

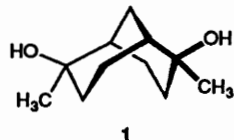
Crystal Structures of Helical Tubulate Inclusion Compounds formed by 2,6-Dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol

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The title compound forms lattice inclusion compounds of the helical tubulate type with a wide range of guest molecules of differing functionality. Crystal structures of the compounds with monoglyme, thiophene and di-iodine are presented. These reveal the relationship of hosts and guests in each compound despite the incongruent symmetry of the two components.

2,6-Dimethylbicyclo[3.3.1]nonane-*exo*-2,*exo*-6-diol **1** is the prototype of a family of alicyclic diol inclusion hosts which crystallise with a hydrogen-bonded structure involving a series of parallel, helical canals running along the length of the needle-like crystals.¹ In the case of **1** these canals have an approximately triangular cross-section (side *ca.* 6.3 Å). This tubuland structure² traps appropriate guest molecules producing multimolecular³ or lattice inclusion⁴ compounds in space group $P3_121$ (or its enantiomorph $P3_221$) with only van der Waals interactions between the host and guest components.

Previously we have reported the crystal structure of the inclusion compound $(\mathbf{1})_3 \cdot (\text{ethyl acetate})$ but, because of guest disorder and the incongruent symmetry of host and guest, a structure factor residual of 0.049 was reached without revealing details of the ethyl acetate molecules within the host canals.⁵ Here we report the first structures for helical tubulate inclusion compounds of diol **1** where the guests have been located.



Screening of the inclusion properties of **1** reveals it to be a potent host molecule. Helical tubulates are formed with a wide range of small guest molecules including alkenes, aromatic hydrocarbons, haloaromatics, ketones, ethers, esters, sulfides, amines and nitriles. Selected examples have been studied in detail by X-ray crystallography.[†]

Crystallisation of the diol **1** from 1,2-dimethoxyethane (monoglyme) gave the helical tubulate $(\mathbf{1})_3 \cdot (\text{monoglyme})_{0.75}$ with the guest molecules situated centrally in the canals and clearly located by the X-ray structural determination (Fig. 1) despite the presence only of light atoms in this guest. Fig. 2 shows a side view of the same guest arrangement where one of the diols has been removed to expose the guest in the canal.

In contrast, the helical tubulate grown from a thiophene

[†] Crystal data for (a) $(C_{11}H_{20}O_2)_3 \cdot (C_4H_{10}O_2)_{0.75}$, $M = 620.4$, trigonal, $P3_121$, $a = 12.0416(3)$, $c = 7.0110(2)$ Å, $U = 880.39(4)$ Å³, $Z = 1$, $D_c = 1.17$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.5418$ Å, $\mu = 5.98$ cm⁻¹. Final $R = 0.043$ for 1082 independent observed reflections [$I/\sigma(I) > 3$] and 96 variables. (b) $(C_{11}H_{20}O_2)_3 \cdot (C_4H_4S)$, $M = 637.0$, trigonal, $P3_121$, $a = 12.4083(5)$, $c = 6.9702(4)$ Å, $U = 929.39(6)$ Å³, $Z = 1$, $D_c = 1.14$ g cm⁻³, $\lambda(\text{Cu-K}\alpha) = 1.5418$ Å, $\mu = 10.58$ cm⁻¹. Final $R = 0.026$ for 1029 independent observed reflections [$I/\sigma(I) > 3$] and 80 variables. (c) $(C_{11}H_{20}O_2)_3 \cdot (I_2)_{0.5}$, $M = 679.8$, trigonal, $P3_221$, $a = 12.068(2)$, $c = 6.984(3)$ Å, $U = 880.8(4)$ Å³, $Z = 1$, $D_c = 1.28$ g cm⁻³, $\lambda(\text{Mo-K}\alpha) = 0.7107$ Å, $\mu = 9.34$ cm⁻¹. Final $R = 0.035$ for 1044 independent observed reflections [$I/\sigma(I) > 3$] and 81 variables.

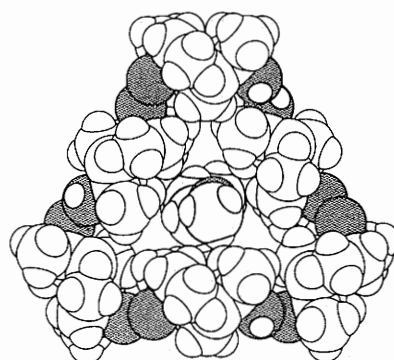


Fig. 1 Projection view in the *ab* plane of one canal only of the crystalline helical tubulate of diol **1** and monoglyme showing the guest positioned centrally in the canal. Oxygen atoms are stippled and carbon atoms of the guest are shaded to aid visualisation of the two components.

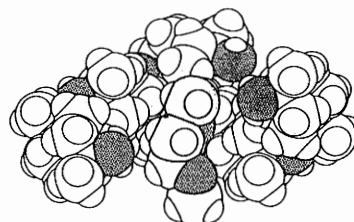


Fig. 2 Side view of the arrangement shown in Fig. 1, with the *c* axis vertical. One of the six molecules of **1** has been removed to show the arrangement of monoglyme guest within the canal.

solution of **1** had the formula $(\mathbf{1})_3 \cdot (\text{thiophene})$ with the planar guest molecules situated along one face of the canal wall. Although once again the guests were clearly located, this example provides a good illustration of the inherent problems associated with determining guest positions in such materials. There are three equivalent canal faces which the guest may choose for its alignment, and for each the thiophene may adopt five different rotational positions as a consequence of its pseudo-fivefold symmetry. One such typical orientation is shown in Fig. 3.

