Different Crystal Structures of Inclusion Complexes formed by *syn*-2,*syn*-7-Dihydroxy-2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane† with Ethyl Acetate and Benzene

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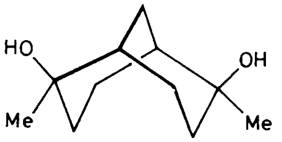
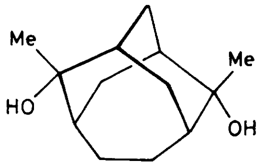
X-Ray structure determinations show that crystals of *syn*-2,*syn*-7-dihydroxy-2,7-dimethyltricyclo[4.3.1.1^{3,8}]-undecane† obtained from ethyl acetate solution possess a spontaneously resolved trigonal network of helical canals containing mobile solvent, while crystals of the same compound obtained from benzene are racemic and tetragonal with the solvent trapped in ellipsoidal cavities.

We have recently reported the formation of crystalline inclusion complexes by the cyclic diol (**1**), in which helical canals containing ethyl acetate or other guest molecules are formed between helical spines of continuous hydrogen bonds.[1,2] As part of a systematic programme to find other such complexes, we have now investigated the tricyclic diol (**2**), prepared by the reaction of tricyclo[4.3.1.1^{3,8}]undecane-2,7-dione[3] with methyllithium. The diol (**2**) is related to (**1**) by addition of an ethano bridge and by reversal of substituent stereochemistry.



(**1**)



(**2**)

When crystallised from ethyl acetate, (**2**) spontaneously resolves as the crystalline inclusion complex (**2E**), with the structure‡ shown in Figure 1. This structure has the same crystallographic symmetry ($P3_121$) as the inclusion complex (**1E**) of (**1**) with ethyl acetate. However, the differences in

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† The term *syn* is used here to define substituents relative to the unique ethano bridge.

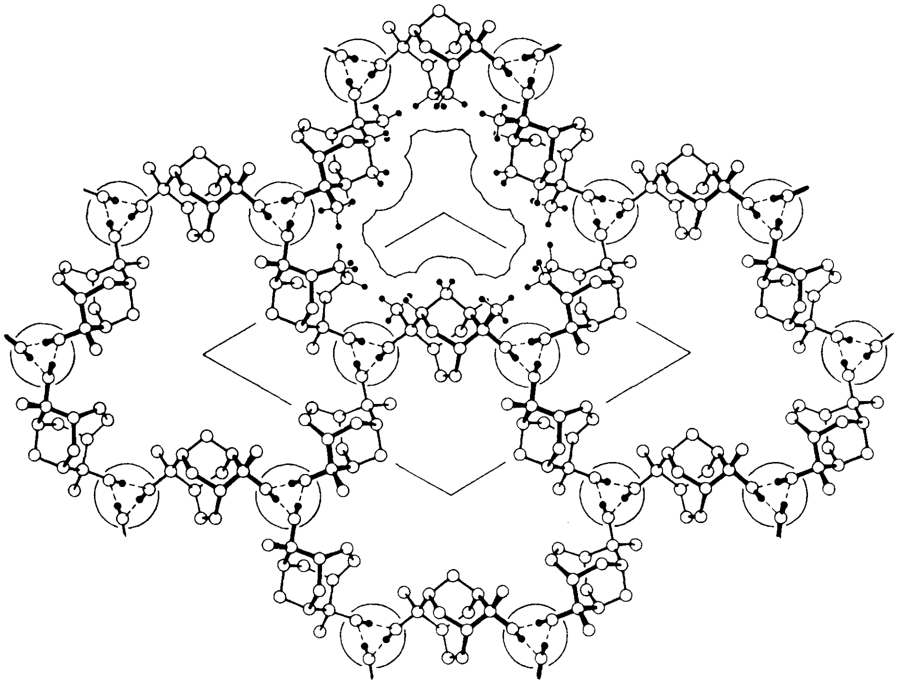

Figure 1. Projection view, parallel to the three-fold screw axes, of the diol host network in the crystal structure of (**2E**). The helical spines of hydrogen bonds are circled. Selected hydrogen atoms included with van der Waals radii define the projected cross section of one canal.

stereochemistry and volume between host molecules (**1**) and (**2**) cause differences in host molecule orientation and lattice dimensions between crystalline (**1E**) and (**2E**). The tri-lobed cross-section available to guests in the helical canals of (**2E**) (see Figure 1) is distinctly different from the triangular cross-section of (**1E**).

When crystallised from benzene, (**2**) forms an inclusion complex (**2B**) with quite different tetragonal crystal structure,‡ represented diagrammatically in Figure 2. The benzene molecules are located in hydrocarbon-lined cavities separated by $c/2$ along crystallographic twofold axes parallel to c. The cross-sectional view in Figure 3 shows the ellipsoidal shape and size of the host cavities, and the positions of the guest benzene molecules within them.§ The empty space which connects the cavities along c is too small to permit the passage of benzene guest molecules.

