Syntheses and Crystal Structures of Seven Alicyclic Diols which Crystallise with Layer Structures Instead of the Helical Tubuland Inclusion Lattice

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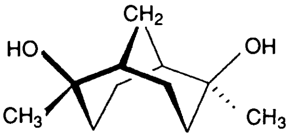
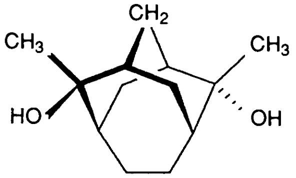
In an exploration of the possibility of modifying the shape and size of the helical canal host structure known to occur in crystals of several bi- and tri-cyclic diols, we report the syntheses and crystal structures of seven further diols: *endo*-2,*endo*-6-dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane (**5**); *endo*-2,*endo*-6-dihydroxy-2,6-dimethyl-9-thiabicyclo[3.3.1]nonane (**6**); 2,6-dihydroxy-2,6-dimethyltricyclo[3.3.1.1^{3,7}]decane (**7**); *anti*-4,*anti*-8-dihydroxy-4,8-dimethyl-2-thiatricyclo[3.3.1.1^{3,7}]-decane (**8**); *syn*-2,*syn*-7-dihydroxy-2,7-diethyltricyclo[4.3.1.1^{3,8}]undecane (**9**); *anti*-2,*anti*-7-dihydroxy-2,7-diethyltricyclo[4.3.1.1^{3,8}]undecane (**10**); and *syn*-2,*anti*-8-dihydroxy-2,8-dimethyltricyclo[5.3.1.1^{3,9}]dodecane (**11**). All seven of these adopt similar layered crystal structures. The properties characteristic of these structures are: two-dimensional hydrogen bonding of diol molecules within the layers, maximised hydrogen bonding for each diol, an absence of inter-layer hydrogen bonding, and the occurrence of cycles of four hydrogen bonds connecting four diol molecules within the layers. The closed cycles of hydrogen bonds are in contrast with the extended helical spines characteristic of the helical canal host lattice. The layered diol structures do not include guests and do not involve spontaneous resolution of the diol molecules.

We have previously reported that diols (**1**)–(**4**) crystallise with a helical tubuland[1] lattice, based on helical spines of inter-diol hydrogen bonds. This lattice is a multimolecular inclusion host system, able to trap guest molecules.[2,3] The helical tubuland structure present in the crystalline state of these diols is extremely unusual amongst multimolecular inclusion systems in that the essential crystallographic features are maintained while the diol building-block (**1**)–(**4**) is altered. This leads to the existence of radically different void spaces and unobstructed cross-sectional areas for the resulting tubular canals in the crystals. We have recently published a detailed structural analysis of the helical tubuland structures formed by these four diols.[4]



(**1**)



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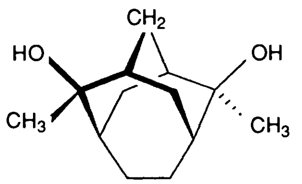

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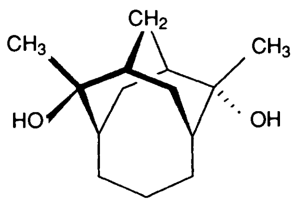
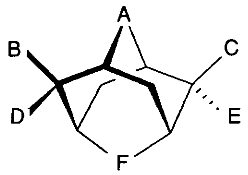


(**4**)

The occurrence of a general helical tubuland lattice-type suggests possibilities for the design and synthesis of further host diols which could also adopt this host lattice type.[5] As part of our investigation into this phenomenon we have examined many other related alicyclic diols with the general structure (**I**),

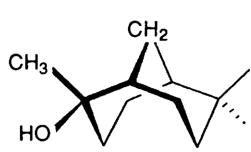


(I)

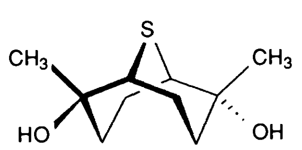
in which the variables **A**, **B**, **C**, **D**, **E**, **F**, are systematically modified. Our intention is to be able to define the structural features necessary for an alicyclic diol of this general type to form the helical tubuland lattice and therefore to place prediction of such behaviour on a more secure footing.[6]

