Pergamon

TETRAHEDRON

Tetrahedron 56 (2000) 6667–6673

Fine-control of Helical Tubuland Inclusion Properties through the Pendant Group Approach

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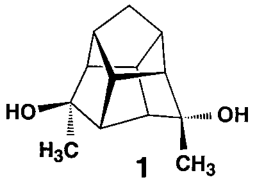
Received 4 November 1999; accepted 4 February 2000

Abstract—The helical tubulands are a family of alicyclic diols which crystallise in chiral space group $P3_121$ and whose lattices can contain guest molecules enclosed within parallel tubes. New examples can be designed following a series of rules based on molecular structure and symmetry. In order to probe the latter requirement, and also to increase host–guest interactions, the behaviour of 2,5,8-trimethyltricyclo[5.3.1.1^{3,9}]dodecane-*syn*-2,*syn*-8-diol **4** was investigated using X-ray methods. Although molecules of **4** have no C_2 symmetry they still form the helical tubuland lattice on crystallisation. In the pure apohost **4** their symmetry-breaking C5 methyl groups protrude into the tube volumes where they randomly adopt one of two equivalent orientations. Although the pendant methyl groups reduce the volume available for guest inclusion, they create irregular tube wall surfaces and interact more effectively with guest molecules. The helical tubulate inclusion compounds of **4** with diisopropyl ketone, benzene, toluene, and *o*-xylene show significant local methyl group ordering around a given guest molecule which performs a crucial templating role in formation of the product. In all cases, however, crystallographic C_2 symmetry results in the solid through overall disorder of these diol orientations. Hence this, rather than strict molecular symmetry, is the true symmetry requirement of the $P3_121$ helical tubuland lattice. © 2000 Elsevier Science Ltd. All rights reserved.

Introduction

Many organic inclusion compounds (such as those formed by hosts like cyclodextrins, cryptands, and carcerands) are unimolecular systems where the guest species interacts with one preformed receptor. These materials lend themselves easily to modelling studies, thus allowing complementary host–guest combinations to be tailored comparatively easily.[1,2] In contrast, other hosts create a crystal lattice containing host-lined voids which are occupied by the guest.[1,3] The supramolecular structures and inclusion properties of these multimolecular materials now are much more complex. Host–host attractions play a major role in addition to host–guest interactions and, in some cases, guest–guest properties will also be significant. Hence the deliberate design of new multimolecular (or clathrate) lattice inclusion hosts, or even fine-tuning the properties of known cases using crystal engineering techniques,[4] represents a significant synthetic challenge.[5]

The compounds **1–5** are examples of a special group of alicyclic diols (the helical tubulands) which crystallise in the chiral space group $P3_121$ (or enantiomorph $P3_221$). Racemic helical tubuland diols undergo enantiomeric self-resolution during crystallisation, thereby producing a 1:1 mixture of chirally pure (+)- and (−)-crystals (a conglomerate).[6] Their lattices contain parallel helical tubes which can trap a wide variety of guests as multimolecular inclusion compounds (helical tubulates).[7]



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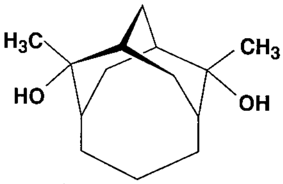

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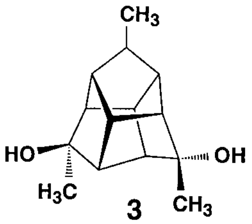

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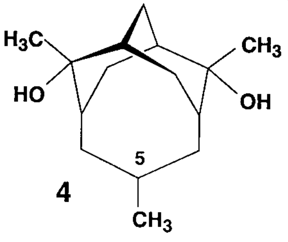

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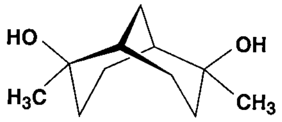

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These clathrate-forming hosts are unique in the degree to which their solid state lattice structures can be designed and engineered. They all have a common intermolecular structural core, a spiral chain arrangement of hydrogen

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Keywords: inclusion; hydrogen bonding; host–guest; template; crystal engineering.

