51 crystal structures containing the heterodimeric hydrogen-bond motif *A* do hydrogen bonds generate both types of ring motif; however, their arrangement in those structures is different from that in (I).

In contrast with the 1:1 adduct, no phenyl–perfluorophenyl stacking interactions are observed in (I) (Fig. 2). The shortest distances between the phenyl-ring centroids [5.1799 (3) Å] correspond to the contacts between molecules related by a unit translation along the *y* axis. The hexameric assemblies interact *via* weak C—H···F and C—H···O hydrogen bonds (Table 2). All intermolecular F···F contacts exceed 2.90 Å.

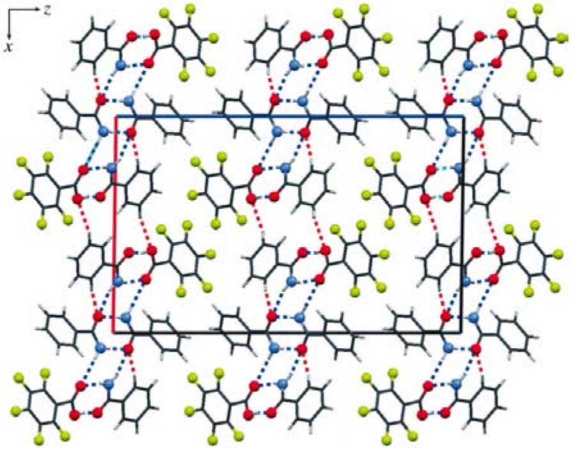

Figure 2
The packing in (I), viewed along the *y* axis, with hydrogen bonds and short C—H···O contacts shown as dashed lines.

Experimental

Compound (I) was prepared from an eqimolar mixture of benzamide and pentafluorobenzoic acid (Aldrich) dissolved in an acetone/water (1:1 *v*/*v*) mixture by slow evaporation of the solvent at room temperature. The first crystallization fraction consisted of (I) in the form of thin plates, whereas the second fraction was a mixture of crystals of (I) and pentafluorobenzoic acid.

Crystal data

$2C_7H_7NO\cdot C_7HF_5O_2$
$M_r = 454.35$
Monoclinic, $P2_1/c$
$a = 15.3195$ (5) Å
$b = 5.1799$ (3) Å
$c = 24.6053$ (8) Å
$\beta = 90.784$ (3)°
$V = 1952.33$ (14) Å^3
$Z = 4$
$D_x = 1.546$ Mg m^{-3}
Mo $K\alpha$ radiation
$\mu = 0.14$ mm^{-1}
$T = 130$ (2) K
Prism, colourless
0.58 × 0.23 × 0.20 mm

Data collection

Kuma KM-4-CCD κ-geometry diffractometer
ω scans
19656 measured reflections
3423 independent reflections
2561 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.040$
$\theta_{\rm max} = 25.0°$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.038$
$wR(F^2) = 0.092$
$S = 1.00$
3423 reflections
319 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0497P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\rm max} = 0.001$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.21$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

O1—C7	1.292 (2)	C1*A*—C7*A*	1.488 (3)
O2—C7	1.222 (2)	O1*B*—C7*B*	1.244 (2)
C1—C7	1.507 (3)	N1*B*—C7*B*	1.335 (2)
O1*A*—C7*A*	1.262 (2)	C1*B*—C7*B*	1.488 (3)
N1*A*—C7*A*	1.320 (2)		
O1*A*—C7*A*—N1*A*	121.03 (17)	O1*B*—C7*B*—N1*B*	121.46 (18)
O1—C7—C1—C6	−40.6 (2)	O1*B*—C7*B*—C1*B*—C2*B*	24.3 (3)
O1*A*—C7*A*—C1*A*—C2*A*	4.1 (3)		

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1—H1O···O1*A*	0.99 (3)	1.49 (3)	2.4733 (18)	169 (2)
N1*A*—H1*AB*···O1*B*	0.86 (2)	2.06 (2)	2.862 (2)	154.9 (18)
N1*A*—H1*AA*···O2	0.89 (2)	2.04 (2)	2.920 (2)	170.1 (16)
N1*B*—H1*BA*···O2$^{\rm i}$	0.87 (2)	2.30 (2)	3.064 (2)	146.6 (17)
N1*B*—H1*BB*···O1*B*$^{\rm i}$	0.88 (2)	2.04 (2)	2.919 (2)	176.0 (19)
C5*B*—H5*BA*···F2$^{\rm ii}$	0.96	2.45	3.382 (2)	163
C3*A*—H3*AA*···O1$^{\rm iii}$	0.96	2.54	3.373 (2)	145

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

All H atoms were located in electron-density difference maps. Positional and isotropic displacement parameters of H atoms from OH and NH$_2$ groups were refined. Carbon-bound H atoms were positioned with idealized geometry, with C—H = 0.96 Å, and refined isotropically using a riding model.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2000); cell refinement: *CrysAlis CCD*; data reduction: *CrysAlis RED* (Oxford Diffraction, 2000); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation Operation Manual* (Siemens, 1989) and *MERCURY* (Version 1.4; Bruno *et al.*, 2002); 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: SQ3027). Services for accessing these data are described at the back of the journal.

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