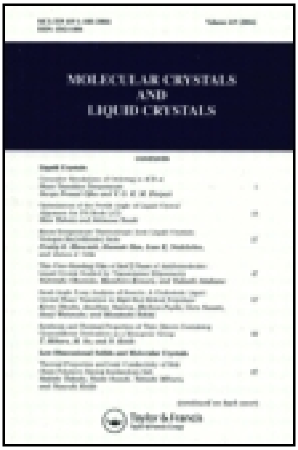

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HELICAL TUBULAND DIOL — PHENOL CO-CRYSTALS

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Abstract A new family of co-crystalline materials formed between helical tubuland diols and phenols has been discovered. Preliminary details of the X-ray structures of (**1**)·(*p* -chlorophenol), (**2**)·(*p* -methoxyphenol), and (**1**)·(hydroquinone)$_{0.5}$ are presented, and the crystal engineering aspects of these compounds are discussed.

INTRODUCTION

Crystallisation of certain alicyclic diols results in three-fold spirals of HO····HO····HO···· hydrogen bonds (termed spines) between diol molecules, as shown in Figure 1 for diol **1**.

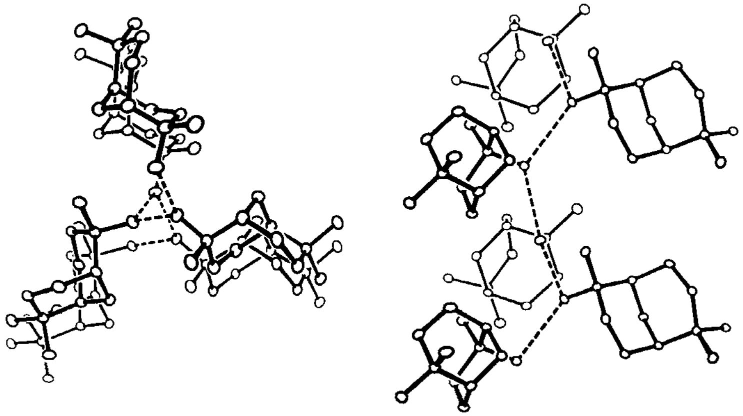

FIGURE 1. Two turns of the hydrogen bonded spine arrangement in crystalline diol **1** viewed (left) as a projection in the *ab* plane, and (right) with the *c* axis nearly vertical. Hydrogen bonds are represented by dashed lines. For clarity, only non-hydrogen atoms are shown.[1]

Similar hydrogen bonding through the second hydroxy group of each molecule produces a network lattice where diol molecules surround a series of parallel canals which can enclose a wide variety of guest molecules. By retaining this hydrogen bonding motif but varying the diol molecular structure we have been able to develop a family of these helical tubuland diols, including **1-3** (Figure 2), which have a considerable range of canal topologies[2-4]. Diols such as **1,2** have canals with considerable cross-sections and are excellent inclusion hosts for small molecules of most functional group types.[5,6] However the canals of **3** are largely occupied by parts of its own structure and the remaining voids are too small for inclusion properties to result.

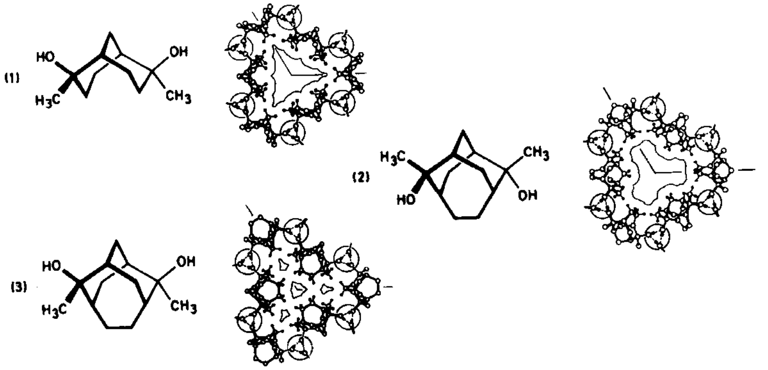

FIGURE 2. Molecular structures of diols **1-3** showing for each helical tubuland host lattice a projection view of one canal only in the *ab* plane. The hydrogen bonded spines are circled and key hydrogen atoms which mark the van der Waals surface of the canals are shown as filled circles.

RESULTS

During our screening of the inclusion properties of **1,2**[5,6] we found anomalous behaviour when phenols were used. In some cases these substances were not included at all despite their small size. On other occasions the crystalline material produced contained both molecular components by IR and NMR spectroscopy, and by combustion analysis, but the X-ray powder diffraction pattern (XRPD) was quite different to those of the lattice inclusion compounds usually formed by these diols.