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PII: S0040-4020(00)00474-9

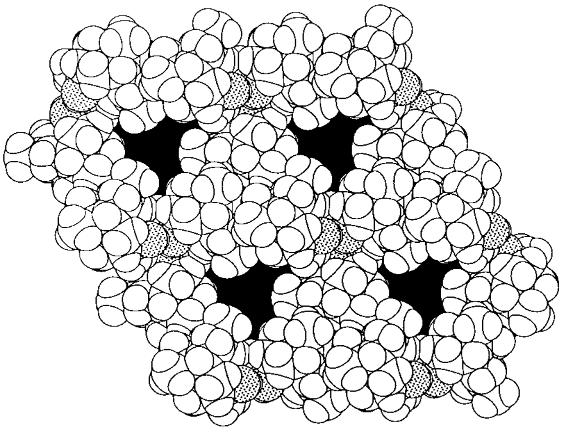

Figure 1. Projection view in the *ab* plane of the guest-free apohost diol **4** showing four tube cross-sections. In this representation all the C5 pendant methyl groups are drawn with the same orientation and the propeller-shaped tubes (UCA=17.3 Å^2) are shaded black.

bonds ···O–H···O–H···O–H···O–H··· surrounding a three-fold screw axis, whose presence in new diols can be predicted if well-defined synthetic rules are followed.[8,9] This hydrogen bonding pattern is therefore a reliable supramolecular synthon[10,11] which we have used to develop this family of hosts. So far 12 of these diols have been synthesised and there is every expectation that more will be obtained. All crystallise with the same hydrogen bonding motif, lattice packing, and even crystal space group, but each differs considerably in its tube dimensions and hence its inclusion properties.

The types of host–guest dispersion forces operating in these compounds cannot be classified easily because the walls of the host tubes have hydrocarbon interiors and relatively smooth surfaces. In general, these diols are all potent hosts of a rather indiscriminate nature. This paper explores fine-tuning the host–guest relationship through deliberate modification of the tube wall surfaces and some consequences of these increased interactions.

Experimental Design

Symmetry and substitution

New helical tubuland diols can be designed, and then synthesised, following a set of crucial structural rules.[8,9] One of these concerns their molecular symmetry. Examples such as **1** and **5** show exact C_2 symmetry in the solid state, but this is impossible for diol **2** due to the non-planar conformational requirements of its propano bridge. Rapid interchange in solution between the two equivalent conformations results in an average C_2 symmetry as demonstrated by its 8-peak (rather than 14-peak) ^{13}C NMR spectrum. Net C_2 symmetry also results in the solid state since the two conformations are adopted randomly during construction of the lattice and because the X-ray experiment records the average of these.

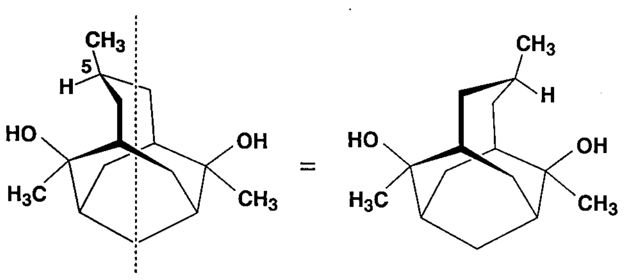

Figure 2. The two equivalent orientations of diol **4** in the solid state showing how the propano bridge and C5 methyl group break the molecular C_2 symmetry thereby creating a pseudo-two-fold axis. Rotation by 180° around this axis (dotted line) converts the first into the second. Both orientations are present randomly in guest-free **4**, this disorder resulting in net crystallographic C_2 symmetry.

The crucial observation here is that diol **2** still adopts the helical tubuland lattice despite no *individual* molecule having C_2 symmetry in the solid state.[12] Therefore, if overall crystallographic C_2 symmetry can be attained somehow in the solid phase, does an individual diol building block really require actual or average C_2 symmetry?

