2,7-Dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol: Structural Analysis of the Ellipsoidal Clathrate and Hemihydrate Crystal Forms

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The ellipsoidal clathrate (containing benzene) **1B** and hemihydrate **1W** crystal structure forms of 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol determined by X-ray crystallography are described and contrasted with the previously reported solvent-free **1** and helical tubulate (containing ethyl acetate) **1E** structures. The superlattice comprising structure **1B** [$(C_{13}H_{22}O_2)_4\cdot(C_6H_6)$ $I4_1/acd$, *a,b* 23.021(1), *c* 18.889(2) Å, *Z* 8, *R* 0.035] is assembled from two identical interpenetrating sublattices which are inversion related. Each of these is constructed from a three-dimensional network of hydrogen bonded diol molecules. Benzene guests occupy D_2 sites in ellipsoidal cavities between neighbouring sublattices. The hemihydrate structure **1W** [$(C_{13}H_{22}O_2)_2\cdot(H_2O)$, *Pbca*, *a* 13.4829(6), *b* 13.6657(5), *c* 26.4388(9) Å, *Z* 8, *R* 0.051] involves diol and water molecules hydrogen bonded together in a spirocyclic manner to create a layer structure. Reasons for formation of the alternative structures in particular circumstances are discussed.

The alicyclic diol 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol **1** exhibits versatile solid state structural behaviour. Crystals grown free from solvent have a hydrogen bonded layer structure with three independent diol molecules, two of which exhibit incomplete hydrogen bonding, in the asymmetric unit.[1]

In contrast, if crystallised from most small solvents the diol **1** yields multimolecular inclusion lattices[2] in which there are arrays of fully hydrogen bonded diol molecules surrounding cavities containing guest molecules. Only non-polar van der Waals interactions are present between host and guest. We have previously communicated briefly that diol **1** forms *two* different types of inclusion lattice dependent on the guest with which it is crystallised.[3]

When crystallised from ethyl acetate the inclusion lattice contains helical canals occupied by guest molecules (the helical tubuland lattice type).[4] In contrast, when crystallised from benzene a quite different inclusion lattice is produced in which there are canals which are periodically constricted to the extent that there are discrete cavities containing one benzene guest each (the ellipsoidal clathrate lattice type).[3] We have described already the details of the helical tubuland crystal structure with ethyl acetate $(\mathbf{1})_3\cdot(C_4H_8O_2)$, **1E**, as part of a discussion of more general helical tubuland behaviour.[5]

In this paper we report structural details of the ellipsoidal clathrate crystal lattice with benzene, **1B**, and of a fourth solid state structure involving the diol and water, **1W**. An attempt to rationalise this multi-faceted crystalline behaviour of diol **1** is also presented.

Results and Discussion

Description of the Lattice Structure of **1B**.—Crystallisation of the diol **1** from benzene gave the inclusion compound **1B** as cubic blocks of composition $(\mathbf{1})_4\cdot(C_6H_6)$ which were subjected to single crystal X-ray determination. Numerical details of the solution and refinement of this structure are shown in Table 1.

The structure has a large tetragonal unit cell, which contains 32 diol molecules and 8 guests, in space group $I4_1/acd$. There is one diol molecule per asymmetric unit with approximate twofold symmetry as indicated by the atom labelling shown in Fig. 1. Intra-diol bond distances and angles are included in Tables 2 and 3 respectively. Table 4 lists details of the hydrogen bonding dimensions for the structure.

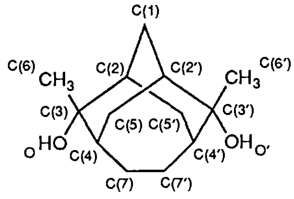

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Fig. 1 Molecular structure of diol **1** showing the crystallographic numbering system used for both X-ray structures **1B** and **1W**

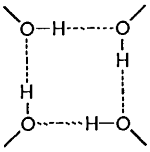


Fig. 2 The hydrogen bonded cycle $(-OH)_4$ present in structure **1B**

All diol molecules are fully hydrogen bonded with one donor and one acceptor bond at each OH group. The first essential feature of the lattice involves fourfold groupings of diol molecules which are hydrogen bonded to form cycles of hydrogen bonds $(-OH)_4$, as shown in Fig. 2. There is disorder of the hydroxy H atoms over the two possible positions in each hydrogen bond, and the refined structure contains half hydrogen atoms in both positions. For this reason the hydrogen bonds are drawn as dashed lines without H atoms in subsequent figures.

The second striking feature involving fourfold assembly of diol molecules is cyclic quartets of diol molecules as shown in Fig. 3. Each cycle has $\bar{4}$ symmetry and surrounds one of the eight $\bar{4}$ sites, at (0, 1/4, 3/8) *etc*., in the cell. Only one $\bar{4}$ site is marked on Fig. 3. Twofold axes relate pairs of cyclic quartets in both the *a* and *b* directions to produce the array shown. The diol molecules in these cyclic quartets are approximately normal to the *c* axis, and approximately horizontal in this diagram.

