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Prediction and Structure of Polymorphic Lattice Inclusion Compounds of 2,7-Dimethyltricyclo[4.3.1.$0^{3,8}$]undecane-*syn*-2,*syn*-7-diol

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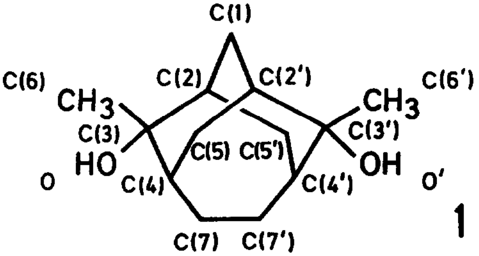
Abstract: The host molecule 2,7-dimethyltricyclo[4 3 1 $0^{3,8}$]undecane-*syn*-2,*syn*-7-diol **1** is known to form two different structural types of lattice inclusion compound dependent on the guest molecule chosen Guests, including 1,2-dichlorobenzene **2**, have now been predicted which result in the formation of both lattice types according to the crystallisation conditions employed. Crystal structures of the ellipsoidal clathrate type. (Racemic-1)$_4$.(1,2-Dichlorobenzene), space group $I4_1/acd$; and the helical tubulate type (Resolved-1)$_3$ (1,2-Dichlorobenzene), space group $P3_121$ are presented The latter polymorph is transformed into the former on heating in a sealed system

Alicyclic diol **1** is a versatile host molecule[1] forming lattice inclusion compounds[2] of two distinct types Mono- or di-substituted benzenes, and small guests, tend to favour a host structure composed of racemic **1** and containing ellipsoidal cavities (the ellipsoidal clathrate type, space group $I4_1/acd$) In contrast, elongated or aliphatic guests, and alkylbenzenes, generally result in a conglomerate[3], crystals of which have a host structure of enantiomerically pure **1** containing parallel helical canals (the helical tubulate type; space group $P3_121$ or enantiomorph)[4,5] Since it is not usually possible to predict crystal structures of pure substances[6-8], and the design of lattice inclusion compounds is in its infancy[9-12], the dual behaviour of this host is especially intriguing There are only van der Waals interactions between hosts and guests in both types of structure, and the nature of the guest is the factor controlling which is adopted



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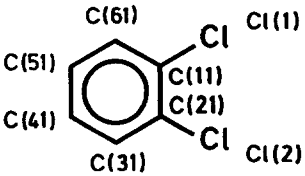

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Crystallographic numbering systems used for diol **1** and 1,2-dichlorobenzene **2**

Crystal polymorphism is a moderately frequent phenomenon, one recent estimate suggesting that about 3% of organic compounds exhibit this property[13] Its prevalence amongst lattice inclusion compounds is less clear. However Chatani has shown[14,15], for example, that urea clathrates of certain small organic guests (which exist at room temperature with the usual hexagonal space group $P6_122$) will undergo a reversible change on cooling to structures with the orthorhombic space group $P2_12_12_1$ These phase transitions are caused by the guest molecules taking up specific orientations in the host canals and occur over a narrow range of temperature. Urea-polyethylene inclusion compounds behave similarly[16,17]

It is axiomatic that the occurrence of polymorphic forms is an unwelcome complication in the already difficult area of design and synthesis of new organic solid materials Equally, in order to gain further insight into the potential of crystal engineering, it is one which cannot be ignored

In the present case, since the two lattice types must have almost identical free energies, we considered that in appropriate cases it might be possible for the same guest molecules to exist within *either* host lattice type as a stable combination Target guests were identified by considering groups of related guests whose lattice types were different, and by modelling experiments based on guest size and shape. As a result, the guest 1,2-dichlorobenzene appeared to be a likely candidate

Racemic 2,7-dimethyltricyclo[4 3.1 $0^{3,8}$]undecane-*syn*-2,*syn*-7-diol[18] **1** was crystallised from 1,2-dichlorobenzene using the Method A described in the Experimental Section Inclusion of guest molecules was confirmed by ^{1}H NMR and IR spectroscopy, and by elemental analysis which supported the composition (**1**)$_4$ (1,2-dichlorobenzene). The crystal lattice type of the inclusion compound was provisionally determined by comparing the X-ray powder diffraction pattern of the material (Figure 1) with the characteristic patterns of examples studied earlier[4] which indicated formation of the ellipsoidal clathrate lattice type.