In 1995 diol **3** was synthesised so we could test this concept. The compound is a methylated analogue of the known helical tubuland diol **1** and has no symmetry (other than its identity element). Being substituted on the former C_2 rotation axis, however, no further isomers can result during its preparation beyond the normal pair of diol enantiomers. We were gratified to find that solid **3** did indeed adopt the helical tubuland lattice.[9] Random selection of two alternative diol orientations during crystallisation gave a disordered solid with an average crystallographic C_2 symmetry. Addition of the pendant methyl group created highly indented tube walls and reduced the tube unobstructed cross-sectional area (UCA) from 22.7 Å^2 for **1** to only 6.6 Å^2. Hence **3** was obtained as an empty microporous solid without inclusion properties.

Diol 4 apohost

A compound with larger tubes was required to study the relationship between the pendant group substitution and host–guest interaction. Diol **2** (toluene inclusion compound) has a UCA of 29.6 Å^2 and therefore its non-symmetric methylated derivative **4** should be ideal. Crystallisation from diethyl ether indeed gave needle-like helical tubuland crystals.[13] Its lattice structure is shown in Fig. 1 where all diol orientations are drawn the same for simplicity. This would result in parallel tubes of propeller-shaped cross-section and UCA=17.3 Å^2 as illustrated. In reality, however, the crystal contains a random mixture of both diol orientations which results in net C_2 symmetry through crystallographic disorder.

The two solid state orientations of diol **4**, illustrated in Fig. 2, involve the type of disorder shown by **3**. Rotation of the left-hand structure by 180° around its pseudo-two-fold axis (dotted line), followed by superposition on the right-hand one, confirms that both are structurally identical. The C5 pendant methyl group is *exo*- since an *endo*-conformation would be some 11 kcal mol^{-1} higher in energy due to steric factors. Hence, in this case, different conformations are ruled out within the crystal structure of **4**. The orientation of a given molecule of **4** is determined at crystal construction and thereafter it cannot change. In contrast, it would

Table 1. Numerical details of the solution and refinement of structures of diol **4** determined by X-ray crystallography

Compound	**4**	**4**–diisopropyl ketone	**4**–benzene	**4**–toluene	**4**–*o*-xylene
Formula	$C_{15}H_{26}O_2$	$(C_{15}H_{26}O_2)_3$ $(C_7H_{14}O)_{0.67}$	$(C_{15}H_{26}O_2)_3$ $(C_6H_6)_{0.75}$	$(C_{15}H_{26}O_2)_3$ $(C_7H_8)_{0.5}$	$(C_{15}H_{26}O_2)_3$ $(C_8H_{10})_{0.33}$
Formula mass	238.4	791.3	773.7	761.2	750.5
Crystal description	{100}(00-1)(011) (1-11)(0-11)(-101) (-111)	[a]	{100}{001}	{100}{001}	{100}(0-11) (101)(-111) (-10-3)
Space group	$P3_121$	$P3_121$	$P3_121$	$P3_121$	$P3_121$
a (Å)	13.708(1)	13.808(2)	13.773(2)	13.729(1)	13.7532(9)
c (Å)	7.0046(8)	6.999(1)	6.998(2)	7.008(1)	7.0104(5)
V (Å^3)	1139.9(2)	1155.7(2)	1149.6(4)	1143.9(2)	1148.4(1)
T (°C)	21(1)	21(1)	21(1)	21(1)	21(1)
Z	3	1	1	1	1
D_{calc} (g cm^{-3})	1.04	1.14	1.12	1.10	1.09
Radiation, λ (Å)	CuKα, 1.5418	CuKα, 1.5418	CuKα, 1.5418	CuKα, 1.5418	CuKα, 1.5418
μ (cm^{-1})	4.91	5.36	5.20	5.15	5.07
Crystal dimensions (mm)	0.35×0.35×0.36	[a]	0.15×0.15×0.42	~0.08×0.08×0.15	0.25×0.25×0.25
Scan mode	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{\max.}$ (°)	140	140	140	140	140
ω scan angle	$0.60+0.15 \tan \theta$	$0.50+0.15 \tan \theta$	$0.50+0.15 \tan \theta$		$0.50+0.15 \tan \theta$
No. of intensity measurements	1613	1693	1687	1671	1681
Criterion for observed reflection	$I/\sigma(I)>3$	$I/\sigma(I)>3$	$I/\sigma(I)>3$	$I/\sigma(I)>3$	$I/\sigma(I)>3$
No. of independent observed reflections	1383	1355	1261	1173	1380
No. of reflections (m)	1383	1355	1261	1173	1380
No. of variables (n) in final refinement	90	126	103	96	102
$R=\sum^m\lvert\Delta F\rvert/\sum^m\lvert F_0\rvert$	0.037	0.040	0.048	0.038	0.038
$R_w=[\sum^m w\lvert\Delta F\rvert^2/\sum^m w\lvert F_0\rvert^2]^{1/2}$	0.058	0.053	0.060	0.047	0.058
$s=[\sum^m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	2.50	2.04	2.05	1.52	2.42
Crystal decay	1–0.96	None	none	none	None
R (for no. of) multiple measurements	0.012 (358)	0.013 (387)	0.039 (361)	0.024	0.011 (393)
Max., min. transmission coefficients	0.87, 0.85	-[a]	0.93, 0.88	0.97, 0.90	0.90, 0.86
Largest peak in final diff. map/e Å^{-3}	0.25	0.27	0.56	0.21	0.17