We have shown previously that hydrogen bonded cycles $(-OH)_4$ are common amongst alicyclic diols and often result in the formation of layer structures.[6] Here, however, a three dimensional hydrogen bonded network is produced. The hydrogen bonded cycles are inclined at a steep angle to the *c*

Table 1 Crystallographic details and diffraction analyses for structures **1B** and **1W**

	1B	**1W**
Formula	$(C_{13}H_{22}O_2)_4\cdot(C_6H_6)$	$(C_{13}H_{22}O_2)_2\cdot(H_2O)$
Formula mass	919.39	438.65
Crystal description		{001}(−111)(−1−11)(1−11)(111)
Space group	$I4_1/acd$ (Origin at $\bar{1}$)	*Pbca*
a/Å	23.021(1)	13.4829(6)
b/Å	23.021(1)	13.6657(5)
c/Å	18.889(2)	26.4388(9)
V/Å^3	10 010.5 (5)	4871.4(3)
T/°C	21(1)	21(1)
D_{obs}/g cm^{-3}	1.20	1.20
Z	8	8
D_{calc}/g cm^{-3}	1.22	1.21
Radiation, λ/Å	Cu–Kα, 1.5418	Cu–Kα, 1.5418
μ/cm^{-1}	5.82	6.05
Crystal dimensions/mm	0.10 × 0.11 × 0.28	0.32 × 0.32 × 0.42
Scan mode	θ/2θ	θ/2θ
$2\theta_{max}$/°	120	140
No. of intens. meas.	4060	5155
Criterion for obsd. reflection	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No. of independent obsd. reflections	1361	3431
No. of reflections (m), variables (n) in final refinement	1361, 151	3431, 298
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_0\rvert$	0.035	0.051
$R_w = [\Sigma^m w\lvert\Delta F\rvert^2/\Sigma^m w\lvert F_0\rvert^2]^{\frac{1}{2}}$	0.045	0.074
$s = [\Sigma^m w\lvert\Delta F\rvert^2/(m - n)]^{\frac{1}{2}}$	1.49	2.57
Crystal decay	1 to 0.95	1 to 0.96
Max./min. transmission coefficient	0.95, 0.90	0.85, 0.81
Largest peak on final diff. map/e Å^{-3}	0.18	0.2
Extinction coefficient	1.69 × 10^{-5}	

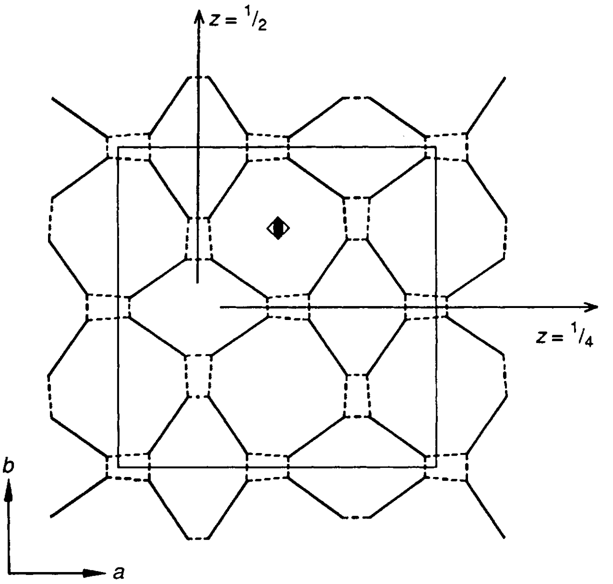


Fig. 3 Projection diagram of one diol sublattice present in structure **1B** viewed down c, with one $\bar{4}$ site shown and twofold axes parallel to a and b. Diol molecules are represented diagrammatically as solid spacer rods and hydrogen bonds as dashed linkages.

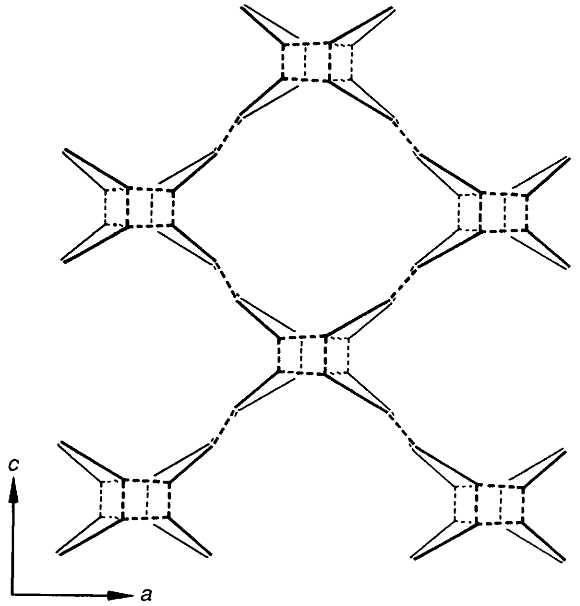


Fig. 4 The same diol sublattice (Fig. 3) viewed down b. Line thickening represents perspective in this diagram. Diol molecules are represented as solid spacer rods and hydrogen bonds as broken lines.

axis, and have two steep edges relative to c and two edges approximately normal to c. Thus the array shown in Fig. 3 represents a flat projection of the three-dimensional achiral lattice resulting from continuation of such hydrogen bonding. This is illustrated in Fig. 4 which shows this array rotated through 90° and viewed down b.

The complete structure consists of *two* of these interpenetrating sublattices which are inversion related. Each sublattice has $I\bar{4}2d$ symmetry as compared with the overall symmetry of $I4_1/acd$. Only van der Waals interactions are present between the sublattices. Figs. 5 and 6 show the two corresponding views with both sublattices included.

