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Helical Tubuland Inclusion Diol Hosts: Fine-Tuning the Canals by Crystal Engineering

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Application of crystal engineering techniques offers the possibility of increasing the host-guest interaction within canals of helical tubulate inclusion compounds and thereby enhancing guest selectivity. New helical tubuland hosts have been synthesised bearing small pendant groups, first to create an irregular canal wall surface and, secondly, to provide a non-hydrocarbon canal interior. The polar fluoromethyl substituent has been found to be particularly effective for these purposes.

Keywords: hydrogen bonding; inclusion compounds; host-guest compounds; molecular tweezers; resolution; conglomerates

INTRODUCTION

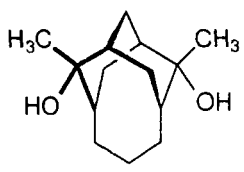
Members of the helical tubuland family of alicyclic diols crystallise in space group $P3_121$ (or its enantiomorph $P3_221$) with a ···H-O···H-O···H-O··· hydrogen bonded lattice containing parallel canals. New examples of this family can be designed and synthesised by adhering to a clearly defined set of structural rules. This enables us to alter the diol skeleton and hence the canal dimensions while, quite remarkably, leaving the crystal space group unchanged.[1]

Those helical tubulands with adequately sized canals enclose guest molecules and yield multimolecular inclusion compounds termed helical tubulates. The inclusion properties of the helical tubulands therefore result from the net lattice packing arrangement of the host molecules rather than on the more common one-on-one modes of host-guest interaction. Furthermore, unlike many other types of inclusion hosts, they trap guests predominantly on a size and shape basis. Therefore, in general, the nature of the guest functionality is of minor significance in determining whether or not a helical tubulate is produced in any given case.

One reason for this behaviour is the ability of the canals to expand or contract their area in the crystal *ab* plane to match the dimensions of potential guests. Another factor is the hydrocarbon nature of the canal walls which permits only weak and relatively unspecific host-guest attractions to occur. In contrast, many of the inclusion compounds studied have quite specific attractions operating between guests lined up in the canals.[2]

RESULTS AND DISCUSSION

In order to probe increased host-guest interaction we are investigating two approaches resulting in modified helical tubuland diol hosts. First, the relatively smooth canal walls can be transformed into less uniform surfaces by the addition of small pendant groups provided these are positioned on the diol pseudo-twofold axis. Substitution elsewhere on the skeleton results in formation of other lattice packing arrangements than the helical tubuland type. These pendant groups protrude into the canals thereby reducing the volume available for guests but creating a highly irregular canal interior. Clearly, group size is an important factor here since adequate canal volume must remain to permit guest inclusion. In this paper the outcome of replacing a hydrogen atom of the known helical tubuland diol **1**[3] by a methyl group to afford the diol **2**[4] will be discussed.



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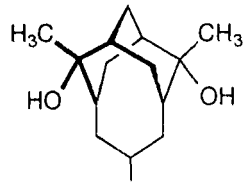

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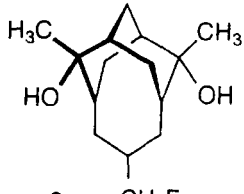

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Secondly, an appropriately functionalised pendant group provides a means of converting the hydrocarbon nature of the canal walls into a more polar environment. However, such a group must not interfere with the helical tubuland hydrogen bonding network otherwise a totally different lattice will be produced. Organofluorine C-F groups do not normally associate with hydroxy groups, particularly if the latter can participate in cooperative ···H-O···H-O···H-O··· hydrogen bonding,[5-7] and therefore the behaviour of the new fluoromethyl diol **3** was synthesised and investigated to test this concept.

The three diols **1-3** were crystallised from benzene and all were found to form inclusion compounds. In each case these proved to be helical tubulates when their crystal structures were determined by single crystal X-ray methods.

Figure 1 shows projection views of one canal of each of these compounds drawn to the same scale and with the benzene guest molecules omitted for clarity. Their unobstructed cross-sectional area (UCA) values are 32.3, 19.5 and 17.1 $Å^2$ respectively, where the UCA value represents the minimum free area of the canal when viewed in projection. The actual area available for guest inclusion at various heights along the canal is actually greater than this since these projections are analogous to the view observed looking along the interior of an indented pipe.

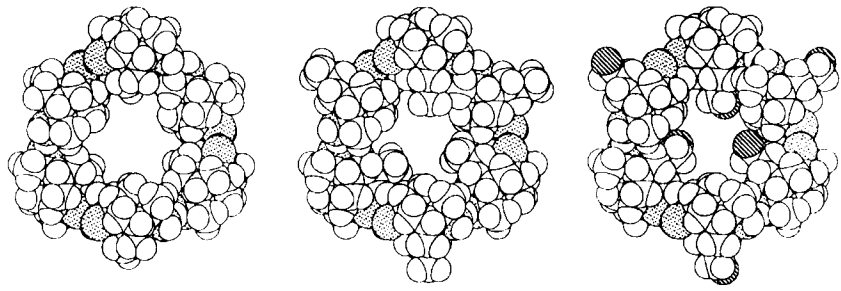

FIGURE 1 Projection views in the *ab* plane of one canal only of the helical tubulate inclusion compounds of diols **1-3** with benzene. These canals, drawn here to the same scale with the guest molecules omitted, have UCA values of 32.3, 19.5 and 17.1 $Å^2$ respectively. Oxygen atoms are stippled and fluorine atoms are diagonally hatched.