In the course of this work we have discovered that alicyclic diols of the general type (**I**) can form crystal structures other than the helical tubuland lattice.[7] However these materials still retain a definite proclivity to crystallise in distinct structural categories. In almost all cases studied so far, lattices with either a helical or a layer structure are produced. We report here the structures of a set of seven diols (**5**)–(**11**) which crystallise with layer structures, but without inclusion capabilities. There is complete hydrogen bonding within but not between these layers. These compounds are as follows: *endo*-2,*endo*-6-dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane (**5**); *endo*-2,*endo*-6-dihydroxy-2,6-dimethyl-9-thiabicyclo[3.3.1]nonane (**6**); 2,6-dihydroxy-2,6-dimethyltricyclo[3.3.1.1^{3,7}]decane (**7**); *anti*-4,*anti*-8-dihydroxy-4,8-dimethyl-2-thiatricyclo[3.3.1.1^{3,7}]decane (**8**); *syn*-2,*syn*-7-dihydroxy-2,7-diethyltricyclo[4.3.1.1^{3,8}]undecane (**9**); *anti*-2,*anti*-7-dihydroxy-2,7-diethyltricyclo[4.3.1.1^{3,8}]undecane (**10**); and *syn*-2,*anti*-8-dihydroxy-2,8-dimethyltricyclo[5.3.1.1^{3,9}]dodecane (**11**).

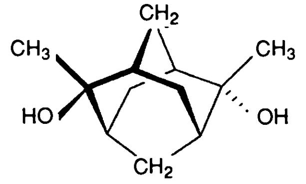
In accord with our previous papers in this area we designate substituent groups as *syn* or *anti* with respect to the unique, largest bridge [or the heteroatom bridge, in (**6**) and (**8**)] of the tricyclic system. Being a derivative of the symmetrical adamantane framework, diol (**7**) is the only stereoisomer possible in this



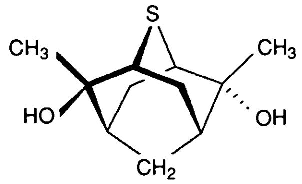
(5)



(6)



(7)



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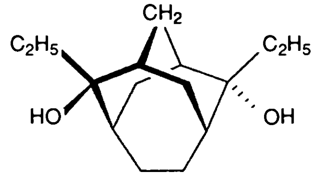

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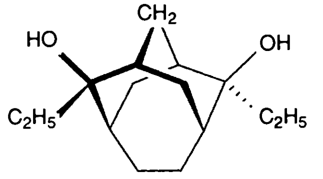
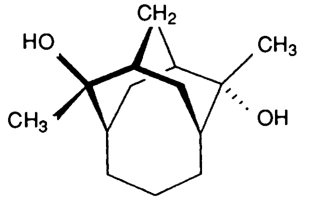


(10)



(11)

case. Diol (**5**) is the double epimer of (**1**), (**9**) is the diethyl homologue of (**2**), (**10**) is the diethyl homologue of (**3**) and (**11**) is the single epimer of (**4**).

Results

Syntheses.—The synthetic routes to the diols (**5**)–(**11**), and several other diols prepared but whose crystal structures were not determined, are outlined in the Scheme. All these diols, except for (**11**), (**13**), and (**18**), have C_2 symmetry and the principal synthetic strategy is based on the two faces of the precursor molecule on the twofold axis being dissimilar. The different steric demands of these two faces allow the appropriate diketone or dialkylidene precursor to be used in generating the required diol stereoisomer with high selectivity. Preparation of the three diols which lack C_2 symmetry, involves the same principles.

Although most of the reactions proved to be straightforward, a few specific comments should be made. The reaction of diones (**12**) and (**16**) with methylmagnesium iodide proved not to be highly selective. Although most reaction took place on the *exo*-face, there was sufficient reaction on the *endo*-face to result in significant amounts of the *exo,endo*-diols, (**13**) and (**18**) respectively, being produced. However, the required major isomers (**5**) and (**6**) were readily obtained by crystallisation.

The additional symmetry of tricyclo[3.3.1.1^{3,7}]decane-2,6-dione (**19**) compared with the other precursors means that reduction to (**20**), or alkylation to yield (**7**) and (**21**), can only result in one diol product and consequently each can be synthesised in one step from (**19**).

