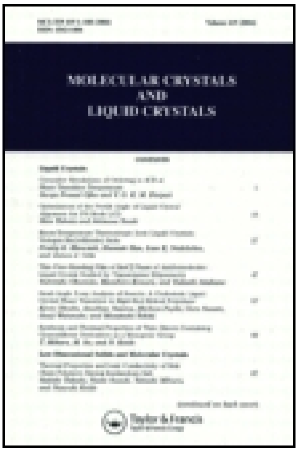

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FORMATION AND STABILITY OF THE HELICAL TUBULAND DIOL INCLUSION LATTICE

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Abstract Alicyclic diols of specific design crystallise with a lattice enclosing a series of parallel helical canals which trap a wide range of guest molecules. Typical structures of these helical tubulate compounds are presented. The canal sizes and geometries vary considerably depending on the actual diol utilised. Lattices with smaller canals retain the helical tubuland structure in the absence of guests, whereas those with larger canals collapse to a close-packed structure.

Keywords: inclusion compounds, crystal structures, host-guest chemistry, helical tubuland hosts, helical tubulate compounds, hydrogen bonding

THE HELICAL TUBULAND LATTICE

The alicyclic compounds (1-3) are members of a family of hosts, the helical tubulands, whose crystal structures feature parallel canals containing trapped guest molecules[1,2]. As illustrated in Figure 1, variation in the molecular structure of the host diol results in considerable modification of the canal topology and dimensions observed in the crystalline material.

The helical tubulands crystallise as conglomerates in space group $P3_121$ and its enantiomorph $P3_221$ as long trigonal needles with the canals parallel to the needle axis c. Tight spiral spines of hydrogen bonds ...O-H...O-H...O-H... (circled in Figures 1 and 2) form the structural core of the crystal lattice. Diol molecules radiate from and interconnect these spines such that a hexagonal arrangement of six spines encloses each canal which is lined only by hydrocarbon hydrogen atoms. The canal walls involve a double helical array of diol molecules hydrogen bonded in the sequence:

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    ...HOC----COH...OC----CO...HOC----COH...OC----CO...
                    H     H              H     H
```

(where C----C represents the diol molecule as a tie-line joining the two hydroxy groups).

Figure 2 shows a projection view in the ab plane of the host network of diol (2) with significant hydrogen atoms drawn with their van der Waals radii. The resulting trefoil-shaped canals have a maximum diameter of 8.3 Å and an unobstructed cross-sectional area of 30.2 Å^2. It should be noted that Figures 1 and 2 represent slices across the needle axis of each crystal and therefore the helical characteristics of the canal construction are lost in these representations[3,4].

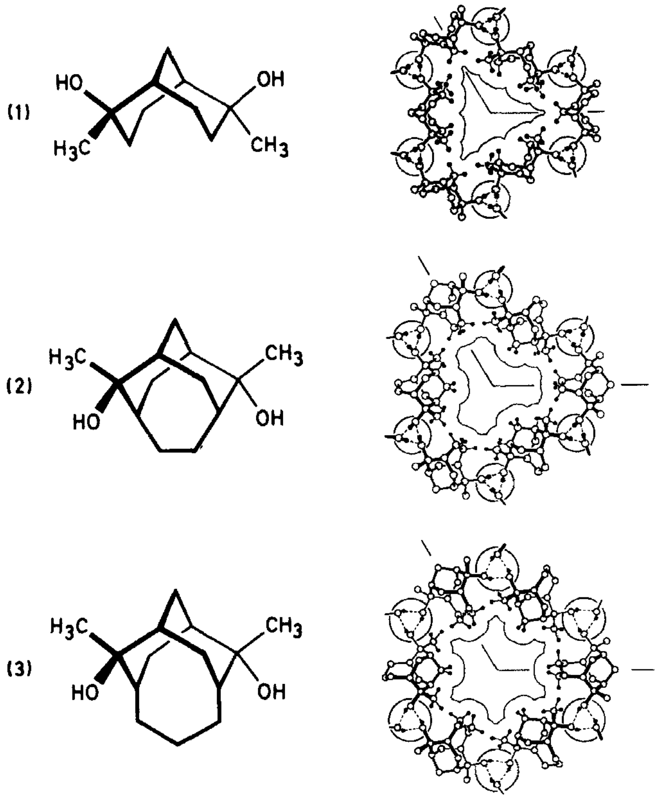

FIGURE 1 Molecular structures of diols (1-3) showing for each helical tubuland lattice a projection view of one canal only in the *ab* plane.

HELICAL TUBULATE COMPOUNDS

Diols (1-3) are all potent inclusion hosts, trapping a wide range of guest molecules when the diol is crystallised from liquid guest. Confirmation of formation of the helical tubuland lattice is conveniently monitored by X-ray powder diffraction, while confirmation of inclusion is available from I.R. spectroscopy and combustion data.

Detailed information on the behaviour of guest molecules in helical tubulate compounds can be difficult to obtain because of the incongruent symmetry of the host and guest components. Figures 3 and 4 show typical arrangements of guest in the (1 - Thiophene) and (2 - Carbon tetrachloride) helical tubulates as derived from single crystal X-ray data. The latter compound is a good illustration of the possible complexity of host-guest relationships in such materials. Six different carbon tetrachloride orientations are repeated every five host unit cells resulting in an overall stoichiometry of $(2)_{15}\cdot(CCl_4)_6$; or $(2)_3\cdot(CCl_4)_{1.2}$ per unit cell[5].

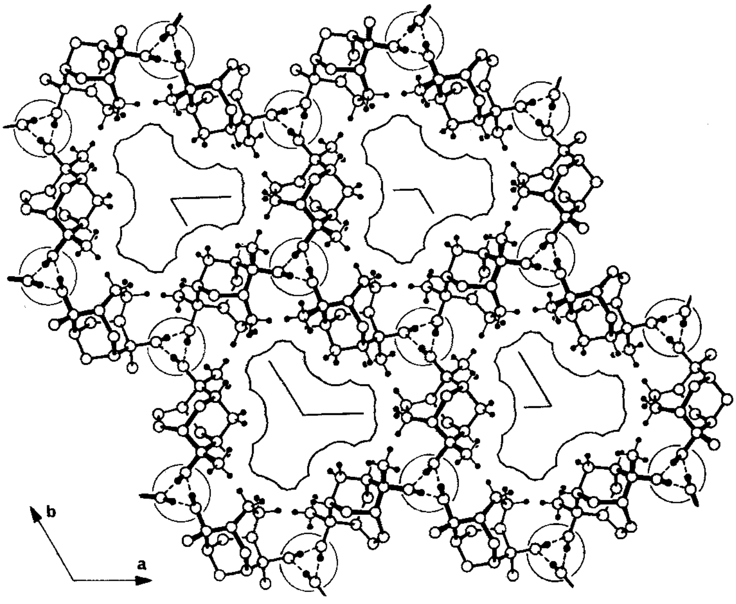

FIGURE 2 Projection view looking along *c* of the diol network in crystalline (2). Dashed lines indicate OH hydrogen bonds comprising the spines (circled), and the filled circles represent significant hydrogen atoms defining the canals.

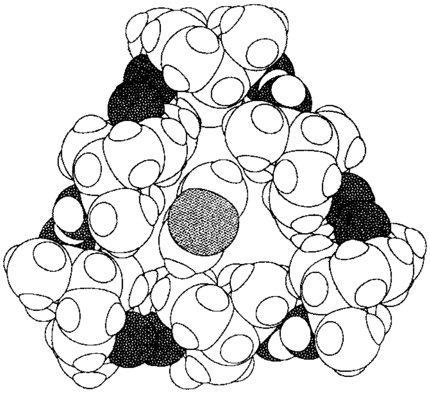

FIGURE 3 Space-filling representation of host-guest interactions in the helical tubulate $(1)_3.(C_4H_4S)$.

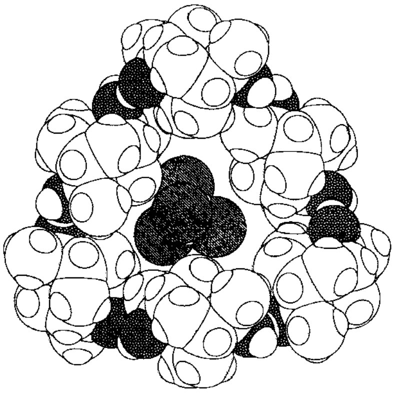

FIGURE 4 Typical arrangement of host and guest in the helical tubulate $(2)_3.(CCl_4)_{1.2}$.

STABILITY OF THE HELICAL TUBULAND STRUCTURE