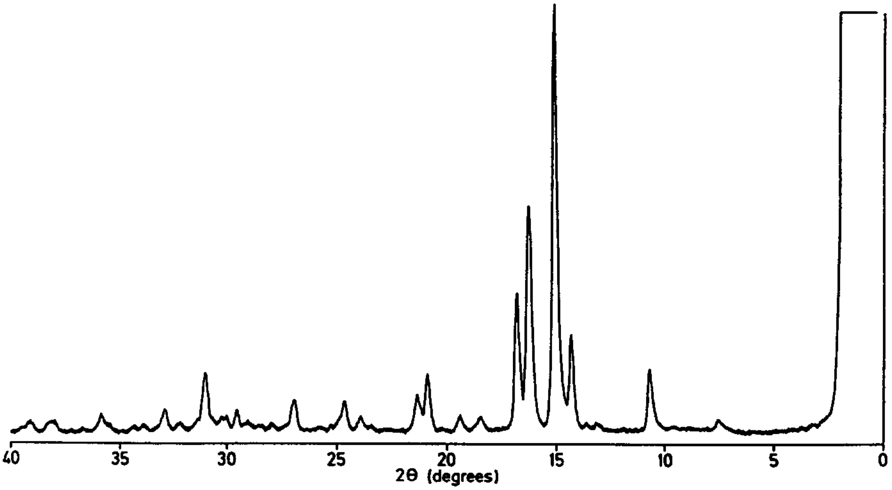

Figure 1. X-Ray powder diffraction pattern of the inclusion compound (**1**)$_4$.(1,2-dichlorobenzene) The peak pattern is characteristic of the ellipsoidal clathrate type

This structural assignment was confirmed by a full single crystal X-ray structure determination (see Experimental Section). Numerical details of the solution and refinement of this structure are shown in Table 1 Figure 2 shows the tetragonal arrangement of four diol molecules around one molecule of guest in the ellipsoidal cavity. Addition of a further turn of four diol molecules in Figure 3 shows how the guest is sealed within the clathrate structure. Atomic positional parameters for the structure are given in Table 2; bond lengths and angles are presented in Table 3 (see Experimental)

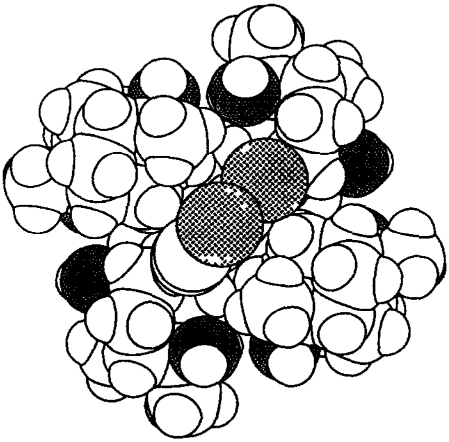

Figure 2. Part of one canal only of the inclusion compound (**1**)4 (1,2-dichlorobenzene) showing how four molecules of the host create an ellipsoidal cavity which is occupied by the guest The top surface has been left open to expose the 1,2-dichlorobenzene molecule to view Oxygen and chlorine atoms are shaded.

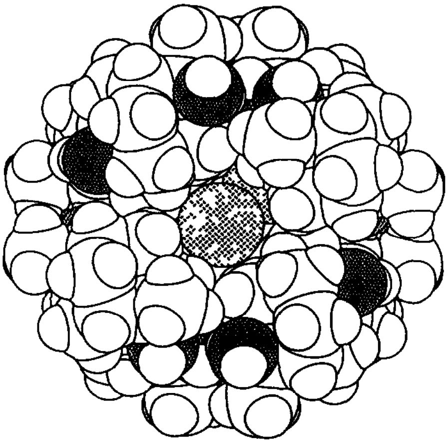

Figure 3. Addition of a further four molecules of **1** to Figure 2 showing the 1,2-dichlorobenzene guest trapped as a clathrate within a typical canal of the inclusion compound Only a small portion of the guest is now visible in the centre of the figure

Table 1. Numerical Details of the Solution and Refinement of the Crystal Structures.