[a] Irregular piece broken from a large crystal.

be possible (in principle) for the two orientations of **2** to interconvert within the crystal simply by conformational ring-flipping.

Despite the small size of the organic building block, the weak nature of the intermolecular forces, and the significant size of the void spaces, some (but not all) helical tubuland hosts can retain their lattice structure when guest free.[7,14] Crystalline **4** obtained from diethyl ether is such a microporous solid containing no guest molecules (an apohost). Since the UCA value represents the minimum cross-sectional area available to guest molecules, rather larger values will be available at differing heights along the tube. In addition, some flexibility in the *ab* plane (tube area) would be expected from previous helical tubuland diol behaviour.[14] Hence, although there is no possibility of trapping the large guests (such as ferrocene) included by diol **2**,[7,15] the tube of **4** should still allow inclusion of moderately sized compounds.

Experimental

Synthesis

2,5,8-Trimethyltricyclo[5.3.1.1^{3,9}]dodecane-*syn*-2,*syn*-8-diol **4** was synthesised as described.[13] Inclusion compounds were prepared by dissolving the solvent-free diol in a small volume of hot liquid guest. The resulting solution was left to stand overnight at room temperature or with slow evaporation of solvent for a longer period. Crystals which had formed were filtered, allowed to dry in air, and then examined by IR (mull) and solution ^{1}H NMR (Bruker ACF300) spectroscopy to determine if guest inclusion had taken place.

Preliminary screening using **4** revealed several positive examples, but others were ambiguous. The latter indicated quantities of guest considerably smaller than normally found in helical tubulate inclusion compounds. Preliminary X-ray data collection (e.g. on **4** recrystallised from norbornadiene) gave cell dimensions close to those of the empty structure. It is believed that in these cases small residual amounts of highly disordered liquid are occluded within crystal faults. We have observed the release of such liquid in other cases while cutting large crystals for X-ray investigation.

Solution and refinement of the X-ray structures

The materials investigated all crystallise in the trigonal space group $P3_121$. For each structure, data were recorded using an Enraf-Nonius CAD4 X-ray diffractometer in $\theta/2\theta$ scan mode. Data collection and processing procedures have been described.[16] Absorption corrections were applied empirically.[17] Numerical details pertaining to the data collection, data processing, and refinement of the structures are given in Table 1.