A rich variety of di-iodine structural chemistry is known. Most instances involve (a) di-iodine complexed with heteroatoms⁶ such as N, S or Se; (b) di-iodine bridging two organometallic halide entities;⁷ or (c) di-iodine units involved in various polyiodide structures.⁸ In contrast, few structures containing discrete di-iodine molecules have been determined by X-ray crystallography. Solid α -cyclodextrin $\cdot I_2 \cdot 4H_2O$ ^{9,10} has the adducts arranged in a herringbone manner which effectively isolates the di-iodine in individual cages. However, even here,

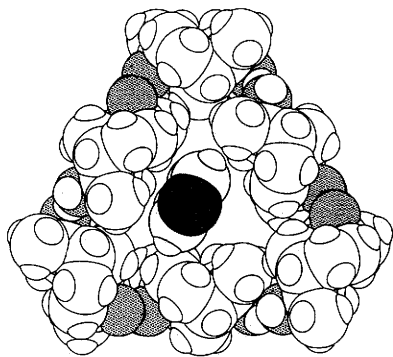


Fig. 3 Projection view in the *ab* plane of a section through one canal of the $(1)_3$ -(thiophene) helical tubulate, showing one typical orientation of the thiophene guest parallel to one canal edge. The sulfur atom of the guest is highlighted using heavy stippling. This figure clearly shows (*cf.* Figs. 1 and 4) the increase in *a, b* lengths and consequent alteration in canal shape with change in guest dimensions.

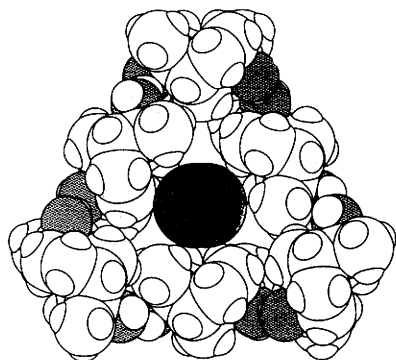


Fig. 4 Projection view of one canal only of the helical tubulate compound of **1** and I_2 , showing the guest molecule located centrally within the host canal, but tilted slightly with respect to the *c* axis

$O \cdots I - I \cdots O$ attractive interactions are present between host and guest. A rather similar topology is found for the hexakis-(2,6-di-*O*-methyl)- α -cyclodextrin- I_2 inclusion compound.¹¹

An inclusion compound of **1** and di-iodine was obtained as needles from a solution of both components in ethanol. Although the bulk material was dark purple, individual crystals were brownish in colour. X-Ray structural determination revealed this material to be the helical tubulate of stoichiometry $(1)_3 \cdot (I_2)_{0.5}$ as shown in Fig. 4. This guest occupancy results in an $I \cdots I$ separation of 11.4 Å, which should be compared with the sum of the van der Waals radii (4.3 Å). We believe this to be the first instance of discrete di-iodide molecules (as opposed to polyiodides) being included in a tubular host structure.

Since the hydroxy groups of the host are not exposed to the canal interior, only $CH \cdots I_2$ interactions can be involved between the guests and the canal walls. The necessity of using a solvent in the preparation of this compound means that co-inclusion of ethanol between the di-iodine molecules must be considered since co-ordination between oxygen and iodine atoms would favour the stability of this inclusion system. Because X-ray and combustion analysis data were equivocal on this question, the material was examined by 1H NMR spectroscopy in both $[^2H_6]$ dimethyl sulfoxide and $[^2H_6]$ acetone solutions. Each spectrum clearly showed an ethanol quartet signal (*ca.* δ 3.5) and integration indicated a probable overall composition of $(C_{11}H_{20}O_2)_3 \cdot (I_2)_{0.5} \cdot (C_2H_5OH)_{0.5}$. Although ethanol was not revealed by the X-ray data, the structure determined does contain adequate volume to accommodate this second guest between the di-iodine units.

These inclusion structures are significant in revealing the spatial relationships of host **1** and its guest partners for the first time. It is particularly noteworthy that the guest occupancy per unit cell changes according to the guest. Our single crystal studies show that *a* and *b* (and hence the canal cross-section) can increase significantly to accommodate bulkier guests but that there is only a very small concomitant decrease in *c* (along the canal). Thus there is a size limit on potential guests with, for example, mesitylene being too large for inclusion in this host structure. Such considerations allow reasonably accurate predictions to be made as to which compounds are likely to be included or excluded.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. For details see 'Instructions for Authors (1992)', *J. Chem. Soc., Perkin Trans. 2*, 1992, issue 1.

Experimental

Diol **1** was synthesised by the published procedure,⁵ and crystals of potential inclusion compounds allowed to grow by slow evaporation of solutions of **1** in the appropriate liquid. Inclusion of guests was screened by IR (mull) spectroscopy and combustion analysis. The X-ray powder pattern (Siemens D500) of each solid was then compared with that of $(1)_3$ -(ethyl acetate) to confirm that the same lattice structure was present.

Diffraction data for all three single-crystal determinations were collected using an Enraf-Nonius CAD4 diffractometer. The procedures used for the collection and reduction of the intensity data have been described.¹² Details of the solution and refinement of the structures will be reported in the full paper.

Acknowledgements

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