

(4-Dimethylaminopyridine)₅(benzoic acid)₃(H₂O)₁₀: a Two-dimensional Clathrate Hydrate

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The title compound forms a unique layered structure in which benzoate anions are two-dimensionally clathrated by water molecules.

At a time when crystal structures are determined in their thousands and when even database analyses of entire families of structures are being incorporated into more general studies of crystal engineering, molecular recognition and supramolecular chemistry,¹⁻⁵ it is pertinent to ask if there is still any scope for the detailed description of a solitary small-molecule crystal structure. In this context, the crystal structure of the title compound is sufficiently arresting to warrant such a description and yet, the results reported in this communication also appear to have some bearing on the larger questions enumerated above.

The title decahydrate, **1**, mp 86–87°, was obtained accidentally during the work-up following a benzylation reaction of PhCH₂CHOHCONHCH(OMe)Ph, **2**. 4-(*N,N*-Dimethylamino)pyridine (DMAP; 1 equiv.), PhCOCl (1.3 equiv.) and Et₃N (1.3 equiv.) were added in CH₂Cl₂ to **2** (0.5 equiv.) to form the *O*-benzoylated derivative. After washing with aqueous NaHCO₃ the organic layer was evaporated. When the resulting residue was recrystallised from diethyl ether–light petroleum at 5 °C, crystals of **1** were obtained.

The crystal structure of **1** was determined at 130 K and satisfactorily refined.[†] There are eighteen residues in the asymmetric unit. Three out of the five DMAP residues are protonated at the heterocyclic N atom and two of these form N–

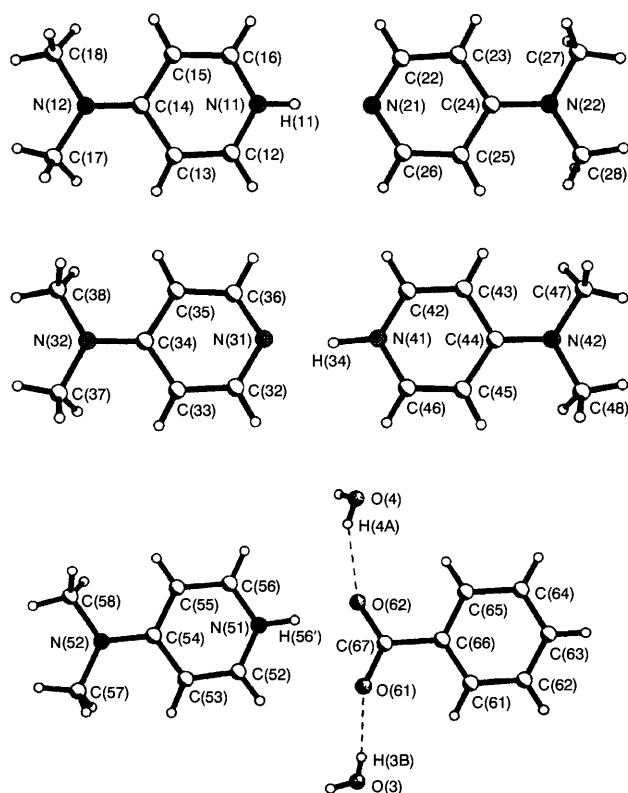


Fig. 1 DMAP building blocks for the herringbone slabs in the crystal structure of **1**. The hydrogen bonds between benzoate anions and water molecules constitute the link between slabs and layers.

H···N hydrogen bonds with the two non-protonated DMAPs as shown in Fig. 1 [N(11)···N(21); N(31)···N(41)]. The third protonated DMAP forms a hydrogen bond [N(51)···O(62)] with a benzoate anion which is also linked to bridging water molecules, *via* hydrogen bonds O(61)···O(3) and O(62)···O(4). The three dimeric aggregates in Fig. 1 form a herringbone slab arrangement as shown in Fig. 2. These slabs alternate with benzoate hydrate layers which are shown in Fig. 3. Notice that the benzoate anions in Fig. 2 form the points of attachment of the slabs to the benzoate hydrate layers *via* O(3) and O(4) which lie within the layers. The planes of the molecules in the slabs and layers are, therefore, nearly perpendicular.

The very high water content in this crystal occurs entirely within the benzoate layers which constitute the heart of this unique structure. Fig. 3 shows that the benzoate anions are arranged with their hydrophobic portions facing each other forming a centrosymmetric dimer. This dimer is hydrophobic on the inside and hydrophilic on the outside. The outer hydrophilic surface is stabilised by a ring of water molecules and the hydrocarbon portions of the dimer are literally a drop of oil in the surrounding pool of water. Appropriately, the dimers are additionally stabilised by C–H···O hydrogen bonds to water molecules O(3F) and O(9A). In a sense, this structure is complementary to that of benzoic acid, wherein hydrogen-bonded centrosymmetric dimers are hydrophilic within and hydrophobic on the outside, being stabilised by herringbone contacts with other phenyl rings from neighbouring dimers. Alternatively, the structure in Fig. 3 may be likened to a two-dimensional equivalent of the polyhedral clathrate hydrate structures,⁶ in which a three-dimensional framework of water molecules surrounds the guest and the basic structural component is a regular pentagon formed by O–H···O hydrogen bonds. The regular solid generated by assembling such pentagons is the dodecahedron, but because space cannot be filled periodically