For **4**, the initial positional parameters were taken from a

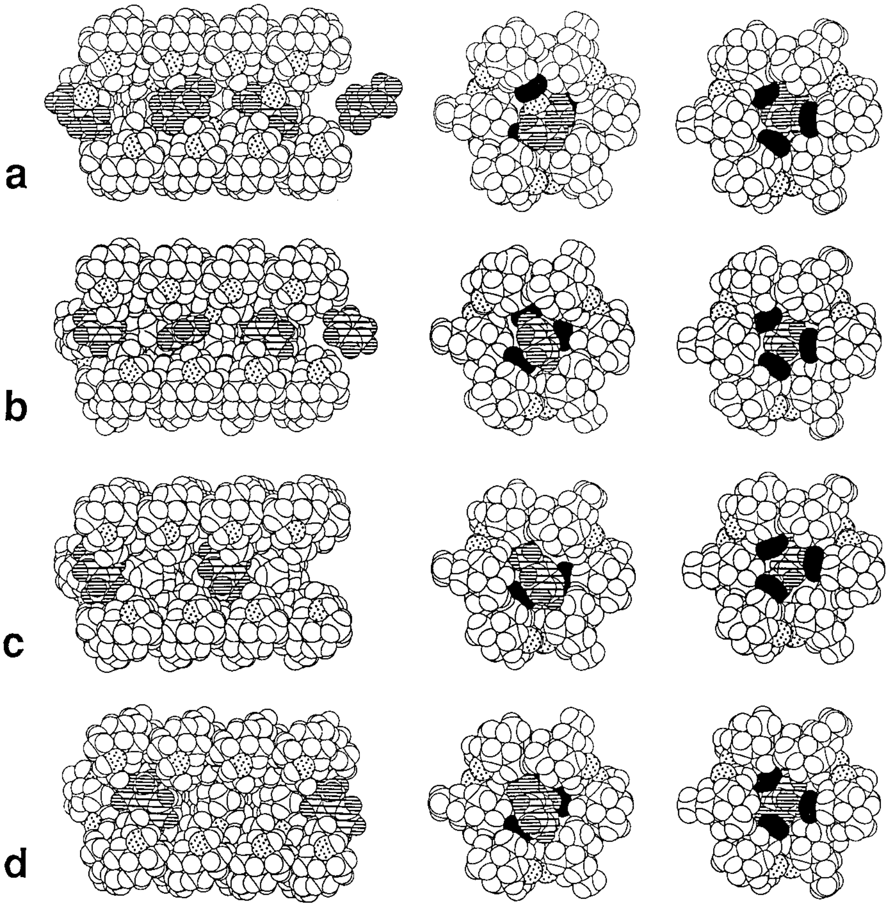

Figure 3. (Left): cut-away views of one tube, with the *c* axis horizontal, for four helical tubulates formed by **4**. The front column of diol molecules has been removed to highlight the guest orientations within. (Centre and right): projection views in the *ab* plane of the top and bottom of one guest molecule within each host tube. These different environments are emphasised by colouring black the C5 methyl groups. Oxygen atoms are indicated by stippling and the guests by horizontal stripes (C light and H heavy). (a) $(\mathbf{4})_3\cdot$(diisopropyl ketone)$_{0.67}$. (b) $(\mathbf{4})_3\cdot$(benzene)$_{0.75}$. (c) $(\mathbf{4})_3\cdot$(toluene)$_{0.5}$. (d) $(\mathbf{4})_3\cdot$(*o*-xylene)$_{0.33}$.

previously determined structure of diol **2**.[12] The position of the additional carbon atom, the C5 pendant methyl group on the propano bridge, was then determined from a difference Fourier synthesis. As discussed above this was disordered over two crystallographically equivalent sites related by a two-fold axis.

We have previously described[14] the general strategy invoked for the location of the guest molecules in inclusion compounds of this type and the evaluation of their stoichiometry. Refinement of each structure utilised the program Raels[18] which has rigid group capabilities. The host diol was refined anisotropically. The position of the hydroxy hydrogen atom was determined from a difference Fourier synthesis, and other hydrogen atoms were included in calculated positions. Guest molecules were refined as rigid groups (except for diisopropyl ketone, which was refined as individual atoms with slack constraints being used to maintain reasonable geometry). Group thermal parameters were used for the guest molecules. Reflection weights used for the refinements were $1/\sigma^2(F_0)$, with $\sigma(F_0)$ being derived from $\sigma(I_0)=[\sigma^2(I_0)+(0.04I_0)^2]^{1/2}$. The weighted residual was defined as $R_w=(\sum w\Delta^2/\sum wF_0^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[19] A DEC Alpha AXP workstation was used for calculations. Full descriptions of the solution and refinement of individual structures are available in the supporting information.

