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HELICAL TUBULATE INCLUSION COMPOUNDS: SIZE, SHAPE, AND STOICHIOMETRY

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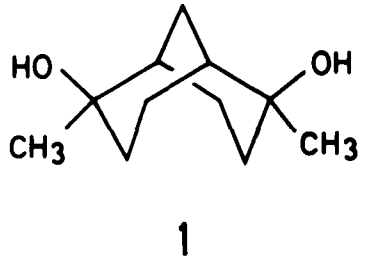
Abstract The X-ray crystal structures of helical tubulate inclusion compounds of the diol host **1** reveal considerable variation in canal size depending on the specific guest entrapped. Examination of this data reveals how such flexibility is achieved through changes in the host orientation and hydrogen bonding angles. The sum of these effects makes **1** a potent inclusion host for a wide range of small molecules and depends little on the guest functional group. Representative helical tubulate stoichiometries, packing, and interactions are explored. The guest-free diol exists with the same lattice type as an empty microporous solid.

INTRODUCTION

Certain alicyclic diols such as **1** crystallise in space group $P3_121$ (or its enantiomorph $P3_221$) with a hydrogen bonded lattice containing parallel chiral canals which can trap guest molecules.[1] This lattice type and its resulting inclusion compounds are described by the terms helical tubuland and helical tubulate respectively.[2-4]



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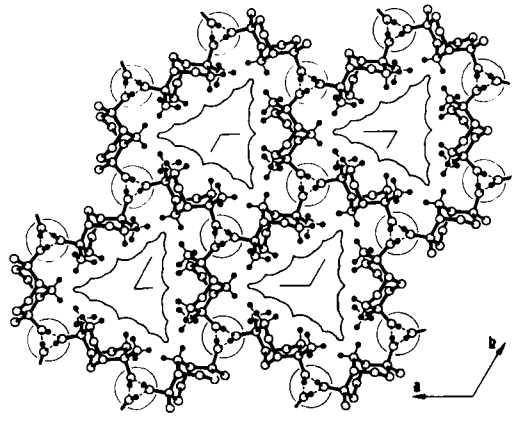

FIGURE 1 Molecular structure of diol **1** and a projection in the *ab* plane of crystalline **1** showing the parallel canals of triangular cross-section and the hydrogen bonding arrangement (dashed lines).[1]

This lattice type involves threefold screw axes of ···O-H···O-H···O-H··· hydrogen bonded spines (circled for emphasis in Figure 1). Such diols can be targeted by deliberate synthetic strategy to yield a family of host molecules. Currently a range of 11 known diols provides a gradation of canal cross-sections from 0 up to 35 Å^2 and the preparation of further potential examples is under way.

The family of helical tubuland diols are potent inclusion hosts which trap guests on the basis of size and shape rather than chemical functionality. Although the structure of the diol lattice would appear at first sight to be inflexible, X-ray examination of a range of helical tubulates formed by the prototype compound, 2,6-dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol **1**, reveals that this is not so. The size of the canal cross-sectional area can actually vary considerably in matching specific guest dimensions.

This paper will explore how these large structural changes can be achieved and will discuss the play-off between host-guest and guest-guest interactions in the various helical tubulate compounds.

RESULTS AND DISCUSSION

Diol Dimensions in Helical Tubulate Compounds of 1

Selected dimensional data from twelve crystal structures of diol **1** helical tubulates are presented in Table 1, listing these inclusion compounds in order of increasing value of the a ($= b$) dimension. It is immediately apparent that the significant increases in this dimension (up to 4.8%) are accompanied by only small decreases in c (up to 0.96%). Hence these changes result in concomitant increases in the unit cell volume V (up to 8.9%) across the series of compounds.

Since the length of a ($= b$) is directly related to the canal cross-section, these areas must increase down the list presented in Table 1. The UCA is the unobstructed cross-sectional area of the host canal when drawn as a projection in the *ab* plane and represents the minimum canal area available for guest occupation in each compound. It is similar to the view seen looking along an indented tube. Therefore the true cross-section at any height may be slightly larger, since the internal surfaces of the host canal walls are themselves indented.