Formula	$(C_{13}H_{22}O_2)_4 (C_6H_4Cl_2)$,	$(C_{13}H_{22}O_2)_3.(C_6H_4Cl_2)$
Formula mass	988.27	777.96
Crystal description	{001}{010}{100}	(00-1)(101)(-111){100}{1-10}{010}
Space group	$I4_1/acd$ (Origin at $\bar{1}$)	$P3_121$
a, b / Å	23.442(4)	13.3717(6)
c / Å	18.928(4)	6.9045(4)
V / Å^3	10401(3)	1069.14(8)
Temp. / °C	21(1)	21(1)
Z	8	1
$D_{calc.}$ / g cm^{-3}	1.26	1.21
Radiation, λ / Å	CuKα, 1.5418	CuKα, 1.5418
μ / cm^{-1}	15.5	19.75
Crystal dimensions / mm	0.09 x 0.09 x 0.51	0.17 x 0.15 x 0.35
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max.}$/ °	120	140
ω scan angle / °	0.50 + 0.15 tan θ	0.60 + 0.15 tan θ
No. of intensity measurements	4194	4048
Criterion for observed reflection	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No. of independent obsd. reflections	992	1260
No. of reflections (m) and variables (n) in final refinement	992, 160	1260, 93
$R = \Sigma^m\|\Delta F\|/\Sigma^m\|F_o\|$	0.065	0.047
$R_w = [\Sigma^m w\|\Delta F\|^2/\Sigma^m w\|F_o\|^2]^{1/2}$	0.081	0.062
$s = [\Sigma^m w\|\Delta F\|^2/(m-n)]^{1/2}$	3.18	3.66
Crystal decay	1 to 0.70	1 to 0.93
Max., min. transmission coefficients	0.88, 0.78	0.78, 0.60
Largest peak in final diff. map / eÅ^{-3}	0.71	0.35
R for reflections (no.) measd. twice	0.019 (1654)	
R for multiple measurements (no.)		0.013 (3665)

In the second experiment, racemic diol **1** was crystallised from 1,2-dichlorobenzene using the different conditions (Method B) described in the Experimental Section. Guest inclusion was confirmed as described previously by ^{1}H NMR and IR spectroscopy. Combustion analysis indicated the composition $(\mathbf{1})_3$ (1,2-dichlorobenzene). The powder diffraction pattern of this sample belonged to the helical tubulate type (see Figure 4), and this was verified by single crystal X-ray structural determination. A projection view of the guest molecule in one canal only of the inclusion compound is shown in Figure 5.

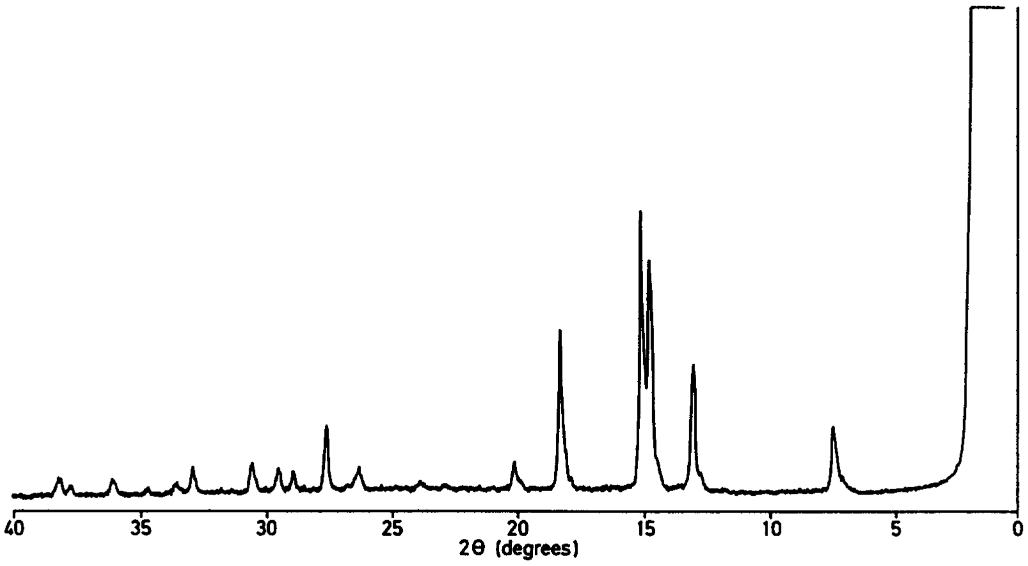

Figure 4. X-Ray powder diffraction pattern of the inclusion compound $(1)_3$ (1,2-dichlorobenzene) The peak pattern is typical of helical tubulate inclusion compounds (Mixtures of the two substances result in powder patterns comprising superposition of the peaks in Figures 1 and 4)