The Brown mercuric acetate method[8] used for Markownikoff hydration of the dienes (**17**) and (**23**) is known to suffer from severe steric limitations in some cases. Here, the diethylidene derivative (**25**) was found to be inert to this procedure. Consequently the *anti,anti*-bisepoxide (**26**) was prepared and reduced using lithium aluminium hydride to afford the required diol (**10**).

Finally, it should be noted that the mercuric acetate hydration of 2,6-dimethylene-9-thiabicyclo[3.3.1]nonane (**17**) produces the diol (**6**) whose stereochemistry is *opposite* to that obtained from the corresponding all-carbon analogue.[2] This is explicable in terms of neighbouring group participation by the sulphur atom requiring the hydration to occur from the *endo*-face of the molecule to regenerate the neutral sulphide grouping from an intermediate sulphonium ion. While such behaviour here is only inferred from the results, similar events are well-known in the chemistry of 2,6-disubstituted derivatives of this ring system.[9,10] The same phenomenon may be involved in the hydration of (**23**) to form diol (**8**). However, the stereochemistry observed in this case would be explicable on simple steric grounds alone.

Test of Inclusion Properties.—The diols (**5**)–(**11**) the crystal structures of which were determined, and also the diols (**13**), (**20**), (**21**), and (**27**) the crystal structures of which were not determined, were subjected to the same test of potential inclusion properties. Each diol was recrystallised from each of six standard solvents (benzene, acetonitrile, ethyl acetate, chloroform, acetone, and ether). The resulting crystals were filtered off, dried for 5 min in a stream of air, and their IR spectra (paraffin mull) recorded and compared with the original diol. In all cases no evidence was obtained indicating inclusion of solvent in the crystalline diol. Diol (**8**) was also tested with ethanol, ethane-1,2-diol, and 1-chloropentane. These solvents also were not included.