Actual experimental values for the unobstructed cross-sectional area (UCA) range from 15.6 Å^2 (for acetonitrile guest) to 25.3 Å^2 (for dioxane guest) which represents a surprisingly large increase of 9.7 Å^2 (or 62%) down the series of compounds.

TABLE 1 Dimensional characteristics of helical tubulate inclusion compounds of diol **1** from single crystal X-ray structural measurements.

Compound	$a = b$ (Å)	c (Å)	V (Å^3)	UCA (Å^2)
$(\mathbf{1})_3$·(acetonitrile)	11.8990(7)	7.0274(4)	861.67(7)	15.6
$(\mathbf{1})_3$·(1,2-dimethoxyethane)$_{0.75}$	12.0416(3)	7.0110(2)	880.39(4)	17.7
$(\mathbf{1})_3$·(diiodine)$_{0.5}$·(ethanol)$_{0.5}$	12.068(2)	6.984(3)	880.8(4)	18.1
$(\mathbf{1})_3$·(1,2-dichloroethane)$_{0.75}$	12.0745(5)	6.9868(5)	882.15(7)	18.1
$(\mathbf{1})_3$·(ethyl acetate)	12.165(1)	7.001(1)	897.3(2)	19.8
$(\mathbf{1})_3$·(chloroacetic acid)$_{1.2}$	12.180(1)	6.9725(8)	895.8(1)	19.8
$(\mathbf{1})_3$·(propanoic acid)$_{1.2}$	12.1832(5)	6.9746(2)	896.54(5)	19.9
$(\mathbf{1})_3$·(trichloroethylene)$_{0.86}$	12.284(2)	6.980(1)	912.2(2)	21.9
$(\mathbf{1})_3$·(thiophene)	12.4083(5)	6.9702(4)	929.39(6)	24.3
$(\mathbf{1})_3$·(chlorobenzene)	12.455(1)	6.960(1)	935.0(2)	24.9
$(\mathbf{1})_3$·(toluene)$_{0.86}$	12.469(2)	6.961(1)	937.3(2)	25.1
$(\mathbf{1})_3$·(dioxane)	12.4699(5)	6.9687(4)	938.43(6)	25.3

The observed variations in canal size do not result from variation in hydrogen bonded distances, as is sometimes the case.[5] Inter-oxygen separations O···O only range from 2.804 to 2.817 Å across the series of twelve compounds with no discernible trend being apparent. Furthermore there are no significant alterations in the interatomic distances or angles of the skeleton of diol **1** itself over the twelve inclusion compounds.

Diol Angles in Helical Tubulate Compounds of **1**

If projections of the smallest canal (15.6 Å^2; acetonitrile compound) and largest canal (25.3 Å^2; dioxane compound) are superimposed (Figure 2) then it becomes clear that the three diol **1** molecules occupying apex sites of the canal occupy almost identical positions. However, the alternating three diols occupying wall sites have been displaced outwards in the latter case. The 3_1 hydrogen bonded ···O-H···O-H···O-H··· spines have a triangular cross-section in the *ab* plane. It is their positional change (hatched to open diagrams) which causes this expansion of the canal.[6]

It is thus clear that the experimental canal dimensional changes must be caused by angular changes in these structures. Four key trends in the angles of these helical tubulate

structures are presented in Table 2. The first three columns describe intermolecular angles involving the hydrogen bonded spine of the host lattice, while the fourth describes the host tilt angle. Values of all four sets of angles show small, but significant, regular alterations across the twelve compounds. It is the combination of these which culminates in the effect seen in Figure 2.

The tilt angle is the angle C2···C6···z axis (where C2 and C6 are the carbons bearing the hydroxy groups and z is the canal direction). Increase in this value signifies that the host becomes less tilted as a increases and this causes the small concomitant decrease in c.