Inclusion compounds formed by diols (1) and (3) are invariably of the helical tubulate type. In contrast, diol (2) commonly forms either helical tubulate compounds or an alternative tetragonal inclusion system (space group $I4_1/acd$) which involves both enantiomers of the diol[5,6]. Guest molecules are now enclosed in ellipsoidal cavities within the host lattice. Clearly both classes of inclusion compound are extremely close in energy. However it is not known why the behaviour of (2) is so different from diol (1) which has smaller canals, and diol (3) which has larger helical tubuland canals.

Certain patterns of inclusion behaviour are apparent for diol (2). The helical tubuland host lattice is generally preferred when the guests are aliphatic or alkylbenzenes more alkylated than toluene. The alternative ellipsoidal clathrate lattice is usually adopted when the guests are small molecules, monosubstituted benzenes, or non-alkylated disubstituted benzenes. A few guests form both inclusion types depending on the exact experimental conditions employed.

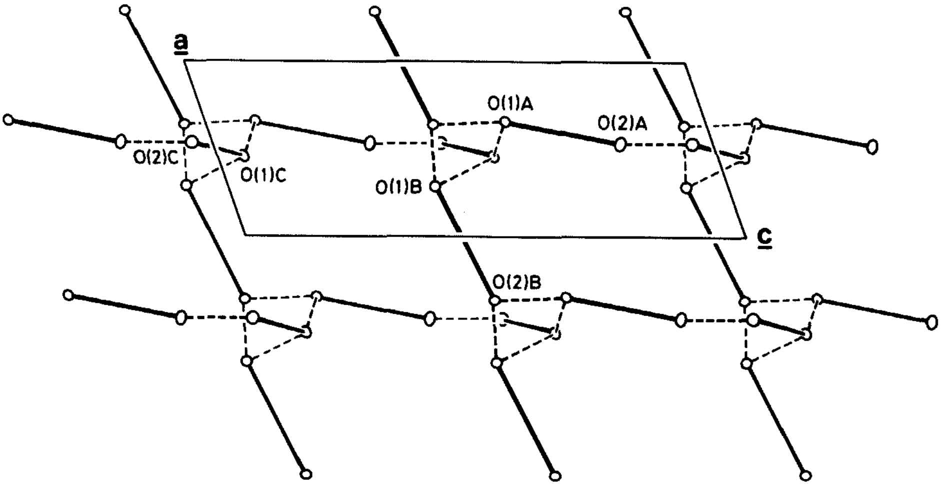

FIGURE 5 The hydrogen bonding network of guest-free (2). For clarity, diol molecules are drawn as as solid spacer rods connecting the two hydroxy groups. Hydrogen bonds are shown as dashed lines.

Guest-free samples of diols (1-3) have been prepared by crystallisation from mesitylene (a solvent too bulky to be included), by sublimation, and by heating the inclusion compounds under reduced pressure[7]. We find that in all cases (1) retains its helical tubuland lattice despite its guest-free canals comprising about 17% of its crystal volume. This structure is reminiscent of zeolites such as laumontite and zeolite L which have canals along only one axis of the solid[8]. However zeolites require guest templates for their formation, whereas the sublimation result reveals that diol (1) itself contains inbuilt features controlling development of the helical tubuland lattice.

Contrary behaviour is exhibited by diols (2) and (3) where the guest-free material no longer has the helical tubuland lattice[7]. Figure 5 shows, in diagrammatic form, the close-packed lattice of guest-free (2). The asymmetric unit contains three independent diol molecules (A-C), of which A and C each are one hydrogen bond short of the normal maximum (i.e. two donors and two acceptors per diol). The resulting hydrogen bonding network links molecules as layers in the *ac* plane.

The switch in guest-free structures correlates well with the canal size of the helical tubuland lattices and the strength of their hydrogen bonding (Table 1).

The larger canals and weaker hydrogen bonding present in the helical tubuland forms of (2) and (3) require the presence of guest molecules to form and maintain this canal lattice type.

TABLE 1 Data for the helical tubuland forms of diols (1-3).

	Melting point (^{0}C)	Canal unobstructed cross-sectional area (Å ^{2})	Intermolecular hydrogen bond O....O distance (Å)
(1)	189-191	22.4	2.81
(2)	146-148	30.2	2.98
(3)	146.5-147	34.7	3.08

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