# Stability of the Helical Tubuland Inclusion Lattice

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Diol **1** maintains its open tubular lattice even in the absence of guest molecules, whereas the crystal structure of guest-free **2** reveals that it collapses to a layer structure involving incomplete hydrogen bonding.

The factors involved in formation of multimolecular or lattice inclusion compounds[1,2] are complex and only partially understood. Most hosts of this type (*e.g.* urea, hydroquinone, cyclophosphazenes) require the presence of neutral guest molecules for formation or maintenance of lattices containing such cavities, and alternative close-packed structures are adopted in their absence.[3] However, in a few cases (*e.g.* Dianin's compound) the same cage host structure is present in either circumstance.[1,3] We report here on the properties of the helical tubuland diol host family[4] where both modes of behaviour are encountered.

Each of the alicyclic diols **1–5** can be crystallised from ethyl

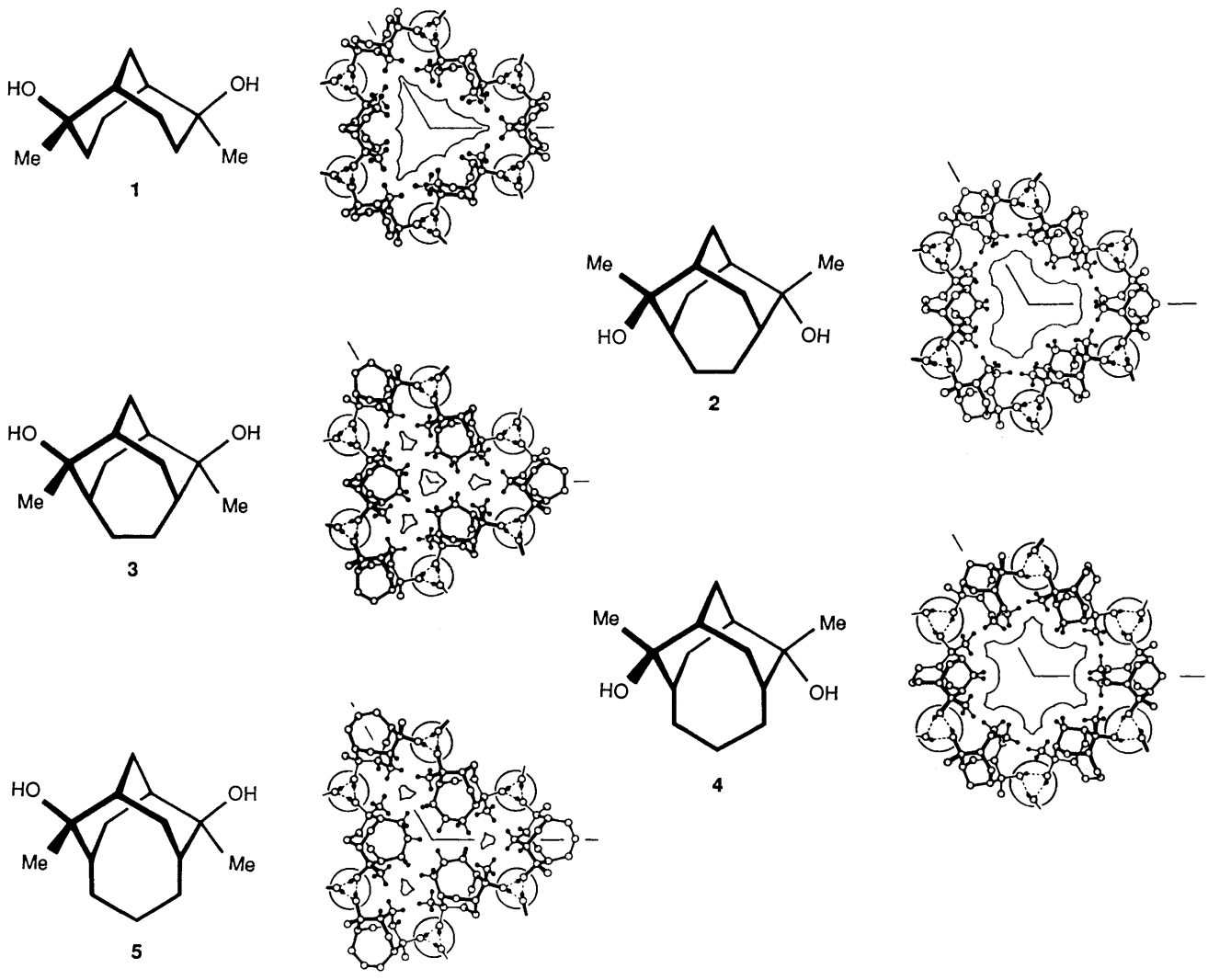


**Fig. 1** Structures of diols **1–5**, showing for each a projection view in the *ab* plane of one canal only of their helical tubuland lattice

acetate as a conglomerate in space group $P3_121$ (or its enantiomorph) with parallel canals whose topologies and dimensions vary considerably (Fig. 1).[4] Diols **1**, **2** and **4** are versatile inclusion hosts trapping a wide range of guest molecules. In contrast, diols **3** and **5** where the canal volume is severely self-restricted, have guest-free helical tubuland lattices as shown by X-ray crystallography.[5]

Guest-free solid samples of **1**, **2** and **4** have now been produced by heating inclusion compounds under reduced pressure, by sublimation, and by crystallisation from mesitylene (a solvent too bulky to be included). The composition and lattice structure of each sample was then investigated by IR (mull) spectroscopy, elemental analysis and X-ray powder diffraction.