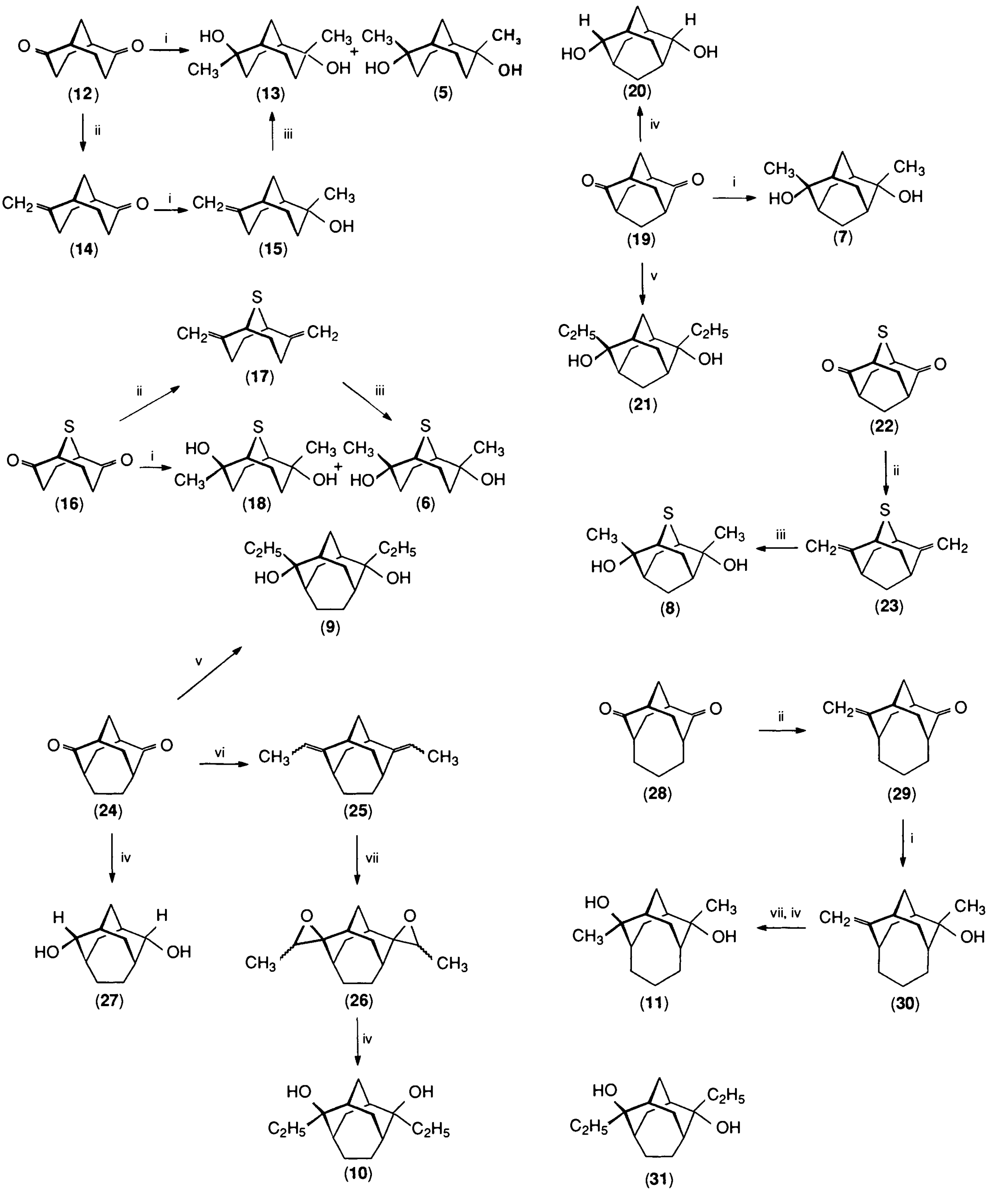
Description of the Structures

The crystal structure of (**10**) could not be fully determined, owing to problems of disorder, but the structures of the other six diols were determined fully without ambiguity. In the crystals of all six there are layers within which the diols are fully linked by intermolecular hydrogen bonds, and each diol molecule is involved in two donor and two acceptor hydrogen bonds. We describe and discuss the structures at three levels: (i) the molecular structures and dimensions; (ii) the network of hydrogen bonded diol molecules in each crystal; and (iii) the orientations of the hydrogen bonds to and from each diol.

Molecular Structures.—The atom labelling is defined in Figure 1. In the crystals of (**5**)–(**8**) and (**11**) there are two molecules in the crystallographic asymmetric unit, with atoms labels distinguished by the addenda A and B.

The bond lengths (Table 1) and angles (Table 2) within the molecules all lie within acceptable ranges, and show no irregularities. The overall sizes and shapes of the molecules are shown comparatively in Figure 2, and are clearly affected by the identity or absence of the linkage F. The contra-molecular dimensions, listed in Table 3, quantify these variations. The C(4)–C(4′) distance is unambiguously dependent on the size (or absence) of the connecting bridge F and is unaffected by substitution of S for CH_2 in the opposite bridge A. The C(4)–C(4′) distance data are summarised comparatively in Table 4.

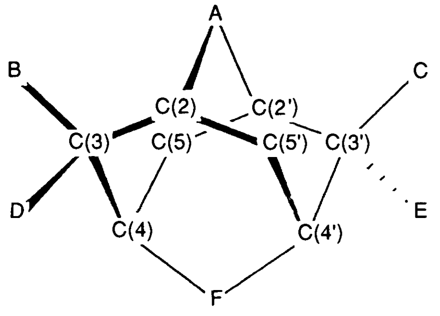
With reference to the data in Table 3, the C(6)–C(6′) distance is affected only very slightly by the differing ring sizes: for the new diols with layer structure it ranges from 5.85 Å in (**7**) to 6.04 Å in (**6**), while it is slightly smaller, 5.75 Å, in (**1**). The variation in the contra-molecular O–O′ distances between the OH groups is appreciable, ranging from 5.24, 5.29 Å in (**5**) to 5.70, 5.73 Å in (**11**), but there is no correlation between this molecular parameter and the crystal structure type. Significant comparisons of these O–O′ distances are: (i) the configurational isomers (**1**) and (**5**), with the latter shorter by 0.35 Å; (ii) the



Scheme. *Reagents:* i, CH_3MgI; ii, $Ph_3P{=}CH_2$; iii, 1. $Hg(OAc)_2/H_2O$, 2. $NaBH_4/NaOH$; iv, $LiAlH_4$; v, C_2H_5Li; vi, $Ph_3P{=}CH{-}CH_3$; vii, *m*-$ClC_6H_4CO_3H$.

configurational isomers (**2**) and (**3**) where there is no difference; (iii) the configurational isomers (**4**) and (**11**) where there is virtually no difference; and (iv) the substitutional isomers (**2**) and (**9**) with the ethyl substituents in (**9**) causing a shorter O–O′ distance.