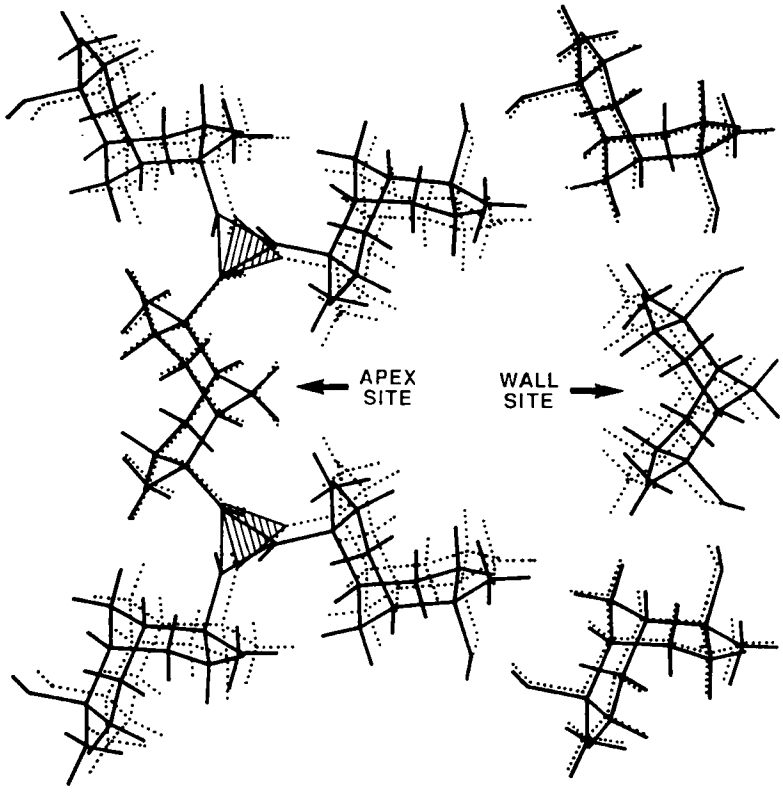

FIGURE 2 Superimposed projections in the ab plane of one canal of $(\mathbf{1})_3$·(acetonitrile) (dotted structure) and $(\mathbf{1})_3$·(dioxane) (solid structure) drawn to the same scale. Apex and wall diols for these canals are labelled; the same molecules have transposed roles in the adjacent canals. One molecule of **1** has its hydrogen bonded spines represented in triangular cross-section. Change from the hatched to open position causes the observed canal expansion.

TABLE 2 Angular characteristics of helical tubulate inclusion compounds of diol **1** from single crystal X-ray structural measurements.

Compound	C-OH···O (donor) (deg.)	C-O···HO (acceptor) (deg.)	OH··OH··OH (deg.)	Tilt angle (deg.)
$(\mathbf{1})_3$·(acetonitrile)	107.8	129.3	122.7	65.6
$(\mathbf{1})_3$·(1,2-dimethoxyethane)$_{0.75}$	107.9	128.9	122.6	66.8
$(\mathbf{1})_3$·(diiodine)$_{0.5}$·(ethanol)$_{0.5}$	108.4	128.6	122.3	66.7
$(\mathbf{1})_3$·(1,2-dichloroethane)$_{0.75}$	108.2	128.7	122.4	66.7
$(\mathbf{1})_3$·(ethyl acetate)	108.5	128.0	122.4	67.3
$(\mathbf{1})_3$·(chloroacetic acid)$_{1.2}$	108.6	128.3	122.0	67.3
$(\mathbf{1})_3$·(propanoic acid)$_{1.2}$	108.6	128.1	122.0	67.4
$(\mathbf{1})_3$·(trichloroethylene)$_{0.86}$	109.2	127.2	122.0	67.9
$(\mathbf{1})_3$·(thiophene)	109.2	126.9	121.5	68.4
$(\mathbf{1})_3$·(chlorobenzene)	109.5	126.3	121.2	68.5
$(\mathbf{1})_3$·(toluene)$_{0.86}$	109.3	126.4	121.4	68.4
$(\mathbf{1})_3$·(dioxane)	109.4	126.2	121.3	68.5

Although each of the series of angular changes is individually small, their combined behaviour provides a most efficient mechanism for the host lattice to expand or contract in the *ab* plane. Hence the diol **1** network has a surprising ability to adjust itself to guests of specific size and shape.

