Crystal Engineering: Helical Tubuland Diol–Phenol Cocrystals

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Phenols can occupy one eclipsed arm of the trigonal hydrogen-bonded spine structure of helical tubuland diols thus producing a new family of cocrystalline solids the X-ray crystal structures of which are described.

Although it is not yet possible to predict crystal structures on purely theoretical grounds,[1] increased understanding of interactions in solids[2] is beginning to provide pointers towards prediction by analogy. Knowledge and understanding of hydrogen bonding and other intermolecular forces offers the potential for new and unconventional forms of synthesis.[3,4]

We have previously shown that crystallisation of each of the alicyclic diols **1–3** results in isostructural lattices (space group $P3_121$) constructed from a series of trigonal hydrogen-bonded spines and containing parallel canals.[5] For **1** and **2** these canals are large in cross-section and enclose guest molecules. By retaining the hydrogen-bonding structure but varying the molecular structure, we have been able to develop a series of these helical tubuland diols with a considerable range of canal topologies and inclusion properties.[6,7]

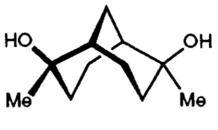
In continuing our studies we wished to employ this hydrogen-bonded spine motif in the synthesis of new self-assembling binary structures. Here, we report preliminary details of a new family of such materials formed by cocrystallisation of helical tubuland diols and phenols.

Slow evaporation of a solution of **1** and *p*-chlorophenol in mesitylene gave crystalline material containing both hydroxylic components (by IR and ^{1}H NMR spectroscopy) in the ratio 1 : 1 (microanalysis). X-Ray structural determination confirmed this composition and revealed the material to have a hydrogen-bonded cocrystalline structure where molecules of *p*-chlorophenol have replaced molecules of **1** in one of the three eclipsed arms (viewed along the *c* axis) of molecules radiating from each trigonal spine (Fig. 1).†

This substitution results in the hydrogen-bonding network changing from a three- to a two-dimensional arrangement involving layers (Fig. 2). Each layer incorporates molecules of **1** with the same chirality around the helical spines, but such layers alternate with those of the opposite chirality. Therefore, unlike the chiral helical tubuland[8] structures, which crystallise as conglomerates,[9] the solid **1**·(*p*-chlorophenol) is centrosymmetric and achiral. The layers of opposite chirality associate by means of ···Cl···Cl···Cl···Cl··· interactions producing pseudomacrocyclic rings comprising four molecules of **1** and four of *p*-chlorophenol. Chlorine interactions are very favourable and have been documented across a wide range of compounds.[10]

In crystal engineering terms, the lattice of **1**·(*p*-chlorophenol) is thus constructed from two major types of intermolecular interaction, namely the trigonal hydrogen-bonded spine and the chlorine–chlorine association. We, therefore, expected to obtain related structures in other cases and this proved correct. Diol **2** also yields a 1 : 1 compound with *p*-chlorophenol, and is isostructural with the first.

Furthermore, we anticipated that use of hydroquinone instead of *p*-chlorophenol would result in formation of a



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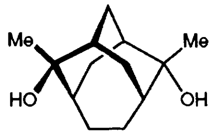

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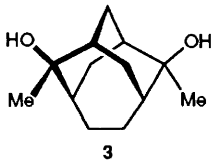

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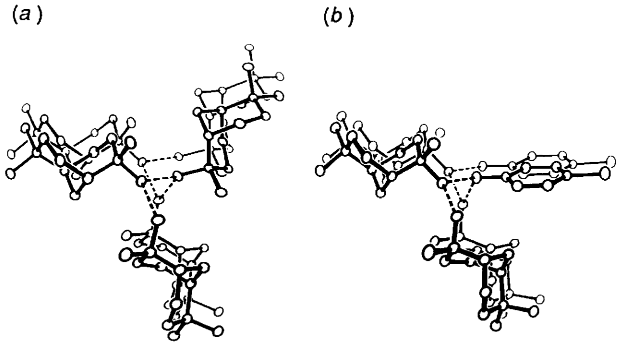

Fig. 1 (*a*) The trigonal hydrogen-bonded spine ···OH···OH···OH··· that constitutes the structural core of the helical tubuland lattice of pure diol **1**. (*b*) The similar spine formed by **1** and *p*-chlorophenol molecules in the cocrystalline material **1**·(C_6H_5ClO). Hydrogen bonds are represented as dashed lines, hydrogen atoms are omitted for clarity.