The directions of the hydroxy groups relative to the molecular framework, as assessed by the C(3′)–C(3)–O angles, are effectively constant over all of the ten diols: apart from the slightly smaller values in (**5**) and (**6**), this parameter varies by only a few degrees. The O–C(3)–C(3′)–O′ torsional angles are differentiated by relatively small amounts in the six new diol molecules: the smaller values (73.5 and 78.8°) characteristic of (**1**) and (**3**), where the OH groups are *syn* to the CH_2 bridge, are reflected slightly in (**5**) and (**6**). The larger value for (**11**) is a



(II)

	(5)	(6)	(7)	(8)	(9)	(10)	(11)
A	C(1)	S	C(1)	S	C(1)	C(1)	C(1)
B	C(6)	C(6)	C(6)	C(6)	C(6)–C(7)	O	O
C	C(6′)	C(6′)	C(6′)	C(6′)	C(6′)–C(7′)	O′	C(6′)
D	O	O	O	O	O	C(6)–C(7)	C(6)
E	O′	O′	O′	O′	O′	C(6′)–C(7′)	O′
F	—	—	C(1′)	C(1′)	C(8)–C(8′)	C(8)–C(8′)	C(7)–C(8)–C(7′)

Figure 1. Atom labelling in (II).

consequence of its unique *syn,anti* configuration of the hydroxy groups.

Overall, there are no features of the molecular or contramolecular dimensions to which we can attribute the difference between the tubuland and layer crystal structure types.

Crystal Structures.—In all seven crystal structures the hydrogen bonding occurs in closed four-membered cycles, $(\text{–OH})_4$. This is entirely different to the extended hydrogen bonding in threefold helices characteristic of the tubuland structure. The dimensions of these cycles are presented in Table 5. In no case is the cycle planar, and in only two structures is there any crystallographic symmetry imposed on the cycle [a twofold axis in both (**9**) and (**10**)]. Deviations from the plane of best fit through the four O atoms range from 0.25 Å in (**6**) to 0.48 Å in (**9**) (see Table 5). The two diagonal O ··· O lengths are equal as in (**9**) and (**10**) or can differ by as much as 0.61 Å as in (**11**).

All of the structures are layered, with diol molecules connected by hydrogen bonds in two dimensions, and van der Waals contacts only in the third dimension. One description of the layered structures is made in terms of the two-dimensional linkages of these hydrogen bond cycles $(\text{–OH})_4$ by diol molecules. An alternative description of the crystal structures focuses on one-dimensional chains of diol molecules, with linkages of the chains occurring at the hydrogen-bond cycles. In all cases the diol molecules form a two-dimensional grid, with the hydrogen-bonding cycles occurring at the grid points where the chains are closest. The two dimensional network also contains larger cycles of four complete diol molecules, $(\text{HO–R–OH})_4$, which are connected at the hydrogen bond cycles $(\text{–OH})_4$. The individual structures differ in the symmetry elements which propagate the diol molecules within the layers, in the weaving of the chains in the layers, and in the crystallographic relationships between the layers, but occur in three groups namely: (i) (**5**) and (**6**); (ii) (**7**), (**8**), and (**11**); and (iii) (**9**).

The crystal structures of (**5**) (space group *Pc*) and (**6**) (space group $P2_1/c$) are closely related, with virtually identical layer structure perpendicular to the *c*-axis, as shown in Figure 3. In both the chains are propagated by cell translation along the *a* and *b* axes, by two independent diol molecules. The chains are woven such that those in the *a* direction lie entirely on one side of the chains in the *b* direction. The layers are relatively flat. In (**5**) there are two layers per 19.9 Å along the *c*-axis, related by the *c*-glide plane of space group, while in (**6**) there are four layers stacked along the 40.4 Å *c* axis of the space group with contiguous layers related alternately by centres of symmetry and twofold axes.