Results

Diol 4—diisopropyl ketone

Crystallisation of **4** from diisopropyl ketone yields the helical tubulate $(\mathbf{4})_3\cdot$(diisopropyl ketone)$_{0.67}$ which corresponds to a stoichiometry of two guest molecules per three unit cells (along *c*) of the host lattice. Pairs of guests are translated along the tube. The different orientations of the molecules comprising the pair are 3_1 related, as illustrated in Fig. 3a (left).

In this structure there is an appreciable free space between adjacent guests since local ordering of the three host pendant groups closest to the guest (all within 3.6 Å) is necessary for guest inclusion at that site. These are located around one end of the guest [Fig. 3a (right)]. Additionally, there is a fourth methyl group at the other end of the guest, one of whose alternate orientations is also within 3.6 Å (of the guest oxygen atom) as shown in Fig. 3a (centre). Here, and in the subsequent structures, the guests now effectively occupy cages rather than the unobstructed tubes which were characteristic of earlier helical tubulate compounds.[7]

Diol 4—benzene

This helical tubulate has the stoichiometry $(\mathbf{4})_3\cdot(\text{benzene})_{0.75}$ corresponding to three guests per four host unit cells. Adjacent guest molecules are translated along the host tube axis by 4/3*c* and are related by a 3_1 screw axis as shown in Fig. 3b (left). The guests are tilted within the tube with the angle between its axis and the normal to the benzene plane being 68.8°. Once again there is significant unoccupied space between adjacent guests. In this case, however, only two of the pendant methyl groups closest to the guest must adopt a specific orientation. The third group is further from the guest and can still adopt either orientation.

Fig. 3b (right), where the guest molecule is situated under the pendant methyl groups, clearly illustrates how areas greater than the UCA value exist within helical tubuland tubes and how such space can be utilised by guests. Viewed from the opposite side, Fig. 3b (centre), the guest comfortably occupies this more exposed environment.

Diol 4—toluene

Crystals of the helical tubulate from toluene have the stoichiometry $(\mathbf{4})_3\cdot(\text{toluene})_{0.5}$. This corresponds to the decreased occupancy, compared to the benzene case, of one guest molecule per two unit cells. Adjacent guests are related by translation by two unit cells along the tubes [Fig. 3c (left)]. The angle between the tube axis and the normal to the guest aromatic plane is 63.3°. As for the benzene example, the two pendant methyl groups closest to the guest adopt a specific orientation in this solid state structure.

Diol 4—*o*-xylene

Crystallisation of diol **4** from *o*-xylene gave the compound $(\mathbf{4})_3\cdot(o\text{-xylene})_{0.33}$ with only one guest per three unit cells. This is the lowest guest occupancy ever observed for a helical tubulate compound, apart from $(\mathbf{2})_3\cdot(\text{squalene})_{0.23}$ which involves a considerably longer guest species.[15] Once again the aromatic guest is tilted with respect to the tube axis, the angle between this and the normal to the aromatic plane being 62.1°. Adjacent guests are translated along the canal with, on average, two empty unit cell sites between them [Fig. 3d, (left)]. All three pendant methyl groups closest to the guest are ordered and once again the opposite ends of the guest within the tube occupy quite distinct environments.

Discussion

The helical tubuland symmetry requirement

In our early work[8] we thought that one key requirement for a diol to be able to form the helical tubuland structure was that it should conform to its crystallographic site symmetry of C_2. As explained in the Experimental Design section, this view was over-simplistic. Examples such as diols **2** and **3** were able to satisfy symmetry requirements by means of random disorder over two crystallographically equivalent sites. This was also true for the guest-free structure of **4**.

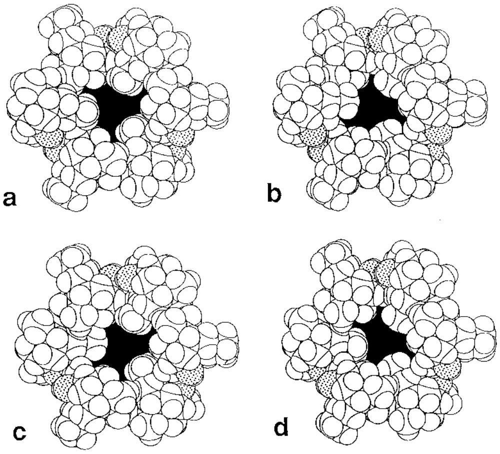

Figure 4. Projection views in the *ab* plane of the helical tubuland lattice of pure diol **4** showing the various canal cross-sections which can result from different ordering of the host C5 pendant methyl groups at a given site in the crystal. **a**–**d**: Groups orientated AAA, BBB, AAB and BBA respectively; the UCA value is 17.3 Å^2 in all four cases.