Samples of **1** prepared by all three methods have the helical tubuland lattice (Fig. 1) with guest-free canals comprising *ca.* 17% of the crystal volume. We are unaware of any other small organic host maintaining an open tubular structure without supporting guest molecules being present. The behaviour of **1** may be compared to those inorganic zeolite lattices (*e.g.* laumontite, zeolite L) with canals along only one axis of the solid which, once formed, possess structures independent of the presence or absence of guests. However, zeolites normally require water and aquated ions as guest stabilisers for their initial formation and their lattices are permanent.[6] The sublimation experiment demonstrates that the inbuilt properties of **1** alone control the growth of its helical tubuland lattice. Similar arguments also apply to the diols **3** and **5**. Since the diol lattices involve hydrogen bonds and van der Waals forces they are non-permanent, and, therefore, collapse on dissolution in solvents.

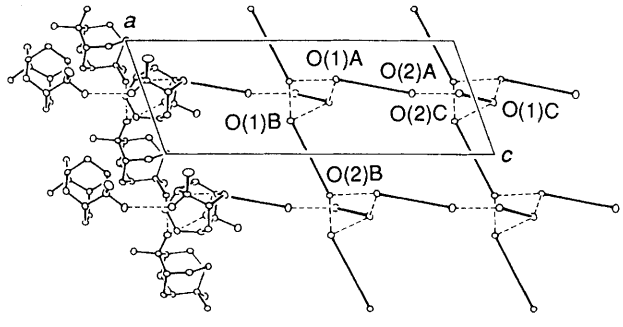


**Fig. 2** The hydrogen bonding network of guest-free **2** projected onto the *ac* plane with hydrogen bonds shown as dashed lines. For clarity, part of the figure reduces the diol molecules to solid spacer rods linking the two hydroxy groups. Only the major component is represented for disordered molecule C.

In marked contrast, guest-free samples of **2** and **4** do not have the helical tubuland structure. Sublimation of **2** gave a

**Table 1** Data pertaining to the helical tubuland forms of diols **1–5**

| | M.p. °C | U.C.A. Å$^{2a}$ | O···O Å$^{b}$ |
|---|---|---|---|
| **1**$^{c}$ | 189–191 | 22.4 | 2.81 |
| **2**$^{c}$ | 146–148 | 30.2 | 2.98 |
| **3**$^{d}$ | 245–247 | 4.7 | 2.84 |
| **4**$^{e}$ | 146.5–147 | 34.7 | 3.08 |
| **5**$^{d}$ | 249–250 | 2.7 | 2.83 |

$^{a}$ U.C.A. = Unobstructed cross-sectional area of canal (see Fig. 1). $^{b}$ Intermolecular hydrogen bond oxygen–oxygen distance. $^{c}$ Ethyl acetate inclusion compound. $^{d}$ Solvent-free structure. $^{e}$ Benzene inclusion compound.

solid suitable for single-crystal structure determination.† The structure in no way resembles the helical tubuland or tetragonal lattices found when **2** includes guest molecules.[7] There are three diol molecules A–C in the asymmetric unit and each takes part in hydrogen bonding (Fig. 2). Both hydroxy groups in the B molecule form two hydrogen bonds; one as donor, and one as acceptor. The A and C molecules exhibit incomplete hydrogen bonding with one hydroxy group participating in two hydrogen bonds, and the other in only one. This hydrogen bonding network is confined to linking molecules in layers in the *ac* plane. Diol molecule C is disordered, having a minor component of 17.6% occupancy which forms a different hydrogen bonding network.

The unprecedented difference in guest-free structural type between diols **1**, **3** and **5** on one hand, and diols **2** and **4** on the other, can be rationalised. Table 1 lists several parameters for the helical tubuland structures of **1–5**.[8] These data clearly show that **2** and **4** support larger canals than the other three diols and that, in addition, their hydrogen bonding is significantly weaker (lower m.p. and increased hydrogen bond oxygen–oxygen distance). These differences correlate exactly with the observed change in guest-free structural type.

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† *Crystal data* for: $C_{13}H_{22}O_2$, $M$ = 210.3, monoclinic, $P2_1/c$, $a$ = 7.398(2), $b$ = 25.166(3), $c$ = 20.076(4) Å, $\beta$ = 109.42(1)°, $U$ = 3525(1) Å$^3$, $Z$ = 12, $D_c$ = 1.19 g cm$^{-3}$, $\lambda$ (Cu-K$\alpha$) = 1.5418 Å, $\mu$ = 5.8 cm$^{-1}$. Anisotropic thermal parameters were refined for all non-H atoms, final $R$ = 0.055 for 3909 independent observed reflections [$I/\sigma(I) > 3$] and 452 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.

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