Diol molecules connected *via* hydrogen bonds on the steep edges of the cycles occur in spiralling chains along the c direction. These spirals of hydrogen bonded diols surround fourfold screw axes (4_1 and 4_3) parallel to c, but each spiral does not itself have 4_1 or 4_3 symmetry as there are no fourfold screw axes in space group $I\bar{4}2d$. Each spiral has a diamond shape in projection. It is the pair of such intertwined and distorted spirals which has the crystallographic screw symmetry. In other words spirals from the two sublattices together generate the fourfold screw symmetry. In the diagrammatic representation in Fig. 5 it appears that there are spiral canals along the fourfold screw axes, but in fact the empty core of these spirals has a radius of

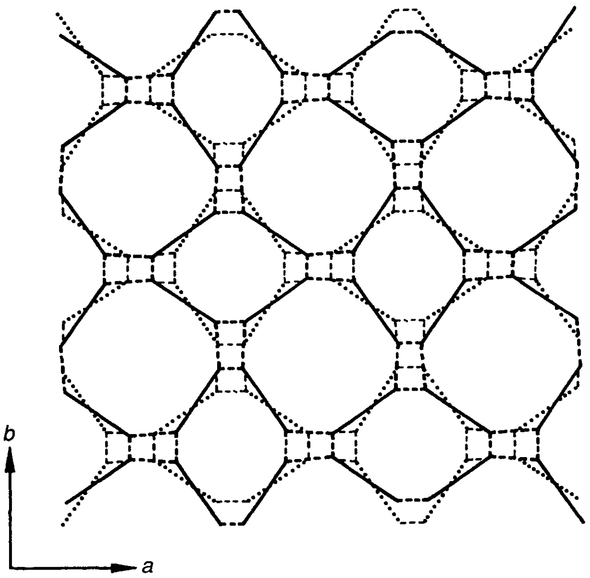


Fig. 5 Projection view with superposition of the two diol sublattices producing the interpenetrating superlattice of **1B** viewed down *c*. No perspective is implied in this Fig. Both sublattices are identical but are related by a centre of symmetry. Line character is different for each of these sublattices with the diol molecules of one represented diagrammatically as solid spacer rods and those of the other shown as dotted spacers. Hydrogen bonds are again represented as broken lines.

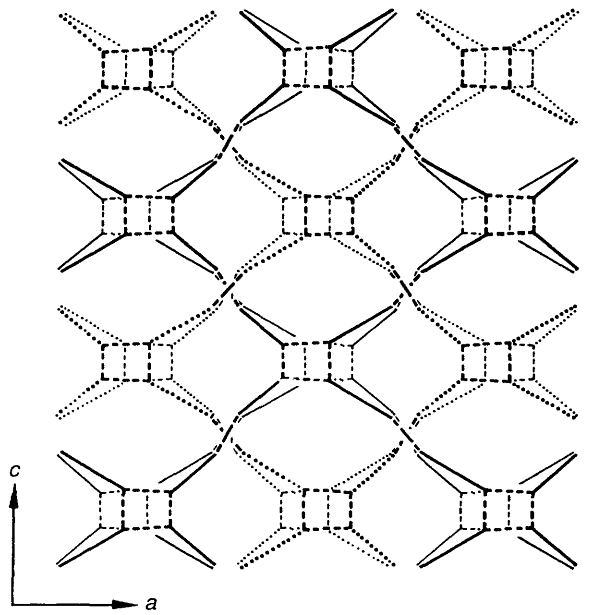


Fig. 6 The same superposition of the two sublattices generating the diol superlattice of **1B** (see Fig. 5) but viewed down *b*. Perspective is shown only where the hydrogen bonded cycles of diol molecules actually cross in this diagram.

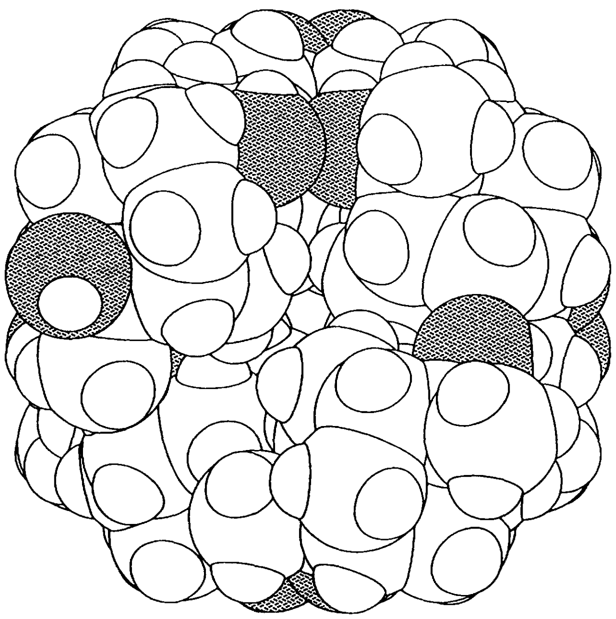


Fig. 7 Projection view along a fourfold screw axis parallel to *c* in structure **1B**. This space filling representation shows that the canals produced at these locations have insufficient volume for inclusion properties to result.