The present results confirm that the presence of a small symmetry-breaking substituent on the former C_2 axis is no impediment to the formation of helical tubulate compounds. Although the pendant group caused significant reduction in the tube cross-section, the diol **4** readily included a number of moderately sized guests. The symmetry properties of these inclusion compounds are particularly interesting. In all these cases net crystallographic C_2 symmetry is achieved through disorder in the crystal, therefore this appears to be the fundamental symmetry requirement.

It is noteworthy, however, that the local symmetry is quite different. Each pendant methyl group can adopt either of the two orientations A or B, and hence there are four local methyl arrangements: AAA, AAB, BBA, and BBB. In guest-free **4** these are all present on a statistical basis.

Fig. 4 shows a slice through a crystal of guest-free diol **4** with one tube cross-section projected onto the *ab* plane. If all three pendant methyl groups at this site are identically ordered (AAA) then the resulting canal cross-sections projected in the *ab* plane have a threefold propeller-shape. Selection of the opposite orientations (BBB) results in the propeller of opposite chirality. In the remaining two cases (AAB and BBA) the projected cross-section has no symmetry.

These alternative possibilities provide enhanced choice and flexibility in host–guest packing which was not possible in earlier examples. In the inclusion compounds examined here local ordering of the closest pendant groups is selected to provide the best fit. For the diisopropyl ketone and *o*-xylene compounds all three are ordered (BBA), while for the benzene and toluene compounds one is random (R) and two are ordered (ABR). In addition, a given guest has two dissimilar extremities within the tube so the ‘top’ and 'bottom' environments are different. These are compared and contrasted in Fig. 3.

It is evident that introduction of the pendant methyl group, accompanied by its choice of orientations in the crystal, has greatly increased the host–guest interaction in these helical tubulates. The host environment is transformed from an open tube to a constricted tube that effectively gives a series of cages. Partial or complete local ordering of the methyl groups occurs depending on the guest included. Indeed, each given guest now plays a crucial templating role during assembly of the inclusion compound.

Unobstructed cross-sectional area (UCA) of the tubes

In the previous work we have used UCA values to provide both a visual and a quantitative measure of helical tubulate tube size. Comparisons were made across the family of hosts, and also within the series of inclusion compounds formed by one particular diol. The UCA is the area seen looking along one tube when the helical molecular structure is projected onto the *ab* plane. It is analogous to viewing along an indented pipe. Hence the UCA value represents the minimum cross-sectional area available for guest inclusion, and greater values will be available at different heights along the tube.

For diols such as **1** and **5** these UCA values are unambiguous and comparisons between them are meaningful. Diols such as **2**–**4**, however, can adopt two different orientations within the crystal and consequently the situation is more complex. First, the protrusions into the tubes mean that the UCA values lead to underestimates of the free volume. Considerably greater areas are available for guest occupation due to the significant indentations created in the tube walls. Secondly, the protrusions may be all disordered, all have the same orientation or, as seen above, there may be local ordering around the included guest. In these situations the UCA shapes, and sometimes their values, are significantly different. Which should be chosen?

Since the concept of UCA is a valuable one we will retain the idea that it represents the minimum cross-sectional area available for guest inclusion. Consequently the values in Table 2 have been calculated using both host orientations for each diol forming the tube. Using Fig. 4 to illustrate and quantify this problem, the UCA value of the AAA (or BBB) arrangements, and also the AAB (or BBA) arrangements, are all 17.3 Å^2. When both disorder components are included for each diol the UCA value falls to 13.8 Å^2.

The UCA values remain useful as both qualitative and quantitative measures of tube size, but for disordered diols such as **2**–**4** their values will considerably underestimate the inclusion potential of the hosts. In future publications we will calculate these using both host orientations unless clearly stating otherwise to illustrate a specific point of interest.