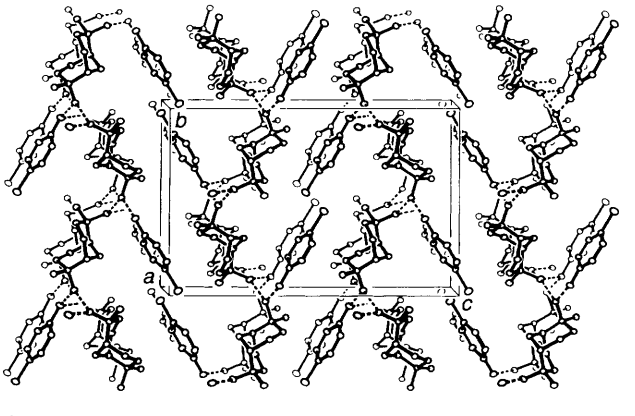

Fig. 2 Arrangement of molecules of diol **1** and *p*-chlorophenol in the unit cell of **1**·(C_6H_5ClO). The hydrogen-bonded spines and chlorine–chlorine interactions, eclipsed packing and pseudomacrocycles are readily visible.

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† *Crystal data* for: $(C_{11}H_{20}O_2)\cdot(C_6H_5ClO)$, M = 312.8, monoclinic, $P2_1/c$, a = 6.927(1), b = 12.696(1), c = 19.286(4) Å, β = 94.825(8)°, U = 1690.1(4) Å^3, Z = 4, D_c = 1.23 g cm^{-3}, λ(Cu-Kα) = 1.5418 Å, μ = 20.71 cm^{-1}. Anisotropic thermal parameters were refined for all non-H atoms, final R = 0.035 for 1375 independent observed reflections [$I/\sigma(I) > 3$] and 199 variables.

$(C_{11}H_{20}O_2)\cdot(C_6H_6O_2)_{0.5}$, M = 239.3, monoclinic, $P2_1/c$, a = 6.8637(5), b = 12.8289(5), c = 15.974(1) Å, β = 103.099(3)°, U = 1370.0(2) Å^3, Z = 4, D_c = 1.16 g cm^{-3}, λ(Cu-Kα) = 1.5418 Å, μ = 6.05 cm^{-1}. Anisotropic thermal parameters were refined for all non-H atoms, final R = 0.046 for 2065 independent observed reflections [$I/\sigma(I) > 3$] and 164 variables.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

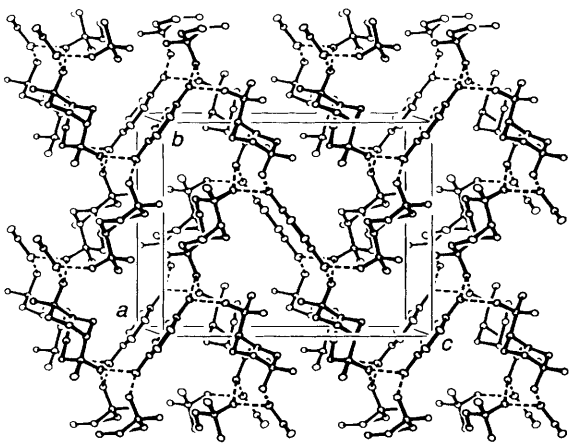

Fig. 3 Unit cell of $\mathbf{1}\cdot(C_6H_6O_2)_{0.5}$ showing the network hydrogen-bonded lattice. Hydrogen atoms are omitted for clarity.

three-dimensional hydrogen-bonded lattice by replacement of each pair of associated *p*-chlorophenols in the pseudomacrocycle by one hydroquinone molecule. The crystal structure of the cocrystalline product **1**·(hydroquinone)$_{0.5}$ (Fig. 3)† was in full accord with these expectations, adopting the same lattice packing and symmetry (space group *P*2$_1$/*c*) as the previous material.

Work is currently underway to delineate the extent and scope of this new series of materials. Early indications are that a number of simple phenols lead to such structures but that more complex phenols, such as Dianin's compound,[11] do not. Diol **3** also does not appear to form cocrystals. Thus, the tentative conclusion is that only those simple phenols and helical tubuland diols that pack poorly by themselves are likely candidates for cocrystalline combination.

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