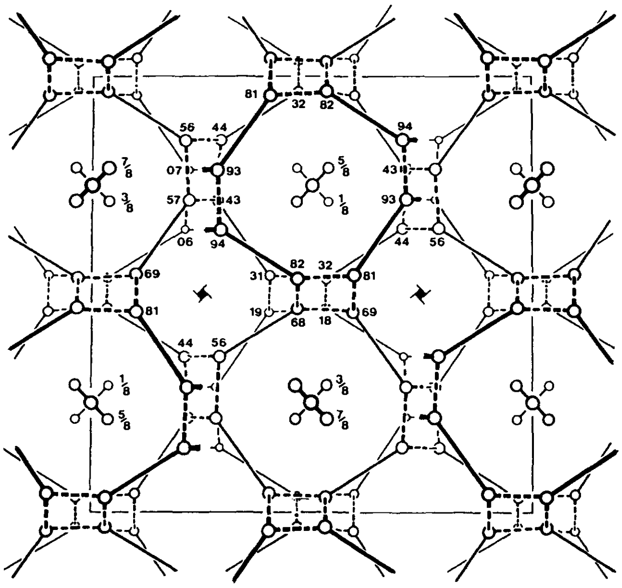


Fig. 8 Diagrammatic representation of the complete unit cell of **1B** viewed down *c*, showing the diol superlattice in perspective. The diol molecules are drawn simply as two oxygen atoms connected by solid lines and hydrogen bonds are marked as broken lines. Benzene guest molecules are viewed end on and are represented by their upper edges. Two of the fourfold screw axes are symbolised. The numbers are 10^2z for oxygen atoms and fractional coordinates for benzene centres. This perspective view should be compared to Fig. 5 to visualise the relationship between the two interpenetrating sublattices.

only *ca.* 0.5 Å to the van der Waals edge of the CH_2 groups which protrude inwards. This constriction of the double spiral canal is evident in Fig. 7 which shows a space filling representation.

Both the sublattice and the superlattice are achiral with both diol enantiomers present. These are arranged alternately around each $\bar{4}$ related cyclic quartet; those around each 4_1 screw axis are of one handedness, and those around 4_3 axes are of the other.

The complete lattice is represented in a perspective view by Fig. 8 which also includes the benzene guest molecules. These are positioned on 222 (D_2) sites at (0, 1/4, 1/8) *etc.*, located midway between the $\bar{4}$ (S_4) sites. The benzene molecules appear in end view in Fig. 8. Contiguous 222 sites along the canal axis are related by the $\bar{4}$ operation, and thus the contiguous guest molecules are rotated by 90° in projection as indicated in Fig. 9.

The separations of the 222 and $\bar{4}$ sites along the canal axis is $c/4$ = 4.72 Å, and the centres of the diol quartets are separated by 9.44 Å. A benzene molecule occupies the position between the pair of diol quartets and there is substantial space between them. Thus adjacent diol quartets are not in contact along the canal axis, as is shown in Fig. 10, a side view of a pair of diol quartets shown in space filling representation.

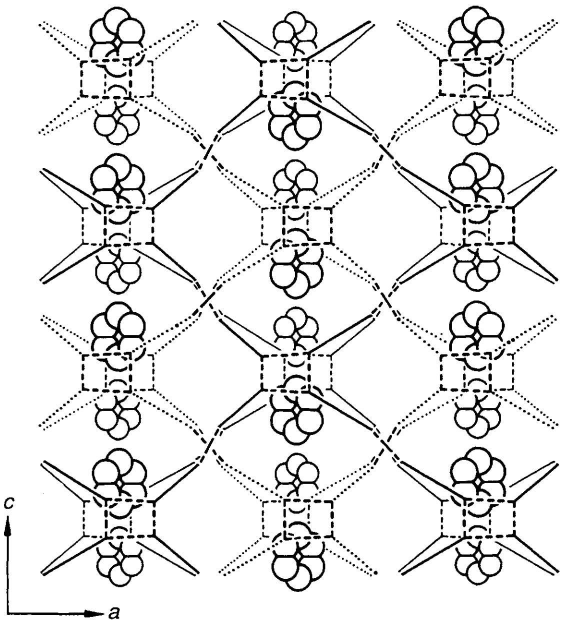


Fig. 9 Representation of Fig. 8 viewed down *b* showing superlattice perspective and the arrangement of benzene guests in space filling representation (hydrogen atoms omitted). As in Fig. 6, the diols of one sublattice are represented diagrammatically as solid spacer rods and those of the other as dotted spacers. Hydrogen bonds are indicated as broken lines. The benzene molecules which make up the vertical columns are alternatively orthogonal. Individual column perspectives are emphasised by different sizes of benzene carbon atoms.

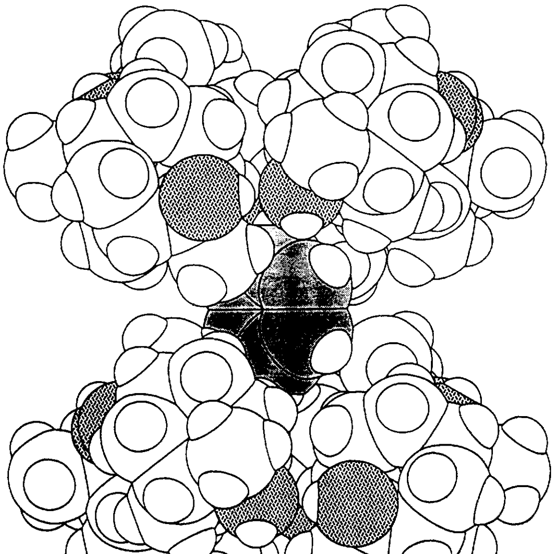


Fig. 10 Space filling representation of a single benzene guest molecule in its ellipsoidal cavity created by two adjacent cyclic quartets of diol **1** molecules in the structure **1B**. The top quartet of diols is from one sublattice and the bottom quartet from the other, with the benzene centre at a 222 site.

If a cyclic quartet of diols surrounding the $\bar{4}$ site is taken as a single object, then each sublattice can be described as a distorted diamond lattice since $I\bar{4}2d$ is a subgroup of $Fd\bar{3}m$ if $a = b = c/\sqrt{2}$.