Dimensional variation within the helical tubulate structures

The above results demonstrate a considerable range of structural characteristics and properties for the tubes of the various compounds formed from diol **4**. Our earlier detailed analysis of diol **5**[14] revealed that the inclusion of increasingly larger guests caused significant increases in the *a* (=*b*) dimension (tube area) but that these were accompanied by only small decreases in *c* (tube length). The unit cell volume (*V*) and UCA values increased regularly in accordance with these dimensional changes. Over a series of 12 helical tubulates the hydrogen bond O···O distance was almost invariant (2.804–2.817 Å), thereby indicating the presence of effective and strong inter-host hydroxy group hydrogen bonding. The variations in tube area resulted from a combination of small angular changes involving the hydrogen bonds and the orientation of the host diols with respect to the tube direction.

The data for the five diol **4** compounds, presented in Table 2, indicate a rather different situation. Concomitant increases in *a* (=*b*), decreases in *c*, and increases in *V* and UCA, are again observed but these changes now are very much smaller. The hydrogen bond O···O distance in these structures is significantly longer and varies more (3.065–3.097 Å), thus indicating much weaker hydrogen bonding than between the molecules of **5**. The hydrogen bonds between molecules of **4** simply stretch to provide greater values of the *a* (=*b*) dimension. This phenomenon has been observed elsewhere, notably for the cage clathrates of 4-*p*-hydroxyphenyl-2,2,4-trimethylthiachroman.[20]

Surprisingly, the values of *a* and UCA do not increase with increasing guest size over the series benzene, toluene, and *o*-xylene. There is, however, a direct correlation between this increased guest size, the decrease in guest stoichiometry

Table 2. Structural data on the helical tubulate inclusion compounds of diol **4** from single crystal X-ray determinations

Compound	*a*=*b* (Å)	*c* (Å)	V (Å)	D_{calcd} (g cm^{-3})	UCA (Å)[a]	O···O (Å)[b]
4	13.708(1)	7.0046(8)	1139.9(2)	1.04	13.8	3.065(1)
(**4**)$_3$·(toluene)$_{0.5}$	13.729(1)	7.008(1)	1143.9(2)	1.10	13.9	3.077(1)
(**4**)$_3$·(*o*-xylene)$_{0.33}$	13.7532(9)	7.0104(5)	1148.4(1)	1.09	14.6	3.081(1)
(**4**)$_3$·(benzene)$_{0.75}$	13.773(2)	6.998(2)	1149.6(4)	1.12	14.7	3.087(1)
(**4**)$_3$·(diisopropylketone)$_{0.67}$	13.808(2)	6.999(1)	1155.7(2)	1.14	15.0	3.097(1)

[a] UCA is the unobstructed cross-sectional area of the host tube when drawn as a projection in the *ab* plane. Both diol orientations have been included for each host molecule in estimating these values.

[b] O···O is the inter-oxygen separation present in the hydrogen bonded spirals of the diol host lattice.

(3:0.75, 3:0.50 and 3:0.33), and decreases in crystal density (1.12, 1.10 and 1.09 g cm^{-3}).

Conclusions

Introduction of a pendant methyl group on the former C_2 axis of helical tubuland diol **2** represents a small molecular change with large supramolecular consequences. Net crystallographic C_2 symmetry, obtained through disorder if necessary, is demonstrated to be the true symmetry requirement of the helical tubuland lattice. Although the pendant group reduces the tube volume this is still ample for guest inclusion. The irregular tube wall surfaces result in greatly increased host–guest interaction and effectively transform the tubes of **2** into the cages of **5**. We are now interested in placement of polar pendant groups within the host tubes and in studying the effect this will have on the host–guest properties of its helical tubulate inclusion compounds.

Supporting information available

Full descriptions of the solution and refinement of individual structures; tables listing fractional coordinates, interatomic distances and angles, and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre [see Notice to Authors, *Tetrahedron* **1984**, *40*(*2*), ii].

Acknowledgements

Financial support from the Australian Research Council is gratefully acknowledged.

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