Host···guest stoichiometry and packing arrangements

The tubular lattice structure of the host diol is such that strict imposition of host···guest stoichiometry or commensurate behaviour may not be required, as would normally be the case for inclusion compounds based on cages or coordination. As is apparent from the formulae quoted in Tables 1 and 2 a variety of arrangements can be accommodated.

Here four such examples (each with a different stoichiometry and packing arrangement) will be considered in detail: $(\mathbf{1})_3$·(thiophene); $(\mathbf{1})_3$·(toluene)$_{0.86}$; $(\mathbf{1})_3$·(diiodine)$_{0.5}$·(ethanol)$_{0.5}$; and $(\mathbf{1})_3$·(chloroacetic acid)$_{1.2}$. Stoichiometric ratios are based on there being three diol molecules per unit cell.

Figure 3 shows comparative projection views across one canal of each of these four inclusion compounds. The guest orientations within the canal are shown in Figures 4-7 respectively where the *z* axis is vertical and one column of diol **1** molecules has been removed to reveal the guest arrangement.

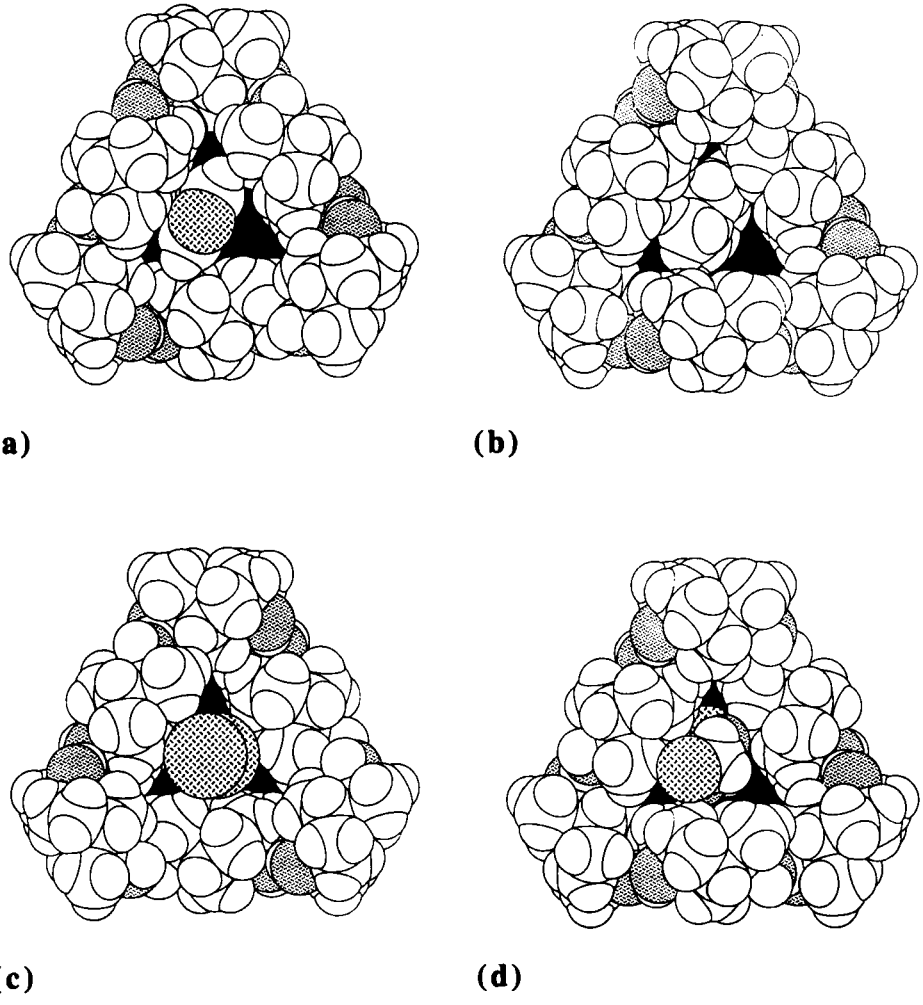

FIGURE 3. Projection views along the canal axis direction *z* for four diol **1** helical tubulates showing for each one molecule of guest in a typical orientation: (a) $(\mathbf{1})_3$·(thiophene); (b) $(\mathbf{1})_3$·$(\text{toluene})_{0.86}$; (c) $(\mathbf{1})_3$·$(\text{diiodine})_{0.5}$·$(\text{ethanol})_{0.5}$; and (d) $(\mathbf{1})_3$·$(\text{chloroacetic acid})_{1.2}$. Non-C/H atoms are stippled and the unoccupied space in each canal has been filled to emphasise the guest.