Description of the Lattice Structure of **1W**.—Crystallisation of solvent-free **1** from damp acetonitrile produced another co-crystalline material **1W**, with the composition $(\mathbf{1})_2{\cdot}(H_2O)$. Numerical details of the solution and refinement of this structure are shown in Table 1. There are two independent diol molecules A and B in the asymmetric unit of **1W**. Bond lengths and interbond angles are presented in Tables 2 and 3. The space group is centrosymmetric and therefore the structure is racemic.

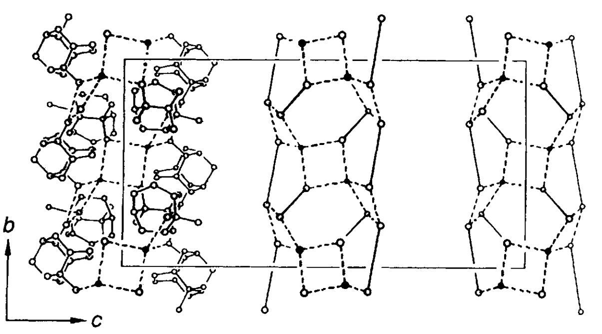


Fig. 11 View of the **1W** structure down *a*. Part of the figure shows the carbon skeletons of diol **1** molecules and part represents these diagrammatically as oxygen atoms separated by solid tie-lines to emphasise the hydrogen bonding arrangement. Hydrogen bonds are represented as dashed lines, diol oxygens as open circles, and water oxygen atoms as filled circles.

Fig. 11 shows a projection of the structure of **1W** viewed down *a*. The structure consists of discrete layers of approximate thickness *c*/2 (*ca.* 13 Å). Purely hydrophobic elements make up the junction between layers at $c = 1/4$ and $c = 3/4$. The water molecule and the hydroxy groups of the diol molecules are all embedded in the centre of the layers, and form a hydrogen bonded network. A view (down *c*) of the structure perpendicular to the layer is shown in Fig. 12.

Each diol hydroxy group takes part in two hydrogen bonds, one as donor and one as acceptor. Each water molecule takes part in four hydrogen bonds, two as donor and two as acceptor. Dimensions associated with hydrogen bonding are given in Table 4.

The water molecules and the hydroxy groups combine to form triplets of the hydrogen bonded cycles $(\text{-OH})_4$ found in **1B** (see Figs. 11 and 12). These triplets are joined in a spirocyclic fashion with the water molecules occupying the shared vertices of the spirocycles. The two halves of the triplet are related by a centre of inversion. Each triplet is connected to four other glide-related triplets by one A and one B type diol molecule of opposite chiralities to yield the layer structure.

Discussion of the diol **1** *structures*.—There are numerous examples of diamondoid lattices, the simplest being cubic diamond itself with a single atom as the repeat unit. The α-cristobalite form of SiO_2 has a distorted diamond latice in which the repeat unit is the SiO_4 tetrahedron whose O···O distances are in the range 2.58–2.64 Å (mean 2.60 Å). The adamantanoid cages in $Cd(SPh)_2$ are also linked in diamondoid fashion. Here the repeat unit is much larger with S···S distances 7.97–8.46 Å (mean 8.22 Å). In this case the large cavities formed within the diamondoid lattice are filled by phenyl substituents on the S atoms.[7] Finally in **1B**, the tetrahedral repeat unit is larger again, and less regular. If the centre of a hydrogen bonded cycle (X) is taken as each vertex of the tetrahedron then X···X distances range from 9.40 to 11.50 Å, with mean 10.1 Å. Since diol molecules lie along the edges of the tetrahedron there is sufficient empty space in this structure for a second, interpenetrating diamondoid lattice.

The concept of sublattices combining through interpenetration to form a molecular superlattice has become widely recognised over recent years, particularly through the elegant

Table 2 Bond lengths (Å) for structures **1B** and **1W**[a]

Bond	**1B**	**1W**(A)	**1W**(B)
C(1)–C(2)	1.530(3)	1.534(3)	1.525(3)
C(1)–C(2′)	1.535(3)	1.532(3)	1.526(3)
C(2)–C(3)	1.533(3)	1.549(3)	1.530(3)
C(2′)–C(3′)	1.537(3)	1.538(3)	1.532(3)
C(3)–C(4)	1.540(2)	1.537(3)	1.546(3)
C(3′)–C(4′)	1.538(3)	1.546(3)	1.541(3)
C(4)–C(5)	1.544(3)	1.534(3)	1.535(3)
C(4′)–C(5′)	1.536(3)	1.541(3)	1.538(3)
C(5)–C(2′)	1.531(3)	1.524(3)	1.533(3)
C(5')–C(2)	1.520(3)	1.513(3)	1.530(4)
C(4)–C(7)	1.522(3)	1.524(3)	1.524(3)
C(4′)–C(7′)	1.526(3)	1.524(3)	1.525(4)
C(7)–C(7′)	1.524(3)	1.522(3)	1.510(4)
C(3)–C(6)	1.533(3)	1.528(3)	1.536(3)
C(3′)–C(6′)	1.528(3)	1.523(3)	1.532(3)
C(3)–O	1.448(2)	1.437(2)	1.439(2)
C(3′)–O′	1.447(2)	1.447(2)	1.442(2)
O–HO	0.91(2) 0.89(2)	0.81(3)	0.87(3)
O′–HO′	0.91(2) 0.89(2)	1.06(3)	0.86(3)
OW–H(1)OW		0.84(4)	
OW–H(2)OW		0.85(3)	

[a] The successive entries for structure **1W** refer to the independent molecules A and B, respectively.