A typical example is the 1:1 compound, m.p. 105-107 °C, formed when diol **1** is crystallised from *p* -chlorophenol. X-Ray structural determination showed this substance to be an intimately hydrogen bonded co-crystalline substance, rather than a lattice inclusion compound with only van der Waals attractions between the two components. Molecules of the phenol have replaced molecules of **1** in one of the three eclipsed stacks of diol molecules in the spines of this structure (Figure 3)[1], thereby changing the three-dimensional hydrogen bonded network to a two-dimensional layer arrangement.

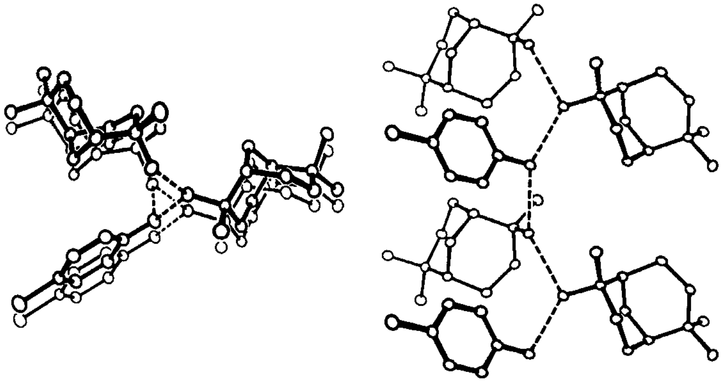

FIGURE 3. The mixed hydrogen bonded spine arrangement in the co-crystalline substance (**1**)·(*p* -chlorophenol) viewed (left) in the *ab* plane and (right) with the *c* axis vertical.[1]

Diol molecules around each spine are of the same enantiomer but alternating layers involve the other enantiomer, yielding an achiral substance in space group $P2_1/c$. These layers associate in part through ···Cl···Cl···Cl···Cl··· interactions[7] producing pseudomacrocyclic rings involving four molecules of each component (Figure 4).[8] Other phenols also produce 1:1 compounds with **1**. From the similarity of their XRPD patterns these compounds adopt the same lattice packing and symmetry.

Diol **2** also forms co-crystals with certain phenols. Another 1:1 compound, m.p. 80-81 °C, is formed between **2** and *p* -methoxyphenol. This material is isostructural with the first in space group $P2_1/c$. Figure 5 shows the unit cell arrangement with the methoxy groups stacked in a very similar manner to the chlorine atoms in the original.

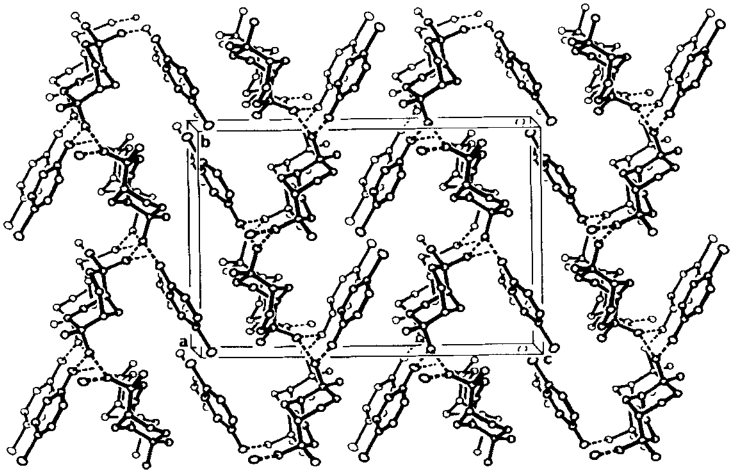

FIGURE 4. The hydrogen bonded lattice of (**1**)·(*p* -chlorophenol) showing the eclipsed stacks of diols and *p* -chlorophenols. Hydrogen bonds are shown as dashed linkages. The spines, layers, pseudomacrocycles, and chlorine close-contacts are readily visible.[1,8]

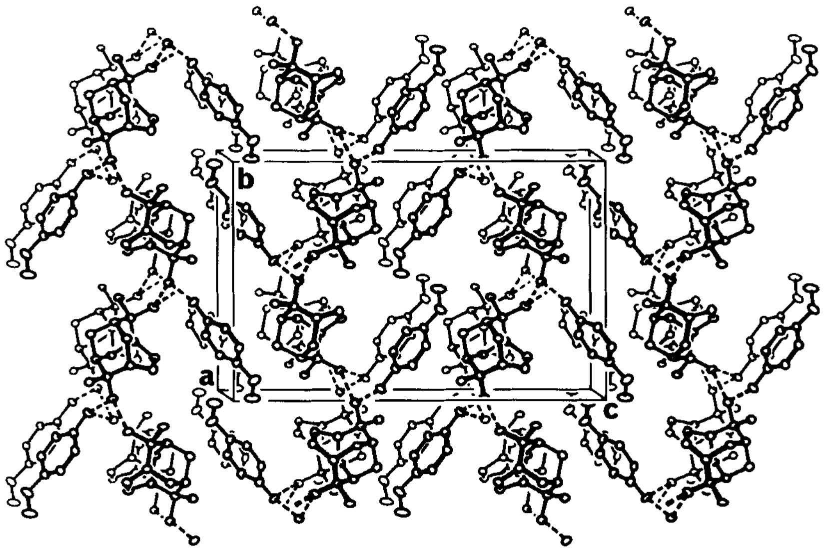

FIGURE 5. Unit cell of the (**2**)·(*p* -methoxyphenol) co-crystalline compound. The remarkable similarity to the structure shown in Figure 4 should be noted.