The compound $(\mathbf{1})_3$·(thiophene) has one guest molecule per unit cell (Figure 4). Adjacent thiophenes are situated along one wall of the canal to maximise host···guest dispersion forces and are related by unit cell translation. Although drawn here in exactly the same orientation it was not possible to distinguish between guest carbon and sulfur atoms in this structure determination. Since thiophene has approximate fivefold symmetry the sulfur must be considered to be random over the five alternative orientations. The shortest C/S···C/S distance is 4.5 Å.

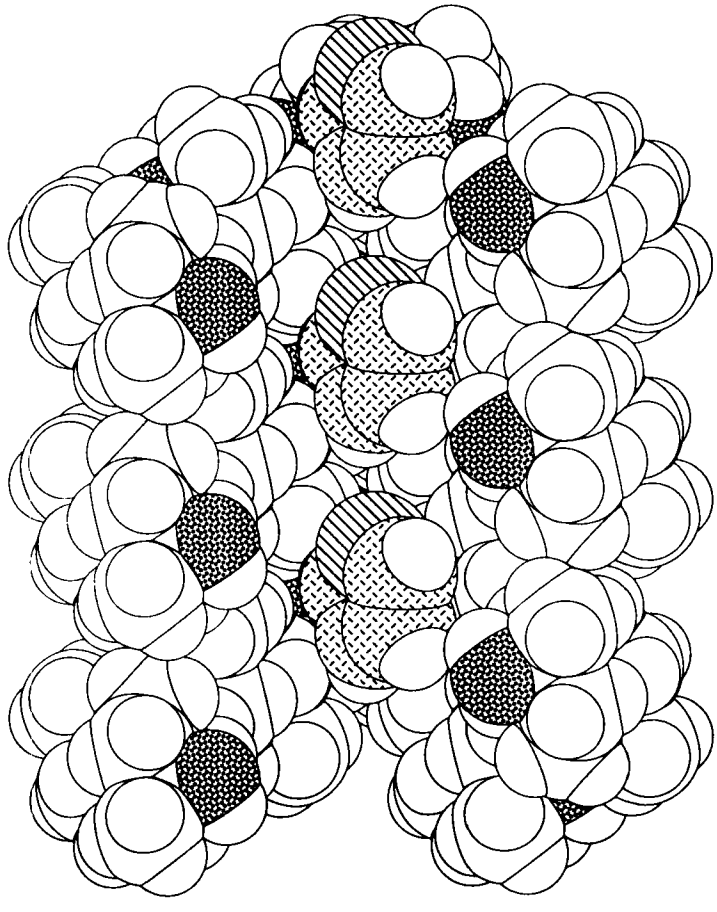

FIGURE 4 Part of one canal of the helical tubulate $(\mathbf{1})_3$·(thiophene) showing the guest arrangement. Host oxygens are stippled heavily, guest carbons are stippled lightly, and the guest sulfur atoms are marked with parallel stripes. The canal axis z is vertical.

In contrast to the first case, the stoichiometry of compound $(\mathbf{1})_3$·(toluene)$_{0.86}$ corresponds to the lesser occupancy of six guests per seven unit cell lengths. In this case the guests now alternate in orientation and therefore the methyl groups of the guests point towards each other (with a C···C distance of 5.2 Å). The shortest aryl-aryl C···C and host···guest distances are both 3.6 Å. Also unlike the first example the guests also exhibit different rotational angles around *z* (Figure 5).

