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MOLECULAR DETERMINANTS OF A NEW FAMILY OF HELICAL TUBULAND HOST DIOLS

Roger Bishop, Ian G. Dance, Stephen C. Hawkins, and
Marcia L. Scudder,
School of Chemistry,
The University of New South Wales,
P.O. Box 1, Kensington,
New South Wales 2033, Australia.

ABSTRACT. The alicyclic diols (1-5) constitute the first members of a family of novel helical tubuland hosts crystallising in space group $P3_121$ but possessing quite different canal shapes and dimensions. Consideration of their structural data has revealed two distinct sub-classes of these materials. The molecular features necessary for a diol to crystallise with the helical tubuland structure are defined and discussed.

1. INTRODUCTION

We have reported previously[1] that the racemic diol (1) forms stable crystalline inclusion complexes with a variety of solvent molecules. A network of host diol molecules (space group $P3_121$) is maintained by continuous helical spines of hydrogen bonds. Other diol molecules radiate from and interconnect these spines enclosing parallel open canals containing the disordered guest molecules. This tubuland structure[2] constitutes an especially interesting example since in each crystal these canals are surrounded by a double helical array of host diol molecules of the same chirality.

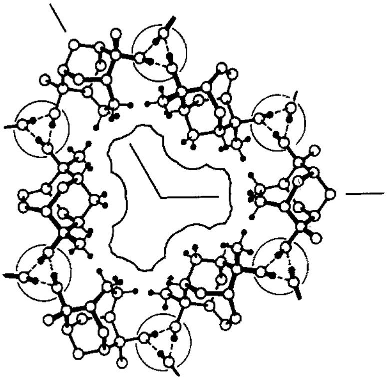
Following this initial discovery we embarked on a program of systematic synthesis in order to demonstrate that additional materials of similar structure could be obtained. Recently we have described the syntheses and crystal structures[3,4] of further alicyclic diols (2-4) of this type which also adopt the crystal space group $P3_121$. Their structural characteristics have been analysed and reported in detail[5]. The previously unreported diol (5) also belongs to this new family of helical tubuland host diols.

Comparative projections along *c* are shown to the same scale for one canal only of diols (1-5). The hydrogen bonded spines are circled and significant hydrogen atoms drawn as filled circles. Bond thickening indicates depth in individual molecules only because the helical characteristic is absent in these projections. The unobstructed canal cross-sections are drawn using projected van der Waals radii of the hydrogen atoms lining each canal.

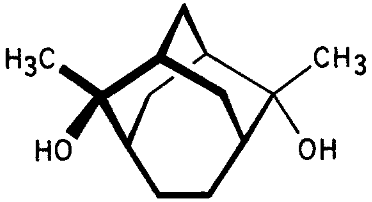
2. STRUCTURAL ANALYSIS

Examination of the various crystal structures reveals two sub-classes of this helical tubuland family. That including (1), (3) and (5) has more efficient hydrogen bonding and smaller canal dimensions while the other, including (2) and (4), has weaker hydrogen bonding and larger canals. For (3) and (5) the canals are constricted so as to produce cages but because of the helical structure considerable void space is still present in these assemblies. Both isomeric diols, one of each sub-class, are prepared from the common diketone intermediate.

Five of the properties allowing distinction between the sub-classes are detailed here, namely: the melting point (M.P.); the hydrogen bond O.....O distance (O.....O); the unobstructed cross-sectional area of the canal (U.C.A.); the unit cell volume (U.C.V.); and the cross-ring O—C ---- C—O torsion angle (Torsion angle).



(2)



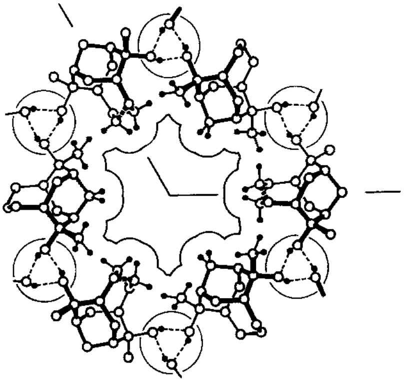
M.P. 146-148°C

O.....O 2.98 $\mathrm{\AA}$

U.C.A. 30.2 $\mathrm{\AA}^2$

U.C.V. 1042 $\mathrm{\AA}^3$

Torsion angle 94.3°



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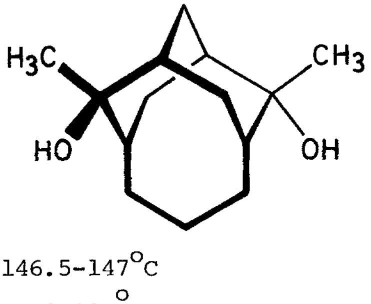