In (**9**) (space group *C*2/*c*) the layers are parallel to the *ab* plane, and the chains form opposing zig-zags across the *a* direction as shown in Figure 4, with the hydrogen bonding cycles occurring where the chains are proximal. There is no interweaving of chains, and thus some similarities with the layers in (**5**) and (**6**). There is one diol molecule per asymmetric unit, with twofold axes relating diols along the chains.

Structures (**7**) and (**8**) are isostructural and isomorphous in space group *Pbca*. The layer type, normal to the long *c* axis, is shown in Figure 5. There is now some weaving of the chains, with all chains along *a* alternating under and over the chains along *b*, but the latter do not weave. There are two molecules per asymmetric unit: molecules A form the chain along the *a* direction, translated by an *a* glide plane normal to the *c*-axis, and molecules B form the zig-zag chain along the *b* direction, by the glide plane normal to the *a*-axis. There are two layers per unit cell, related by the *a*-glide plane normal to the *c* axis. Centres of symmetry occur within the $(\text{HO–R–OH})_4$ cycles.

Figure 6 is a view normal to one layer in the crystal structure of (**11**), in space group $P2_1/c$. The *c*-glide plane propagates chains of molecules labelled A along the *c* direction in the layer, while the 2_1 axis propagates the chains of molecules labelled B in the *b* direction. There is one layer per unit cell, and thus contiguous layers are related by translation. Chains in the *c* direction lie alternately above and below the chains that progress in the *b* direction, in a pattern very similar to that in (**7**) and (**8**).

The layers have different profiles. The layers in (**5**), (**6**), and (**9**) are nearly flat, but those in (**7**), (**8**), and (**11**) which are propagated by glide and screw operations are undulating and thicker in profile. Figure 7 shows the undulations of one layer in (**11**), a consequence of the 2_1 screw axis along *b*.

Orientation of the Hydrogen Bonds Relative to the Diol Molecules.—In attempting to analyse the crystal structures of this series of diols, and to identify factors which cause structure types other than the helical tubuland to occur, the directions of the hydrogen bonds relative to the diol molecule are significant. In the helical tubuland structure type these directions are relatively invariant. In Figure 2 these directions are shown for

Table 1. Bond lengths Å for (**5**)–(**9**) and (**11**).[a]