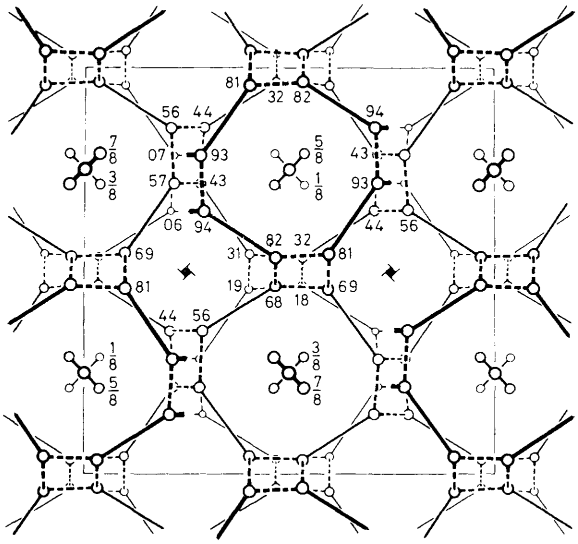

Figure 2. Diagrammatic representation of the crystal structure of (**2B**), projected along c, with host molecules drawn simply as oxygen atoms connected by solid lines, and hydrogen bonds marked as broken lines. Two of the four-fold screw axes are symbolised. The numbers are 10^2z for oxygen atoms and fractional co-ordinates for benzene centres. The upper edges only of the benzene molecules can be seen.

The crystal structure of (**2B**) is maintained by cyclic hydrogen bonds (broken lines in Figure 2) in approximate squares (tilted with respect to the *ab* plane) which connect four host molecules. Diol molecules connected in cyclic quartets by hydrogen bonds on the 'level' edges of the squares surround the channels of linked guest cavities. Molecules connected *via* hydrogen bonds on the 'steep' edges of the hydrogen-bond squares occur in double spiralling chains around the 4_1 and 4_3 screw axes parallel to c. The empty core of these helical columns has a radius of *ca.* 0.1 Å to the van der Waals edge of the CH_2 groups which protrude inwards. The crystal is racemic, with the diol enantiomers aggregated around the right- and left-handed screw axes.

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‡ *Crystal data.* (**2E**): trigonal, space group $P3_121$ or $P3_221$, hexagonal, $a = 13.192(1)$, $c = 6.9137(3)$ Å; $D_m = 1.19(2)$ g cm^{-3}, cell contents $3(C_{13}H_{22}O_2) + xC_4H_8O_2$, x variable, *ca.* 1; 1056 intensity measurements (Cu-K_α), intensity decay (corrected) $1 \rightarrow 0.71$ (x decrease), 694 observed reflections; $R = 0.056$ (currently for $x = 0$, $\sin\theta/\lambda > 0.3$, 596 data). (**2B**): tetragonal, space group $I4_1/acd$, $a = 23.021(1)$, $c = 18.889(2)$ Å; $D_m = 1.20(2)$ g cm^{-3}, cell contents $32(C_{13}H_{22}O_2) + 8(C_6H_6)$, $D_c = 1.22$ g cm^{-3}; 1859 intensity measurements (Cu-K_α), 1361 observed data, $R = 0.041$. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

§ The benzene guests, at 222 (D_2) sites in the crystal, are 12% disordered by rotation 30° about the ring six-fold axis. Contiguous 222 sites along c are related by the crystallographic $\bar{4}$ (S_4) operation.

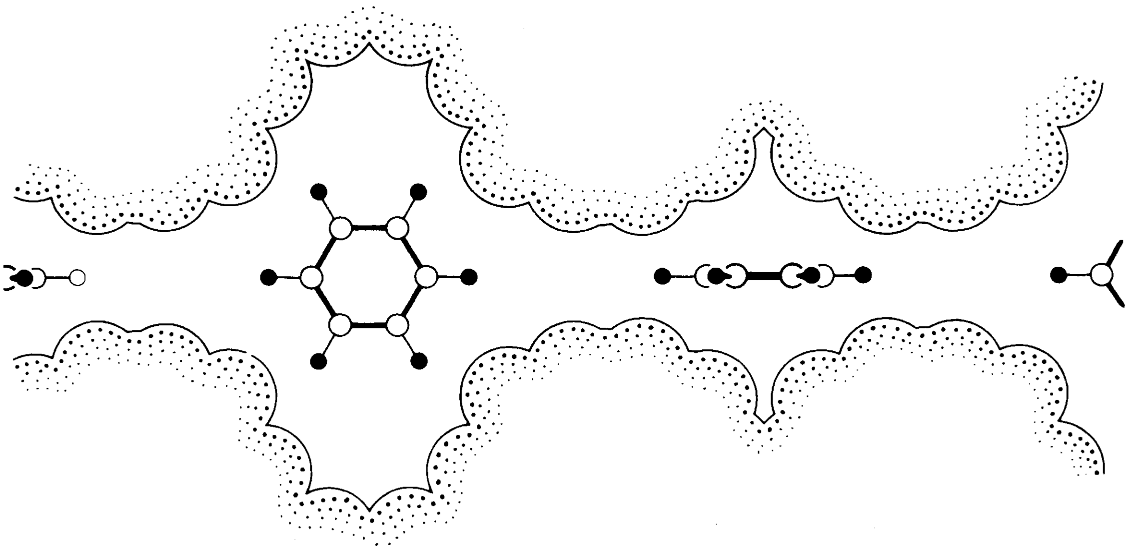

Figure 3. Cross-sectional representation of the cavities in (**2B**), linked along crystallographic two-fold axes parallel to *c*, showing the van der Waals surface due to hydrogen atoms of the host molecules, and the major (88%) orientation of the benzene guest molecules.

Powder diffraction data reveal that inclusion complexes of (**2**) with carbon tetrachloride, diethyl ether, and *o*- and *p*-xylene possess the trigonal crystal structure of (**2E**). Further investigations of inclusion complex formation by this and related host molecules are in progress.

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References

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3 B. R. Vogt, *Tetrahedron Lett.*, 1968, 1579.