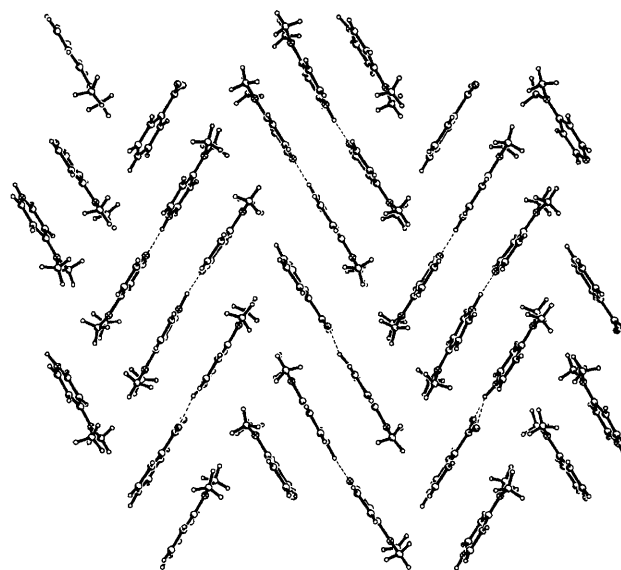


Fig. 2 Herringbone slab arrangement in the crystal structure of **1**. [010] is vertical and [001] is horizontal.

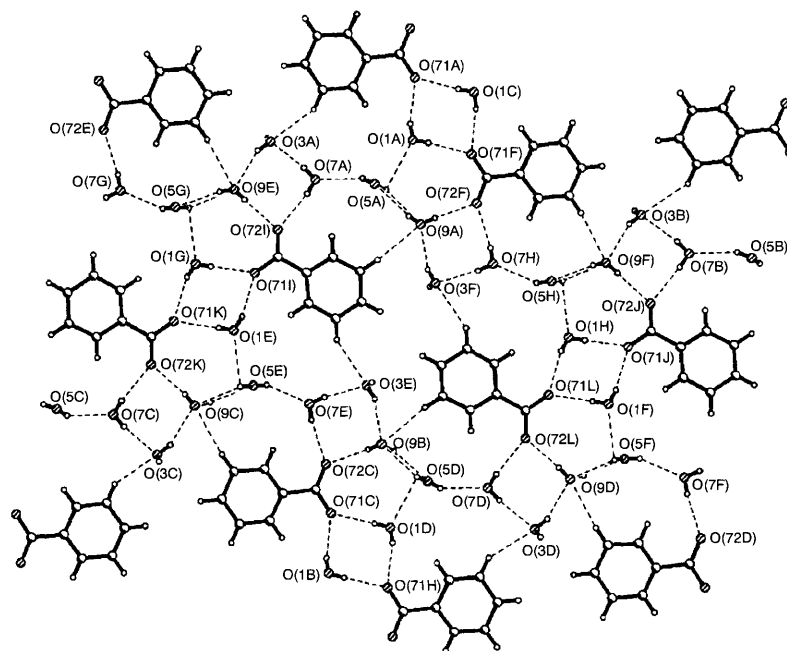


Fig. 3 Hydrated benzoate layer in the crystal structure of **1**. The layers are parallel to [011] and symmetry-independent, although geometrically identical layers may be found at $x = 0$ and at $x = 0.5$. Symmetry-related atoms have the same numerical code. [001] is along the translation $O(71K) \cdots O(71L)$ and [010] is perpendicular to this direction. Notice that the centrosymmetric benzoate dimer is completely encircled by water molecules.

with these dodecahedra, hexagons are incorporated, resulting in tetradeca-, pentadeca- and hexadeca-hedra which alternate with the dodecahedra to generate the three-dimensional structure. In the two-dimensional benzoate hydrate layer seen in **1**, the polyhedra above reduce to quadrilaterals and other polygons formed by $O-H \cdots O$ hydrogen bonds. These include the parallelogram $O(71K)-O(1E)-O(71I)-O(1G)$, the quadrilateral $O(72I)-O(7A)-O(3A)-O(9E)$ and the distorted pentagon $O(1G)-O(71I)-O(72I)-O(9E)-O(5G)$. Different polygons are required for layer filling just as different polyhedra are required for space filling in the three-dimensional clathrate hydrates. Interestingly, one or two benzoate O atoms are included in each of these polygons as in the three-dimensional polyhedral clathrate structure of tetra(butyl)ammonium benzoate hydrate, which seems to be the only reported crystal structure even remotely resembling the title compound.^{6,7}

There are other unusual features in the crystal structure of the title decahydrate. (i) The herringbone slabs consist of twice the number of cations as they do of anions while the layers consist of anions only. There are, in effect, fairly large concentrations of charge in different regions of the structure, and anions and cations do not tend to make a maximum number of close contacts as would be expected in a salt. A possible reason for this is the presence of a large amount of water in the crystal which, with its high dielectric constant, may disperse the charge effectively. (ii) The two hydrated layers which sandwich each herringbone slab are crystallographically independent though they are, geometrically speaking, virtually identical. (iii) The presence of eighteen residues (five DMAPs, three benzoates and ten water molecules) in the asymmetric unit is unprecedented for a small-molecule structure.