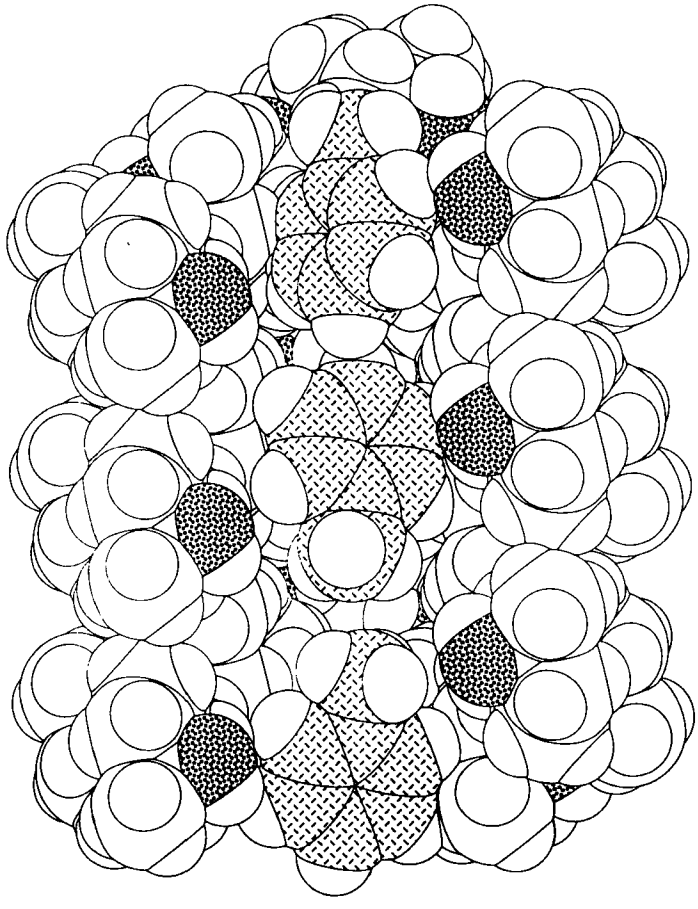

FIGURE 5 The guest arrangement within one canal of the helical tubulate inclusion compound $(\mathbf{1})_3$·(toluene)$_{0.86}$. Host oxygens are stippled heavily and guest carbons are stippled lightly. The toluene guest molecules are arranged in head-head pairs along the length of the canal.

The inclusion compound $(\mathbf{1})_3$·(diiodine)$_{0.5}$·(ethanol)$_{0.5}$ has one diiodine-ethanol complex per two unit cell lengths as illustrated in Figure 6. Since only poor CH···I_2 interactions would be possible between host and guest, the co-inclusion of ethanol solvent provides greater interactive stabilisation as is observed in diiodine-cyclodextrin compounds.[7-9]