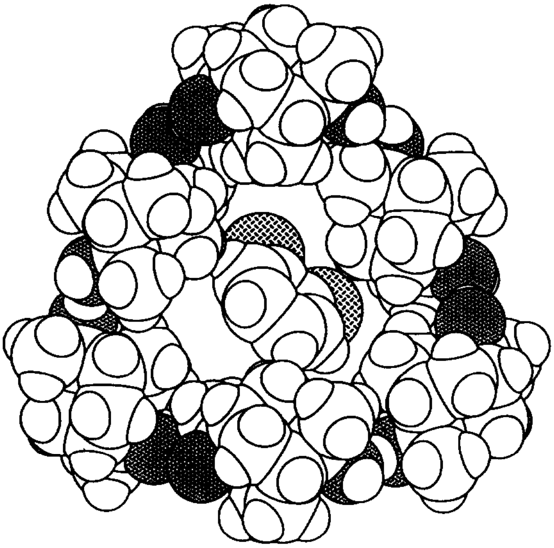

Figure 5. A slice across one canal only of the trigonal inclusion compound showing the trefoil-shaped unobstructed cross-sectional area of the host diol **1** lattice with the 1,2-dichlorobenzene guest located centrally in the canal.

Numerical details of the solution and refinement of this structure are shown in Table 1 Fractional coordinates are listed in Table 4; bond lengths and angles are given in Table 5 (see Experimental)

The ^1H NMR spectra of the two inclusion compounds were very similar, each comprising an addition of the spectra of **1** and **2** though in differing ratios Both IR spectra showed the presence of the guest by means of the strong absorption at 755 cm^{-1}. More importantly, however, these spectra reveal a number of detailed differences which can be used to identify which polymorph is present (Figure 6)

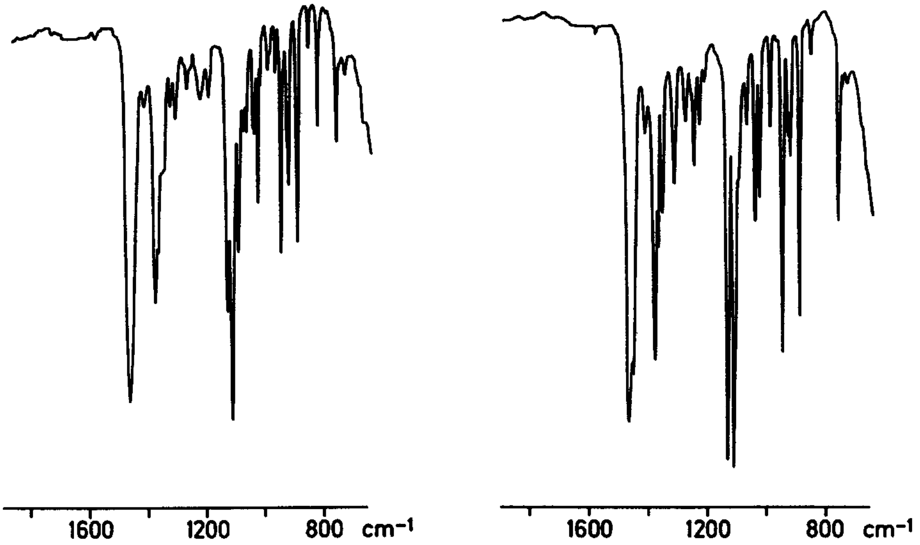

Figure 6. IR spectra (paraffin mull) of the two inclusion compounds in the fingerprint region. Left: the ellipsoidal clathrate type $(\mathbf{1})_4(\mathbf{2})$, and right. the helical tubulate type $(\mathbf{1})_3(\mathbf{2})$ Differences in detail are present in a number of locations

The present results are significant because both structures are stable at room temperature and their existence could be predicted To investigate this phenomenon further, samples of each crystal form were sealed in separate capillary tubes and heated at 60-65°C for 20 hours The newly-measured powder diffraction patterns showed that the ellipsoidal clathrate sample remained unchanged, but that the helical tubulate material had been almost completely transformed into the alternative polymorph These experiments indicate that the ellipsoidal clathrate structure is of lower energy and the one preferred when allowed by constraints of guest size and shape