Table 3 Interbond angles (°) for structures **1B** and **1W**[a]

Angle	**1B**	**1W**(A)	**1W**(B)
C(2)–C(1)–C(2′)	108.8(2)	108.9(2)	108.8(2)
C(1)–C(2)–C(3)	110.7(2)	109.6(2)	110.4(2)
C(1)–C(2′)–C(3′)	110.4(2)	109.7(2)	110.7(2)
C(1)–C(2)–C(5′)	107.4(2)	107.5(2)	108.3(2)
C(1)–C(2′)–C(5)	107.8(2)	109.3(2)	107.9(2)
C(3)–C(2)–C(5′)	115.3(2)	115.4(2)	115.0(2)
C(3′)–C(2′)–C(5)	114.7(2)	114.7(2)	115.1(2)
C(2)–C(3)-·C(4)	112.2(2)	112.3(2)	112.0(2)
C(2′)–C(3′)–C(4′)	112.0(2)	112.1(2)	111.9(2)
C(2)–C(3)–O	107.9(1)	106.9(2)	106.7(2)
C(2′)–C(3′)–O′	108.2(1)	108.7(2)	109.7(2)
C(4)–C(3)–O	108.6(2)	111.0(2)	110.4(2)
C(4′)–C(3′)–O′	108.6(2)	107.4(2)	107.7(2)
C(3)–C(4)–C(5)	111.8(2)	112.0(2)	111.9(2)
C(3′)–C(4′)–C(5′)	111.6(1)	111.3(2)	111.5(2)
C(4)–C(5)–C(2′)	115.0(2)	114.3(2)	114.6(2)
C(4′)–C(5′)–C(2)	115.0(1)	115.3(2)	114.8(2)
C(3)–C(4)–C(7)	115.6(2)	115.6(2)	114.8(2)
C(3′)–C(4′)–C(7′)	115.7(2)	115.7(2)	114.8(2)
C(5)–C(4)–C(7)	111.0(2)	111.8(2)	111.7(2)
C(5′)–C(4′)–C(7′)	111.7(2)	111.4(2)	111.8(2)
C(4)–C(7)–C(7′)	119.7(2)	119.3(2)	119.5(2)
C(4′)–C(7′)–C(7)	119.2(2)	119.6(2)	120.4(2)
C(4)–C(3)–C(6)	110.1(2)	109.4(2)	109.6(2)
C(4′)–C(3′)–C(6′)	110.1(2)	110.0(2)	110.7(2)
C(2)·-C(3)–C(6)	110.8(2)	110.3(2)	111.0(2)
C(2′)–C(3′)–C(6′)	110.8(2)	111.5(2)	109.9(2)
C(6)–C(3)–O	107.1(2)	106.7(2)	107.0(2)
C(6′)–C(3′)–O′	107.0(2)	107.0(2)	106.8(2)
C(3)–O–HO	123 132	106(3)	105(2)
C(3′)–O′–HO′	109 112	106(2)	105(2)
H1OW–OW–H2OW		110(3)	

[a] The successive entries for structure **1W** refer to the independent molecules A and B, respectively.

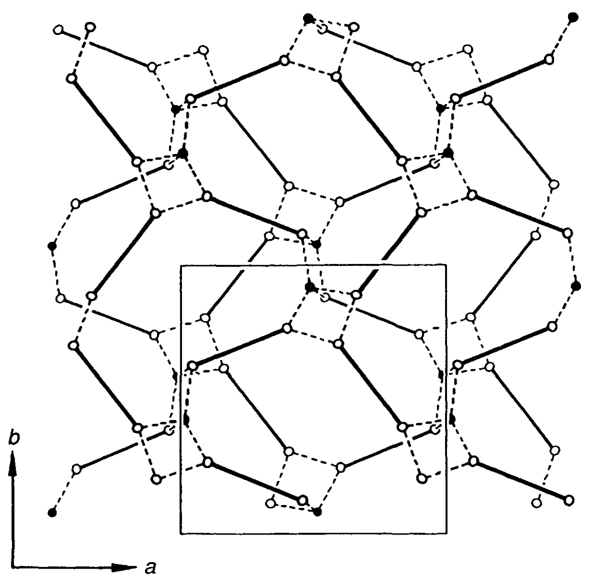
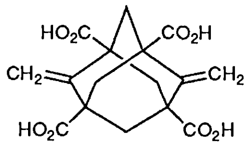


Fig. 12 A single layer of **1W** viewed down *c* with the diol molecules represented as solid tie-lines. Diol oxygen atoms are represented by open circles and water oxygens by filled circles. Hydrogen bonds are shown as dashed lines.

work carried out by Robson and by Ermer. In many of the known cases such as $Zn(CN)_2$, $Cd(CN)_2$ and their relatives,[8] and also the tetrahedrally-substituted tetracarboxylic acid derivatives,[9] interpenetrating but translationally equivalent diamondoid lattices are present.

In some of these structures a relatively open structure remains despite the interpenetration of two or more sublattices and in these cases inclusion compounds can result. The best known of these is the β-hydroquinone inclusion lattice where Powell[10] showed that interpenetration of two simple cubic lattices produces void spaces sufficiently large to trap small guests. Other more recent examples include the 2,6-disubstituted adamantane-1,3,5,7-tetracarboxylic acids.[11,12]

The structure **1B** differs from most of these in that the two sublattices are related by a centre of symmetry rather than by translation. Ermer and Lindenberg have recently reported formation of inclusion compounds between 2,6-dimethylideneadamantane-1,3,5,7-tetracarboxylic acid **2** and a range of guest molecules.[12] Two of these, (**2**)·$(mesitylene)_2$ and (**2**)·$(mesityl\ oxide)_{0.4}$·$(mesitylene)_{1.6}$, also form in space group $I4_1/acd$ and these authors have pointed out the similarity of such structures to **1B**.