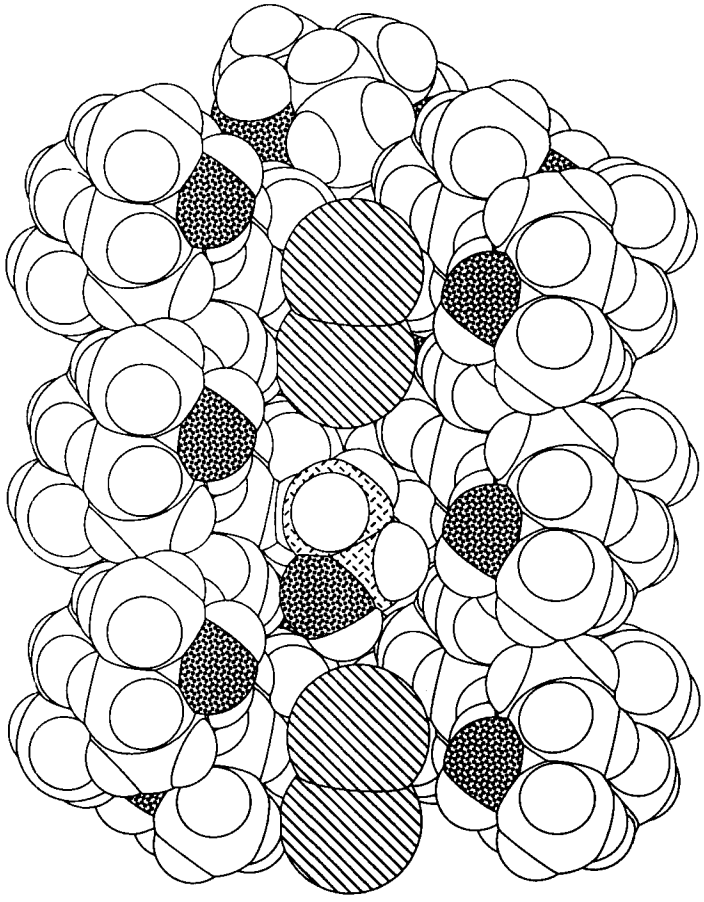

FIGURE 6 Helical tubulate $(\mathbf{1})_3$·(diiodine)$_{0.5}$·(ethanol)$_{0.5}$ showing the diiodine-ethanol complex arranged along the horizontal canal. Oxygens are stippled heavily, guest carbons are stippled lightly, and iodines are designated with parallel stripes. The different host lattice orientation in this figure results from this structure being refined in space group $P3_231$ whereas the enantiomer $P3_121$ was employed for the other examples.

The stoichiometry of the chloroacetic acid inclusion compound was found to be $(\mathbf{1})_3$·(chloroacetic acid)$_{1.2}$ which corresponds to the greater occupancy of six guest molecules per five unit cell lengths. The guests are arranged within the canal as hydrogen bonded dimers with a twofold axis perpendicular to the plane containing the two carboxyl groups. Thus while the four oxygen atoms lie in a plane roughly parallel to one of the canal walls, both chlorines are directed towards the canal wall. It is noteworthy that the stable form of pure crystalline chloroacetic acid is a cyclic hydrogen bonded tetramer (the α-form).[10,11] The dimer is normally a metastable structure (the β-form).[12]