Further predictions of appropriate guests indicated that chloroform and bromobenzene probably would be suitable. Once again, diol **1** produces both types of polymorphic inclusion compound with either of these substances and the ellipsoidal clathrate type was favoured during slow or higher temperature crystallisations[19]

We conclude that, although the phenomenon of polymorphism is a complicating factor in the deliberate design, synthesis, and application of organic solid materials[13], it may be predictable and even controllable in at least some systems

EXPERIMENTAL

^{1}H NMR spectra were recorded in $CDCl_3$ using a Bruker AC300F and IR spectra using a Hitachi 260-10 instrument. X-Ray powder diffraction analysis was made using a Siemens D500 X-ray diffractometer ; scan mode θ, 2θ, scan rate 2° min^{-1}, scan range 2θ = 2° to 40°. Combustion analyses were carried out at U.N.S.W. by Dr. H.P. Pham.

*(2,7-Dimethyltricyclo[4.3.1.$0^{3,8}$]undecane-*syn-2,syn*-7-diol)$_4$ (1,2-Dichlorobenzene)*

Method A. Racemic diol **1**[18] (*ca.* 40 mg) was dissolved in 1,2-dichlorobenzene (*ca.* 2 ml) at about 100°C in a sample tube. The tube was capped and allowed to cool slowly to room temperature. After 3 days, the crystals produced were collected by suction filtration and air dried, m.p. 116-118°C [Found: C, 70.90, H, 9.12. $(C_{13}H_{22}O_2)_4$ $(C_6H_4Cl_2)$ requires C, 70.49, H, 9.38%]

*(2,7-Dimethyltricyclo[4.3.1.$0^{3,8}$]undecane-*syn-2,syn*-7-diol)$_3$ (1,2-Dichlorobenzene)*

Method B. Racemic diol **1** (*ca.* 40 mg) was slowly dissolved under warming in 1,2-dichlorobenzene (*ca.* 2 ml) in a sample tube. The capped tube was allowed to cool rapidly in a refrigerator (0°C). After storage for about 2 hours, the crystals were filtered off and air dried, m.p. 119-120°C [Found: C, 69.80; H, 9.00. $(C_{13}H_{22}O_2)_3$ $(C_6H_4Cl_2)$ requires C, 69.48, H, 9.07%]

Data were recorded for both inclusion compounds using an Enraf Nonius CAD4 X-ray diffractometer. Numerical details pertaining to the collection of data, data processing, and solution of the structures are given in Table 1. Procedures adopted for data collection and processing have been described[20]

Solution and Refinement of the Structure $(C_{13}H_{22}O_2)_4$ $(C_6H_4Cl_2)$

The positional parameters for the diol in the inclusion compound $(\mathbf{1})_4$ (C_6H_6) were used as input for the initial Fourier calculations[5,21]. The 1,2-dichlorobenzene guest was located by careful consideration of the peaks in this and subsequent difference Fourier maps. Unlike the included benzene[5], the guest could not conform to the 222 symmetry of its site. A single representation of the disordered molecule was included and refined as a rigid group[22] with occupancy 1/4 of that of the diol molecule, and C-Cl distances set at 1.70Å. The position and orientation of the guest were allowed to vary. Its thermal motion was described as a 12 parameter TL group (where T is the translation tensor and L the libration tensor). The atoms of the host diol were refined in the normal way with anisotropic thermal parameters. Refinement converged with R = 0.065 (with that for data with $\sin\theta/\lambda<0.1$ equal to 0.049). The hydroxyl hydrogen atoms were included in their map positions and their positions were refined. All other H atoms were included in calculated positions and were not refined. All hydrogen atoms were assigned temperature factors equal to those of the atoms to which they were bound. The largest peak in the final difference map was 0.71 eÅ^{-3} in the vicinity of one of the Cl atoms of the guest.

