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The 2:1 cocrystal of benzamide and pentafluorobenzoic acid

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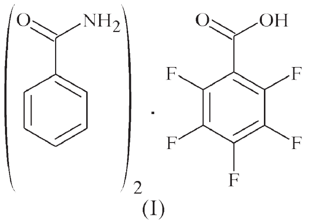
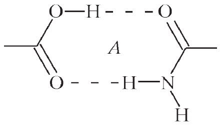
The crystal structure of the title compound, benzamide–2,3,4,5,6-pentafluorobenzoic acid (2/1), $2C_7H_7NO\cdot C_7HF_5O_2$, consists of centrosymmetric hexameric supermolecules composed of four amide and two carboxylic acid molecules connected *via* O—H···O and N—H···O hydrogen bonds. No phenyl–perfluorophenyl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

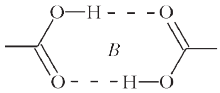
Comment

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

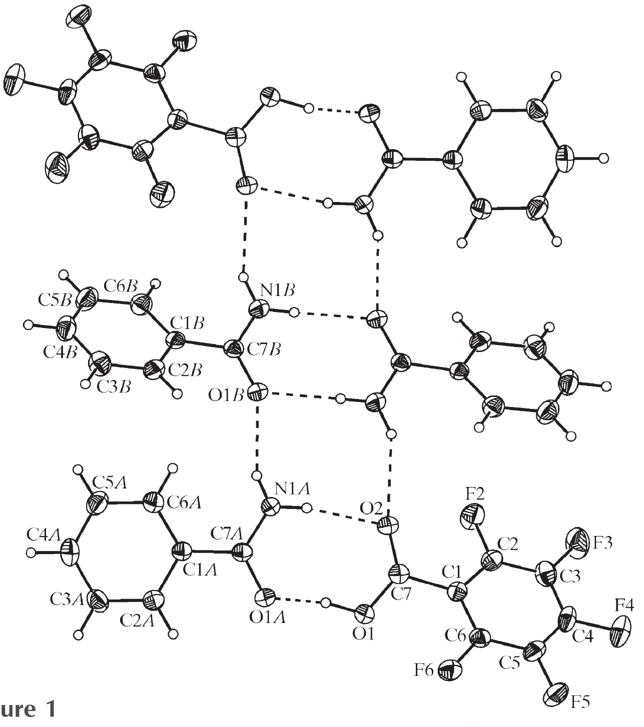


Figure 1
The centrosymmetric hexameric supermolecule in (I), with displacement ellipsoids drawn at the 50% probability level and hydrogen bonds shown as dashed lines. Unlabelled atoms are related to labelled atoms by the symmetry operation ($-x$, $-y + 1$, $-z + 1$).

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