Why is such a structure formed at all? In this context, it is pertinent to mention that all subsequent attempts to crystallise **1** from solutions of DMAP and benzoic acid in water, proved futile. Rather, two simpler crystals, a DMAP benzoate monohydrate, mp 101–103 °C, and an anhydrous acid benzoate, (DMAP)(PhCO₂H)₂, mp 128–129 °C, were obtained. The crystal structures of these substances were also determined, but their packing patterns proved to be straightforward. It is possible that the highly unusual crystal structure of **1** is a result

of low concentrations of benzoate anion formed by hydrolysis of PhCOCl by NaHCO₃ in the work-up. If so, it may be expected that polymorphic or related crystalline forms of other substances may also be obtained by generating the relevant material(s) *in situ*. It is well known that crystals of better quality are obtained when low concentrations of material are generated electrochemically.⁸ That low concentrations are important in crystal growth is also shown by the efficacy of the gel diffusion method in obtaining crystals of organic donor–acceptor complexes.⁹ The present example shows that entirely different and novel crystalline forms may be obtained when the crystallisation conditions are such that low concentrations of material are generated chemically.

It is sobering to note that, even with the considerable recent advances in experimental and computational crystal engineering, it would be impossible to predict the details or even the occurrence of a crystal structure such as the one reported here. It is preferable to reflect on the fact that constituents of such simplicity as DMAP, benzoic acid and water can form a crystal structure of such artistry and intricacy.

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Footnote

[†]Crystal data for **1**: C₅₆H₈₈N₁₀O₁₆, $M = 1157.36$, monoclinic space group $P2_1/c$, $a = 18.055(8)$, $b = 19.964(5)$, $c = 17.198(2)$ Å, $\beta = 99.27(5)^\circ$, $V = 6118(3)$ Å³, $D_c = 1.26$ g cm⁻³, $Z = 4$, crystal size $0.70 \times 0.42 \times 0.20$ mm, $\mu(\text{Cu-K}\alpha) = 0.764$ mm⁻¹, $F(000) = 2488$, $T = 130(2)$ K, Siemens P4 diffractometer, ω scans, 6494 reflections collected, 3148 observed at 2σ level, structure solution with SHELXS-86, refinement with SHELXL-93 on F^2 for 808 parameters, non-H atoms anisotropic, H-atoms

in calculated positions, $R = 0.0951$, $wR = 0.2164$. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

- 1 G. R. Desiraju, *Crystal Engineering: The Design of Organic Solids*, Elsevier, Amsterdam, 1989; G. R. Desiraju, *Angew. Chem., Int. Ed. Engl.*, 1995, in press.
- 2 J. C. MacDonald and G. M. Whitesides, *Chem. Rev.*, 1994, **94**, 2383.
- 3 R. Taylor and F. H. Allen, in *Structure Correlation*, ed. H.-B. Bürgi and J. D. Dunitz, VCH, Weinheim, 1994, vol. 1, pp. 111–204.
- 4 D. Braga, F. Grepioni, P. Sabatino and G. R. Desiraju, *Organometallics*, 1994, **13**, 3532; D. Braga, F. Grepioni, K. Biradha, V. R. Pedireddi and G. R. Desiraju, *J. Am. Chem. Soc.*, 1995, **117**, 3156.
- 5 T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1993, **115**, 4540.
- 6 T. C. W. Mak and G.-D. Zhou, *Crystallography in Modern Chemistry*, Wiley, New York, 1992, pp. 1175–1206; G. A. Jeffrey and W. Saenger, *Hydrogen Bonding in Biological Structures*, Springer, Berlin, 1991, pp. 479–486.
- 7 M. Bonamico, G. A. Jeffrey and R. K. McMullan, *J. Chem. Phys.*, 1962, **37**, 2219.
- 8 V. Enkelmann, B. S. Morra, C. Kroehnke, G. Wegner and J. Heinze, *Chem. Phys.*, 1982, **66**, 303; M. D. Ward, P. J. Fagan, J. C. Calabrese and D. C. Johnson, *J. Am. Chem. Soc.*, 1989, **111**, 1719.
- 9 G. R. Desiraju, D. Y. Curtin and I. C. Paul, *J. Am. Chem. Soc.*, 1977, **99**, 6148.