Table 2. Fractional Coordinates for Non-CH Atoms of Structure $(1)_4$ $(C_6H_4Cl_2)$

	x	*y*	*z*		*x*	*y*	*z*
O	0 4632(2)	0.0350(3)	0.1828(3)	C(6')	0 3586(3)	0.1665(3)	-0.0360(3)
O'	0.2911(2)	0.1516(2)	0.0562(2)	C(7')	0 3718(3)	0.1431(3)	0.1644(3)
C(1)	0.4054(3)	0.0486(2)	-0.0016(3)	HO	0 4816(40)	0.0227(42)	0.1954(48)
C(2)	0.4452(2)	0.0564(3)	0.0610(3)	HO'	0 2857(30)	0.1877(28)	0.0622(39)
C(3)	0 4264(2)	0.0205(3)	0.1240(3)	Cl(1)	0 5070(9)	0 2453(8)	0.0181(3)
C(4)	0.3645(3)	0.0329(3)	0.1460(3)	Cl(2)	0.4351(5)	0 3182(2)	-0.0790(6)
C(5)	0 3244(3)	0.0337(3)	0.0807(4)	C(11)	0.5127(7)	0.2369(6)	-0.0708(3)
C(6)	0.4351(3)	-0.0434(3)	0.1089(3)	C(21)	0.4796(6)	0.2703(4)	-0.1161(3)
C(7)	0.3553(3)	0.0852(3)	0.1917(3)	C(31)	0 4843(9)	0.2634(8)	-0.1892(3)
C(2')	0 3453(3)	0 0706(3)	0.0183(3)	C(41)	0 5220(12)	0.2231(11)	-0 2169(4)
C(3')	0 3469(2)	0 1339(2)	0.0322(3)	C(51)	0 5550(11)	0 1897(11)	-0.1716(6)
C(4')	0 3913(2)	0 1501(2)	0.0885(3)	C(61)	0 5503(9)	0 1966(9)	-0 0985(5)
C(5')	0.4487(2)	0.1203(3)	0.0750(3)				

Table 3. Bond Lengths (Å) and Angles (°) for 1 in Structure $(1)_4$ $(C_6H_4Cl_2)$

O-C(3)	1.448(8)	C(4)-C(7)	1 517(8)	C(3')-C(4')	1 538(8)
C(1)-C(2)	1.519(7)	C(2)-C(5')	1 524(8)	C(4')-C(5')	1 537(7)
C(2)-C(3)	1 526(8)	C(7)-C(7')	1 501(8)	C(3')-C(6')	1 524(8)
C(3)-C(4)	1 536(8)	O'-C(3')	1 444(6)	C(4')-C(7')	1 516(8)
C(4)-C(5)	1 554(8)	C(1)-C(2')	1 547(8)	C(2')-C(5)	1.545(8)
C(3)-C(6)	1 539(8)	C(2')-C(3')	1 506(8)		

C(2)-C(1)-C(2')	109.2(5)	C(3)-C(4)-C(5)	111 0(5)	O'-C(3')-C(6')	106 6(5)
C(1)-C(2)-C(3)	111 4(5)	C(3)-C(4)-C(7)	116 3(5)	C(2')-C(3')-C(4')	112 3(5)
C(1)-C(2)-C(5')	106 7(5)	C(5)-C(4)-C(7)	110 9(5)	C(2')-C(3')-C(6')	110 5(5)
C(3)-C(2)-C(5')	114 9(5)	C(4)-C(5)-C(2')	115 0(5)	C(4')-C(3')-C(6')	109.9(5)
O-C(3)-C(2)	107.4(5)	C(4)-C(7)-C(7')	119 8(5)	C(3')-C(4')-C(5')	111.5(5)
O-C(3)-C(4)	108 1(5)	C(1)-C(2')-C(3')	110 5(5)	C(3')-C(4')-C(7')	115.2(5)
O-C(3)-C(6)	107.0(5)	C(1)-C(2')-C(5)	106 7(5)	C(5')-C(4')-C(7')	111.9(5)
C(2)-C(3)-C(4)	112 4(5)	C(5)-C(2')-C(3')	115 2(5)	C(2)-C(5')-C(4')	115.3(4)
C(2)-C(3)-C(6)	110 7(5)	O'-C(3')-C(2')	108 5(5)	C(7)-C(7')-C(4')	120.1(5)
C(4)-C(3)-C(6)	111 1(5)	O'-C(3')-C(4')	108 9(5)		