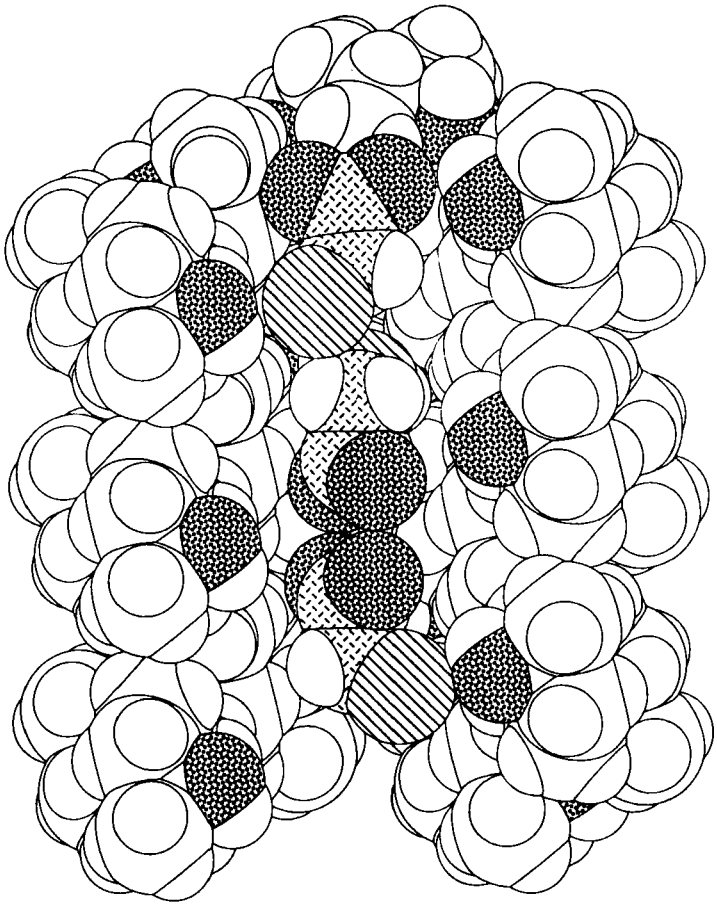

FIGURE 7 The $(\mathbf{1})_3$·(chloroacetic acid)$_{1.2}$ dimer within a diol **1** canal. Oxygens are heavily stippled, guest carbons lightly stippled, and chlorines designated by parallel stripes. A Cl···Cl contact of 3.86 Å between neighbouring dimers indicates weak guest-guest interaction.[13]

Guest-free diol **1**

Samples of guest-free diol **1** have been obtained from helical tubulate compounds by heating under reduced pressure, by sublimation under reduced pressure, and by recrystallisation from mesitylene which is too bulky to be included. All available evidence[6] indicates that **1** retains its helical tubuland lattice with a genuine empty microporous structure in this resulting material.

Perhaps the most convincing single piece of evidence is the X-ray powder diffraction (XRPD) data. For the helical tubulates the predominant peaks are observed at roughly 8.3, 14.5, 15.2, 16.5, 19.2 and 22.4° in 2θ. Of these, the 8.3 and 16.5° values are the *100* and *200* reflections which move to higher values with decreasing guest size, consistent with reduction in a (= b). If no guest is present then the *100* reflection moves to 8.6° and the *200* reflection becomes extremely weak (as expected from calculation).

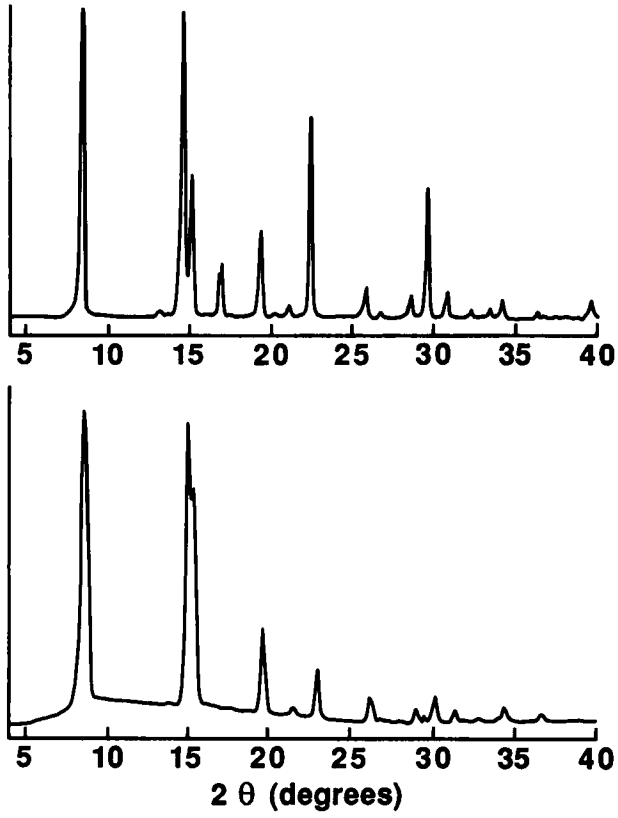

FIGURE 8 Comparison of the X-ray powder diffraction patterns of (top) $(\mathbf{1})_3$·(1,2-dimethoxyethane)$_{0.75}$ and (bottom) guest-free diol **1**.

Figure 8 shows the experimental XRPD data for a typical helical tubulate containing small guest molecules (acetonitrile) and the guest-free form of **1**. The extreme similarity of the two results indicates that the same diol lattice is present in both cases.

Although diol **1** is a small and apparently simple molecule it therefore is self-programmed to yield the same consistent host lattice with or without the intervention of other chemical species such as guest molecules or solvent. It represents a most remarkable illustration of molecular assembly in action.

ACKNOWLEDGEMENTS

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