Given the propensity of the *para* -substituents to associate in a near linear fashion in both these structures, we argued that replacement of these phenols by hydroquinone should result in production of a further co-crystalline solid where each dihydric hydroquinone molecule should replace a pair of the monohydric phenols.

Single crystal X-ray structural determination fully confirmed these ideas. The substance produced with diol **1**, m.p. 189-190 °C, has the same lattice packing and symmetry ($P2_1/c$) as found previously (Figure 6). One significant difference is that now each pseudomacrocycle is composed of four diol molecules but only two phenols, resulting in the changed stoichiometry $(\mathbf{1}).(\text{hydroquinone})_{0.5}$. Consequently the lattice arrangement has altered from two-dimensional layers to a three-dimensional network, as reflected in the sharp increase in m.p.

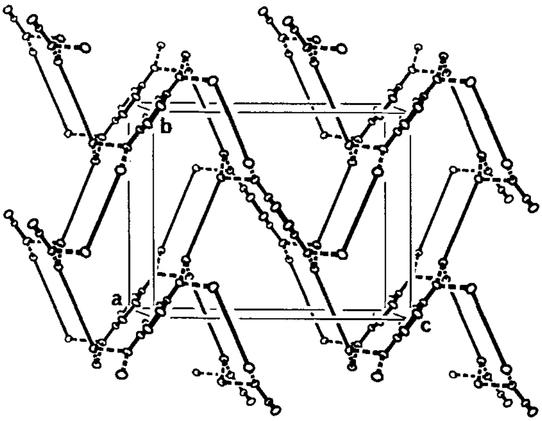

FIGURE 6. The three-dimensional hydrogen bonded lattice present in $(\mathbf{1})\cdot(\text{hydroquinone})_{0.5}$ represented in diagrammatical fashion. For simplicity all hydrogen atoms are omitted and each diol molecule is represented just as a heavy spacer linking two oxygen atoms. The hydrogen bonded spines are indicated by dashed linkages.

DISCUSSION

This paper describes preliminary details of examples of a new family of materials formed by stoichiometric combination of helical tubuland diols with phenols. At present some 15 examples of these substances have been identified and characterised using methods including IR and ^1H NMR spectroscopy, elemental analysis, XRPD pattern, and in some cases X-ray structural determination.

In these compounds the phenols have replaced molecules of the diol in one of the three eclipsed arms of molecules radiating from each three-fold hydrogen bonded spine. However, it has been observed that by no means all phenols (for example calix[4]arene, Dianin's compound, and many more commonplace phenols) have this ability. Similarly all attempts to obtain co-crystals using diol **3** have failed. Furthermore it is known[5] that that strongly hydrogen bonding guests such as propanoic acid and diethylamine are trapped as typical lattice inclusion compounds within the helical tubuland lattice of **1** without intercepting the diol hydrogen bonding array in any way.

We are interested in understanding the crystal engineering factors[9] involved in formation of these stoichiometric combinations, and infer that the likelihood for preparation of new examples of these co-crystalline materials depends on the combination of a helical tubuland diol and a phenol with similar packing difficulties. Thus pure diol **3**, m.p. 245-247 ^oC, is an unlikely candidate. Its canals are nearly completely filled by parts of its own structure and effective intermolecular van der Waals interactions are present. In contrast the diols **1**,**2** normally resort to formation of lattice inclusion compounds to bolster their packing density arrangements.

A number of pure simple phenols suffer surprising problems in forming simple, close-packed lattices. Such difficulties are revealed by the propensity of these compounds to form co-crystalline materials of various types[10] and to show polymorphic behaviour[11].

In the case of *p* -chlorophenol, inclusion compounds are formed with noble gases and low molecular weight hydrocarbons.[12,13]. Pure *p* -chlorophenol crystallises in two polymorphic structures[14], both of which are in space group $P2_1/c$. Hydroquinone forms both inclusion compounds and different crystal modifications.[10] The most stable polymorph at room temperature (α-hydroquinone) contains 54 molecules in each unit cell: an amazing number for such a small, highly symmetrical molecule.[15]

Such simple phenols thus find it advantageous to combine with helical tubuland diols such as **1** or **2** in an intimate co-crystalline solid such as those described here. However, there will be a size restriction on the molecules able to infiltrate the diol hydrogen bonded spine network which will bar more complex phenols from participating in structures of this general type.

ACKNOWLEDGEMENTS

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