Solution and Refinement of the Structure $(C_{13}H_{22}O_2)_3$ $(C_6H_4Cl_2)$

The published positional parameters for the diol in the inclusion compound $(1)_3$ (ethyl acetate) were used as input for the initial Fourier calculations[18] The largest peak in a difference map was taken to be one Cl atom A subsequent Fourier map revealed a second peak at a suitable distance from the first (*ca* 3 0Å) Study of subsequent Fourier maps gave an approximate position for the benzene ring of the guest. The 1,2-dichlorobenzene was refined as a rigid group[22], with the C-Cl distances set at 1.70Å. The position and orientation of the guest were allowed to vary. Its thermal motion was described as a 15 parameter TLX group (where T is the translation tensor, L is the libration tensor, and X the origin of libration). The atoms of the host diol were refined anisotropically in the usual way Refinement converged with $R = 0.047$ (with that for data with $\sin\theta/\lambda<0\ 1$ equal to 0.079). The hydroxyl hydrogen atom was included in its map position and its position was refined. All other H atoms were assigned temperature factors equal to those of the atoms to which they were bound Refinement of the other enantiomer gave an indistinguishable *R* factor *R* for the host structure alone was 0.082 (with that for the 6 reflections with $\sin\theta/\lambda<0\ 1$ which are most sensitive to omitted electron density, equal to 0.37) The guest must be disordered and its occupancy depends on the length of canal which it occupies. The guest occupancy refined to a value close to 1/6, representing one guest molecule per unit cell volume. It was therefore fixed at 1/6 for the final refinement The largest peak in the difference map was 0 35 eÅ^{-3} in the vicinity of the Cl atoms of the guest

Table 4. Fractional Coordinates for Non-CH Atoms of Structure $(\mathbf{1})_3$ ($C_6H_4Cl_2$)

	x	*y*	*z*		*x*	*y*	*z*
O	-0 2395(1)	0 3946(1)	0 1321(2)	Cl(1)	-0 1151(16)	-0 1433(9)	-0.1915(40)
C(1)	-0.0005(1)	0 7017(3)	0 1667(0)	Cl(2)	0 1323(17)	0 0470(27)	-0.1378(64)
C(2)	-0 1005(1)	0 5847(2)	0 2301(3)	C(11)	-0 0740(16)	-0 0704(9)	0 0220(43)
C(3)	-0 1467(1)	0 5021(2)	0 0576(2)	C(21)	0 0401(19)	0 0176(16)	0 0484(54)
C(4)	-0 0513(2)	0 4850(2)	-0 0355(3)	C(31)	0 0738(27)	0 0774(18)	0.2238(58)
C(5)	0 0601(2)	0 6021(2)	-0 0686(3)	C(41)	-0 0065(33)	0 0492(16)	0.3729(49)
C(6)	-0 2007(2)	0 5455(2)	-0 0929(3)	C(51)	-0 1205(29)	-0 0388(18)	0.3465(39)
C(7)	-0 0274(2)	0.3984(2)	0 0667(3)	C(61)	-0 1543(20)	-0 0986(15)	0 1711(38)
HO	-0 2772(25)	0 3498(27)	0 0428(48)				

Table 5. Bond Lengths (Å) and Angles (°) for **1** in Structure $(\mathbf{1})_3$ ($C_6H_4Cl_2$)

O-C(3)	1 444(2)	C(3)-C(4)	1 545(2)	C(4)-C(7)	1 519(3)
C(1)-C(2)	1 529(3)	C(4)-C(5)	1 547(3)	C(7)-C(7')	1.519(4)
C(2)-C(3)	1 529(2)	C(3)-C(6)	1 535(3)	O-HO	0 83(3)

C(2)-C(1)-C(2')	108 4(2)	O-C(3)-C(6)	106 6(1)	C(3)-C(4)-C(7)	115.0(2)
C(1)-C(2)-C(3)	110 3(1)	C(2)-C(3)-C(4)	111 4(1)	C(5)-C(4)-C(7)	112.2(2)
C(1)-C(2)-C(5')	108 3(1)	C(2)-C(3)-C(6)	110 5(2)	C(4)-C(5)-C(2')	115 7(1)
O-C(3)-C(2)	106 1(1)	C(4)-C(3)-C(6)	110 7(2)	C(4)-C(7)-C(7')	119 9(1)
O-C(3)-C(4)	111 3(2)	C(3)-C(4)-C(5)	111 1(2)	C(3)-O-HO	111(2)

Equivalent Position Indicators ' -x, y-x, 1/3-z

Supplementary material available Thermal parameters, fractional coordinates for the CH atoms, and structure factors for both structures. See Notice to Authors, *Tetrahedron*, **1984**, *40(2)*, ii.

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