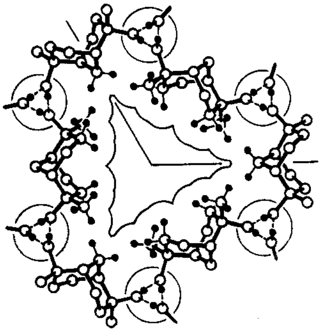
M.P. 146.5-147°C

O.....O 3.08 $\mathrm{\AA}$

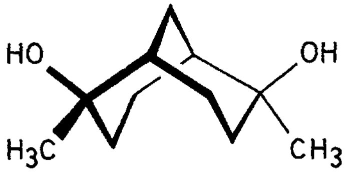
U.C.A. 34.7 $\mathrm{\AA}^2$

U.C.V. 1150 $\mathrm{\AA}^3$

Torsion angle 97.2°



(1)



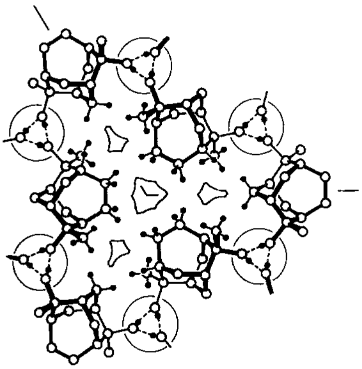
M.P. 189-191°C

O.....O 2.81 Å

U.C.A. 22.4 Å^2

U.C.V. 897 Å^3

Torsion angle 73.5°



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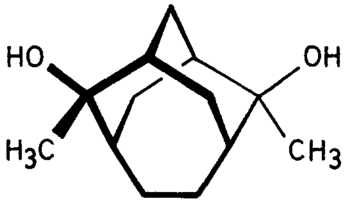


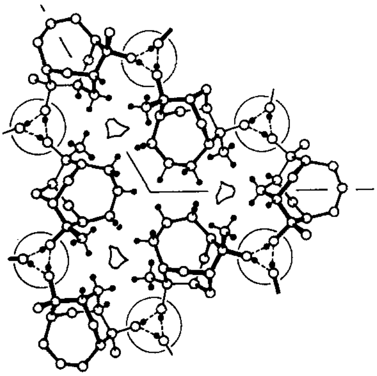
M.P. 245-247°C

O.....O 2.84 Å

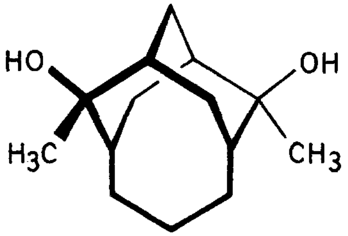
U.C.A. 4.7 Å^2

U.C.V. 858 Å^3

Torsion angle 79.0°



(5)



M.P. 249-250°C

O.....O 2.83 Å

U.C.A. 2.7 Å^2

U.C.V. 901 Å^3

Torsion angle 71.3°

3. MOLECULAR DETERMINANTS

Our program of synthesis has been planned to define the molecular features required in a host diol molecule for it to crystallise with the helical tubuland structure. The following molecular determinants have been found to be necessary.

(i) The diol molecules must have C_2 rotational symmetry in solution. However it is not necessary that this be adopted completely in the crystal. For example the diols (4) and (5) cannot adopt exact twofold symmetry in the solid because of the propano bridge.

(ii) The alicyclic structure must be capable of a small degree of flexibility. This allows the skeleton to twist slightly aiding the conformation imposed by the lattice. Thus the rigid adamantane analogues adopt a different crystal structure.

(iii) Substituent groups around the periphery appear so far to be deleterious. Polar groups may disrupt the hydrogen bonding of the host, while substituents in some positions will prevent the diol packing in a helical fashion.

(iv) A bridge on the opposite side to the hydroxy groups is optional. It can therefore be removed or modified in size to control the canal dimensions.

(v) The two hydroxy groups must be separated by a molecular bridge. This performs a key function in buttressing the canal walls against collapse to a denser structure. Thus, for example, the double epimer of (1) adopts a totally different crystal structure involving hydrogen bonded sheets.

(vi) The tertiary alcohol groups must have a methyl substituent. This appears to have just the correct size, shape and rigidity to support the canal wall structure. All attempts to replace these groups with others have so far led to new crystal structures being produced.

Although further factors are probably involved, the discovery of these structural requirements means that, within certain limits, new members of the helical tubuland family can be predicted with a reasonable degree of confidence.

4. REFERENCES

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