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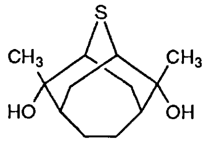

3

Our chief interest in molecules such as the diol **1** is with regard to aspects of crystal engineering.[13] To what extent can new multimolecular lattice inclusion compounds be designed, modified, and applied? Our work has led to the synthesis of a family of helical tubuland diols which exhibit a wide variety of canal dimensions and topologies,[4] and with varying resultant inclusion properties.[14] In the present context, two questions arise. First, why is diol **1** unique amongst this group of compounds in also forming the ellipsoidal clathrate structure? Secondly, what influences diol **1** to adopt each of its four known crystal structures in varying circumstances?

Despite careful screening of many helical tubulate inclusion compounds formed by other diols we have not encountered the ellipsoidal clathrate structure in compounds other than **1** until

Table 4 Hydrogen bonding dimensions (Å and °) for structures **1B**[a] and **1W**

Structure **1B**			
O···O[b]	2.974(3)	C(3)–O···O[b]	122.9(1)
O···O′[c]	3.044(2)	C(3)–O···O′[c]	131.5(1)
		C(3′)–O′···O[e]	111.5(1)
O′···O′[d]	2.896(3)	C(3′)–O′···O′[d]	109.3(1)
O[b]···O···O′[c]	88.80(4)		
O[e]···O′···O′[d]	90.25(4)		
Structure **1W**			
OA···O′A[f]	2.850(2)	C(3)A–OA···O′A[f]	151.7(1)
OA···HO′A[f]	1.81(3)	OA···O′A[f]–C(3′)A[f]	115.4(1)
		OA···HO′A[f]–O′A[f]	165(3)
OA···O′B[g]	2.894(2)	C(3)A–OA···O′B[g]	119.9(1)
HOA···O′B[g]	2.12(3)	OA···O′B[g]–C(3′)B[g]	135.0(1)
		OA–HOA···O′B[g]	160(3)
O′A···OW[h]	2.799(2)	C3′A–O′A···OW[h]	110.4(1)
O′A···H(2)OW[h]	1.96(3)	O′A···H(2)OW[h]–OW[h]	171(3)
OB···OW	2.802(2)	C(3)B–OB···OW	159.5(1)
OB···H(1)OW	1.99(4)	OB···H(1)OW–OW	163(3)
OB···OW[h]	2.851(2)	C(3)B–OB···OW[h]	114.7(1)
HOB···OW	2.00(3)	OB–HOB···OW[h]	166(3)
O′B···OW[i]	2.825(2)	C(3′)B–O′B···OW[i]	127.1(1)
HO′B···OW[i]	2.06(3)	O′B–HO′B···OW[i]	147(3)
OB···OW···O′A[h]	109.6(1)		
OB···OW···O′B[f]	138.2(1)		
OB···OW···OB[h]	95.3(1)		
O′A[h]···OW···O′B[f]	89.8(1)		
O′A[h]···OW···OB[h]	104.7(1)		
O′B[f]···OW···OB[h]	115.6(1)		

[a] Hydrogen atoms have been excluded from these dimensions because they are disordered. [b] $x, -y, 0.5 - z$. [c] $0.75 - y, -0.25 + x, 0.25 - z$. [d] $0.5 - x, y, -z$. [e] $0.25 + y, 0.75 - x, 0.25 - z$. [f] $1.5 - x, -0.5 + y, z$. [g] $1 - x, -y, -z$. [h] $2 - x, -y, -z$. [i] $1.5 - x, 0.5 + y, z$.

very recently. We now know that diol **3**, a sulfur analogue of **1**, is isostructural with **1B** when crystallised from chloroform.[15] However, why the other diols behave differently is currently far from clear.

A recent estimate has suggested that about 3% of organic compounds exhibit crystal polymorphism.[13] This phenomenon is, to say the least, an unwelcome complication in the already difficult business of designing new lattice inclusion compounds through crystal engineering principles. However, at least to some extent, the behaviour of the diol **1** can be rationalised and understood.

The solvent-free structure **1** may be obtained by sublimation or by recrystallisation from mesitylene (which is too large to be included). Diol molecules in this structure are poorly arranged. There are three independent molecules in the asymmetric unit and two of these exhibit incomplete hydrogen bonding.[1]

When organic solvent is included in either the benzene ellipsoidal clathrate **1B** or ethyl acetate helical tubulate **1E** inclusion lattices, all hydroxy groups obtain full hydrogen bonding arrangements (one donor and one acceptor per hydroxy group). This is also the case in the hemihydrate structure **1W**. The calculated densities[1,5] for these four structures are 1.19, 1.20, 1.19 and 1.20 g cm^{-3} respectively suggesting that increased packing density is unimportant in determining which is produced. However, structure **1** is disfavoured over the others by the hydrogen bonding consideration and will form only when there is no alternative.

Since the solvent-free structure is quite different to the ellipsoidal clathrate structure, it seems reasonable to propose that the presence of solvent guest molecules is obligatory in this lattice. The function, therefore, of the benzene in structure **1B** is to increase packing density and interactions between the two independent sublattices. Fig. 10 indicates how this is achieved. Without guest molecules this structure is energetically unfavourable.