The large decrease in UCA on introducing the methyl group is reflected in the stoichiometries of the first two compounds, these being $(\mathbf{1})_3{\cdot}(C_6H_6)$ and $(\mathbf{2})_3{\cdot}(C_6H_6)_{0.75}$ respectively. These values correspond to one guest per unit cell for the former, but only three guests per four unit cells in the latter case.

In the crystal structure of guest-free **2** the pendant methyl groups are randomly orientated over two possible positions in order to create average C_2 symmetry in the crystal.[4] However, in $(\mathbf{2})_3{\cdot}(C_6H_6)_{0.75}$ the presence of the planar guest molecule requires increased local ordering for the best fit. The two groups closest to the guest adopt a specific orientation while the third can still be positioned randomly. Consequently, as can be seen in Figure 2, there is significant empty volume between adjacent guest molecules in the inclusion compound and successive benzene molecules along the canal are related by a 3_1 screw axis.

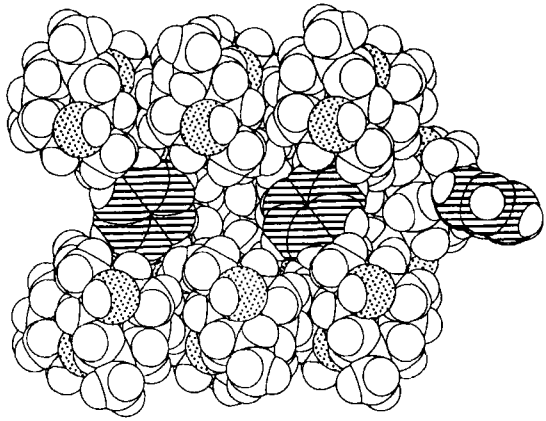

FIGURE 2 One canal of the helical tubulate compound $(\mathbf{2})_3 \cdot (C_6H_6)_{0.75}$ with the *c* axis horizontal and highlighting the pendant methyl group and guest orientations. The front column of diol molecules has been removed to provide this cut-away view. Oxygen atoms are indicated by stippling and benzene carbons by horizontal hatching.

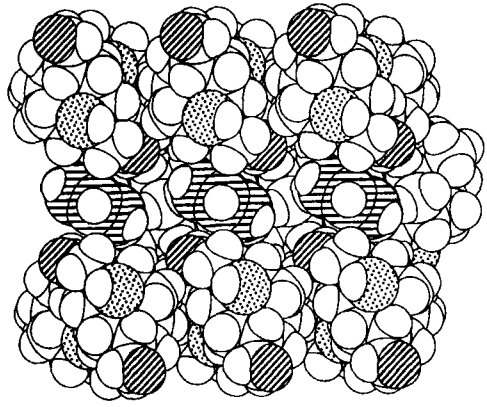

FIGURE 3 One canal of the helical tubulate compound $(\mathbf{3})_3 \cdot (C_6H_6)$ with the *c* axis horizontal and the front column of diol molecules removed to provide this cut-away view. The unit cell translation of the guest molecules and C-F···π aromatic interactions should be noted. Oxygen atoms are indicated by stippling, benzene carbons by horizontal hatching, and fluorine atoms by diagonal hatching.

Modification of the host diol pendant group from the $-CH_3$ of **2** to the slightly larger $-CH_2F$ of **3** results in the *increased* guest occupancy of $(\mathbf{3})_3{\cdot}(C_6H_6)$ for the helical tubulate inclusion compound. This stoichiometry corresponds to one benzene molecule per unit cell with neighbouring guests related by simple unit cell translation along the canal as illustrated in Figure 3.

This increase in packing density results from the polar $-CH_2F$ groups interacting more strongly with the guest molecules than was previously possible employing just a hydrocarbon canal interior. Furthermore, all three pendant groups in $(\mathbf{3})_3{\cdot}(C_6H_6)$ are specifically orientated relative to the benzene guest. Two of the $-CH_2F$ groups form host-guest C-F···π aromatic attractions with opposite faces of the benzene ring, such that their C-F···C aryl distances range between 3.8-4.3 and 3.8-4.8 Å respectively. Other neighbours at differing heights along the canal provide additional stabilisation through C-F···H-Ar interactions of approximately 3.5-3.7 Å.

The former type of interaction is widespread. A search of the Cambridge Structural Database[8] specifying a F atom less than 4 Å from all six carbon atoms of an aromatic ring located 782 examples with a mean C-F···C distance of 3.5 Å. As regards the second type, it has been reported previously[9] that C-H···halogen attractions can be an alternative to the more familiar halogen···halogen interaction,[10] and that these are preferred for aromatic (rather than aliphatic) compounds.[11] A nice example of Ar-H···Cl interactions in molecular assembly is provided by our helical tubulate compound (2,6-dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol)$_3$·(chlorobenzene) where it results in adoption of head-to-tail guest packing, in marked contrast to its head-to-head packed toluene analogue.[2,12]

In the structure $(\mathbf{3})_3{\cdot}(C_6H_6)$ two independent $-CH_2F$ groups behave cooperatively like a pair of hands cupping the guest benzene molecule or, alternatively, they may be regarded as functioning together as molecular tweezer units. However, in this instance a much greater complexity of molecular assembly is involved compared to previously described examples of molecular tweezers.[13-16] Here, the two arms of each tweezer unit belong to different molecules which are separated by a further intervening molecule of diol **3**. All three diols constituting this unit are linked by hydrogen bonding. Furthermore, as outlined above, additional stabilisation of the inclusion compound is provided by neighbouring diol molecules by means of C-F···H-Ar interactions.

We regard the new diol **3** as a proof of concept model which demonstrates the validity of our canal fine-tuning approach and believe that it is only the prototype of possible developments in this field.

Acknowledgement

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