Similarly the solvent-free helical tubuland lattice of **1** is also energetically disfavoured, though this may not be so for other diols.[1] The most important property here is the shape and size of the canals in **1B** and **1E** containing the guest molecules, in relation to the shape and size of the guest. In recent preliminary work we have shown that both ellipsoidal clathrate and helical tubulate inclusion compounds are commonplace for diol **1**, and each can be obtained with a wide range of guest molecules. In essence, small molecules favour the ellipsoidal clathrate structure and larger ones the helical tubulate arrangement.[16]

In a few cases, *both* crystal types may be obtained for the same guest.[17] The clear indication is that there is a critical limit to guest size in the ellipsoidal clathrate structure. Once the guest pushes the two independent lattices too far apart there is either too little host–guest interaction or the sublattices are pressed too close elsewhere in the structure. The alternative helical tubulate inclusion compound is then produced. In turn, there is another size limit here. If the potential guest is too large (*e.g.* mesitylene) it is excluded and the solvent-free structure is produced. Alternatively, if water is present then structure **1W** can form. Desiraju[18] has pointed out the remarkable frequency with which organic hydrates are formed despite water being used less frequently as a recrystallisation solvent. This is no doubt a result of its unparalleled hydrogen bonding properties and compact size.

Experimental

X-Ray powder diffraction patterns were recorded using a Philips PW1050 powder diffractometer. The patterns of the two substances **1B** and **1W** were different from each other, and also from the solvent-free structure **1**[1] and the ethyl acetate inclusion compound **1E**.[5]

(2,7-Dimethyltricyclo[4.3.1.1^{3,8}]*undecane*-syn-2,syn-7-*diol*)$_4$·(C_6H_6) **1B**.—This inclusion compound was prepared from solvent-free diol **1** and benzene as described earlier.[5] Slow concentration of a benzene solution afforded cubic blocks suitable for single crystal structure determination. The density of crystalline **1B** was found to be equal to that of nitrobenzene, 1.20 g cm^{-3} by flotation.

(2,7-Dimethyltricyclo[4.3.1.1^{3,8}]*undecane*-syn-2,syn-7-*diol*)$_2$·(H_2O) **1W**.—Slow concentration of a solution of solvent-free **1**[5] from reagent grade acetonitrile (which proved to be damp) gave a mixture of crystals as needles and rectangular blocks. The X-ray powder diffraction pattern of the needle crystals was similar in general form to that of **1B** (and is now known to be the ellipsoidal clathrate containing acetonitrile guest). Physical separation of the block crystals gave material suitable for single crystal X-ray work which proved to be the hemihydrate **1W**.

Crystal structure Solution and Refinement of **1B** *and* **1W**.—The data for both structures were recorded using an Enraf-Nonius CAD4 diffractometer. Numerical details of the crystals, diffraction data and analyses are given in Table 1. The data for both structures were corrected for absorption using a 12 × 12 × 12 Gaussian grid. Reflection weights used in refinement were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{\frac{1}{2}}$. The weighted residual was defined as $R_w = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$. Anomalous dispersion parameters (for C and O) and atomic scattering factors were from International Tables for X-ray Crystallography.[19]

For **1B**, the positions of all 15 non-hydrogen atoms of the diol molecule were found using direct methods (MULTAN80).[20]

Preliminary refinement included the diol molecule with methyl and hydroxy hydrogen atoms in positions determined from a difference map and all other hydrogen atoms in calculated positions.

Part of the hydrogen bonding network in this structure includes a hydrogen bond between two diol oxygen atoms which are related by twofold symmetry. The hydroxy hydrogen atoms must therefore be disordered. Two alternate positions for each hydroxy hydrogen atom were included in subsequent refinement, each with half occupancy.

There were two residual peaks on a difference map which were near the 222 site. These two peaks generated a complete benzene molecule by application of space group symmetry. Refinement was continued including these atoms, along with their respective hydrogen atoms in calculated positions.

A difference map computed at this stage indicated an alternate orientation for the benzene molecule, in which it was rotated in its plane by 30°. Refinement continued including both disorder components. The occupancies of the two components refined to 0.88 and 0.12, respectively. There was also some indication in the difference map of disorder of the methyl hydrogen atoms. This disorder was not incorporated into the final model, instead the methyl hydrogen atoms were included in calculated positions assuming a staggered conformation.

In the final refinement (using BLOCKLS[21]), all non-hydrogen atoms of the diol molecule and the carbon atoms of the major component of the benzene ring were assigned anisotropic thermal parameters. The thermal parameters of the carbon atoms of the minor component of the benzene ring were kept isotropic and equivalent to those of the atoms of the major component. Thermal parameters of all hydrogen atoms were fixed at the isotropic equivalent of those of the atom to which they were bound. The final residual was 0.035. The largest peak in the final difference map was 0.18 e Å^{-3}. If the occupancies of the two disorder components of the benzene molecule were changed to 1.0 and 0, *i.e.* the minor component was eliminated, then R (and R_w) increased to 0.036 (0.046).

The positions of all 31 non-hydrogen atoms of **1W** were determined using direct methods (MULTAN[20]). Standard anisotropic refinement[21] followed. The hydrogen atoms of the hydroxy groups and of the water molecule were included in the refinement in positions in which they were observed on a difference map. Their positions were refined. All other hydrogen atoms were included in calculated positions. All hydrogen atoms were given isotropic temperature factors equal to those of the atoms to which they were bound. Refinement converged with $R = 0.051$. In the final difference map, the largest residual peak was 0.2 e Å^{3}.

Lists of positional parameters, anisotropic thermal parameters for the non-H atoms, torsional angles, and structure factors for structures **1B** and **1W** have been deposited at the Cambridge Crystallographic Data Centre (CCDC). For details, see 'Instructions for Authors (1993),' *J. Chem. Soc., Perkin Trans. 2*, in the January issue.

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