	(**5**)	(**6**)	(**7**)	(**8**)	(**9**)	(**11**)
C(1)/S–C(2)	1.525(3) 1.532(3)	1.811(3) 1.820(4)	1.535(2) 1.539(2)	1.825(3) 1.823(3)	1.519(6)	1.537(6) 1.503(6)
C(1)/S–C(2′)	1.530(3) 1.532(3)	1.815(3) 1.823(3)	1.540(2) 1.534(2)	1.819(3) 1.820(3)	1.531(6)	1.498(7) 1.531(6)
C(2)–C(3)	1.548(3) 1.547(3)	1.532(5) 1.535(4)	1.536(2) 1.538(2)	1.533(4) 1.544(4)	1.552(7)	1.546(7) 1.520(7)
C(2′)–C(3′)	1.540(3) 1.537(3)	1.533(5) 1.536(5)	1.537(2) 1.538(2)	1.539(4) 1.539(4)	1.540(6)	1.527(7) 1.504(6)
C(3)–C(4)	1.530(3) 1.528(3)	1.521(4) 1.540(5)	1.541(2) 1.540(2)	1.540(3) 1.543(4)	1.537(6)	1.501(7) 1.563(7)
C(3′)–C(4′)	1.533(3) 1.540(3)	1.534(5) 1.531(5)	1.542(2) 1.540(2)	1.549(3) 1.538(4)	1.552(6)	1.542(7) 1.554(7)
C(4)–C(5)	1.531(3) 1.530(3)	1.523(5) 1.522(5)	1.531(2) 1.532(2)	1.554(3) 1.529(4)	1.560(6)	1.561(7) 1.564(7)
C(4′)–C(5′)	1.523(3) 1.525(3)	1.519(5) 1.547(5)	1.542(2) 1.539(2)	1.537(4) 1.542(4)	1.547(6)	1.578(7) 1.583(7)
C(5)–C(2′)	1.535(3) 1.531(3)	1.524(5) 1.520(5)	1.526(2) 1.529(2)	1.531(3) 1.535(4)	1.536(7)	1.515(7) 1.540(7)
C(5′)–C(2)	1.533(3) 1.539(3)	1.532(5) 1.519(5)	1.531(2) 1.532(2)	1.534(4) 1.527(4)	1.527(6)	1.529(7) 1.494(7)
C(3)–O	1.439(2) 1.438(3)	1.443(4) 1.428(4)	1.447(2) 1.442(2)	1.445(3) 1.445(3)	1.444(5)	1.464(6) 1.442(6)
C(3′)–O	1.442(3) 1.437(3)	1.437(4) 1.456(4)	1.451(2) 1.438(2)	1.447(3) 1.439(3)	1.459(5)	1.417(6) 1.441(6)
C(3)–C(6)	1.532(3) 1.535(3)	1.517(5) 1.529(5)	1.526(2) 1.526(2)	1.518(4) 1.523(4)	1.546(7)	1.522(7) 1.503(7)
C(3′)–C(6′)	1.532(3) 1.525(3)	1.517(5) 1.530(5)	1.523(2) 1.530(2)	1.514(4) 1.520(4)	1.521(7)	1.572(7) 1.547(7)
C(1′)/S–C(4)			1.529(2) 1.534(2)	1.525(4) 1.526(4)		
C(1′)/S–C(4′)			1.532(2) 1.527(2)	1.523(4) 1.526(4)		
C(4)–C(7)/C(8)					1.508(7)	1.578(8) 1.521(8)
C(4′)–C(7′)/C(8′)					1.513(7)	1.522(8) 1.535(9)
C(8)–C(8′)					1.518(7)	
C(6)–C(7)					1.459(8)	
C(6′)–C(7′)					1.529(7)	
C(7)–C(8)						1.534(9) 1.508(9)
C(7′)–C(8)						1.473(9) 1.499(9)
O–HO	0.85(3)	0.93(2) 0.84(2)	0.82(2)	0.84(1)	0.93(3) 1.01(3)	1.05(3)
	0.76(3)	0.90(2) 0.94(2)	0.82(2)	0.83(1)		0.86(3)
O′–HO′	0.72(4)	0.86(2) 0.95(3)	0.81(2)	0.77(1)	1.07(3) 0.87(3)	0.90(3)
	0.76(3)	0.98(2) 0.86(2)	0.81(2)	0.84(1)		0.80(3)

[a] The successive entries for structures (**5**)–(**8**) and (**11**) refer to the independent molecules A and B, respectively.

(**1**) as representative of the helical tubuland structure, and for the diols in the layer structure types reported here. The hydrogen bond directions are discussed in terms of the molecular cartesian axial system previously defined[7] in which *X* is C(4) ⟶ C(4′), *Y* is C(2) ⟶ C(2′), and *Z* passes through the A bridge atom, as defined in (**II**). In all of the diagrams in Figure 2 the *Y* axis is vertical. Note that the differentiation of *X* and *Y* is dependent on the differentiation of the bridges A and F, and is absent in (**7**).*

In (**1**) one hydrogen bond lies virtually within the *YZ* plane, and the other is directed from O at about 40° to the *XZ* plane, towards the *X* axis. The pattern of hydrogen-bond directions in (**5**) is similar [taking account of the interchange of *X* and *Y* axes which is equivalent to the epimerisation of (**5**) from (**1**)*], with one significant exception: one hydrogen bond involving both molecules (O′A ··· OB) in (**5**) is in a direction which is approximately *anti* rather than *gauche* relative to the CH_3 group about the C–O bond. The OA ··· O′B hydrogen bond in (**5**) is very similar to that in (**1**). Hydrogen-bond directions in (**6**) are very similar to those in (**5**). In (**7**) and (**8**) the directions of the hydrogen bonds at one OH (OA, O′B) of each independent molecule are very similar to those in (**1**), but at OA′ and OB there are new orientations. In (**9**) there is a standard pattern at O′, but the direction of the O ··· O hydrogen bond is unique. In

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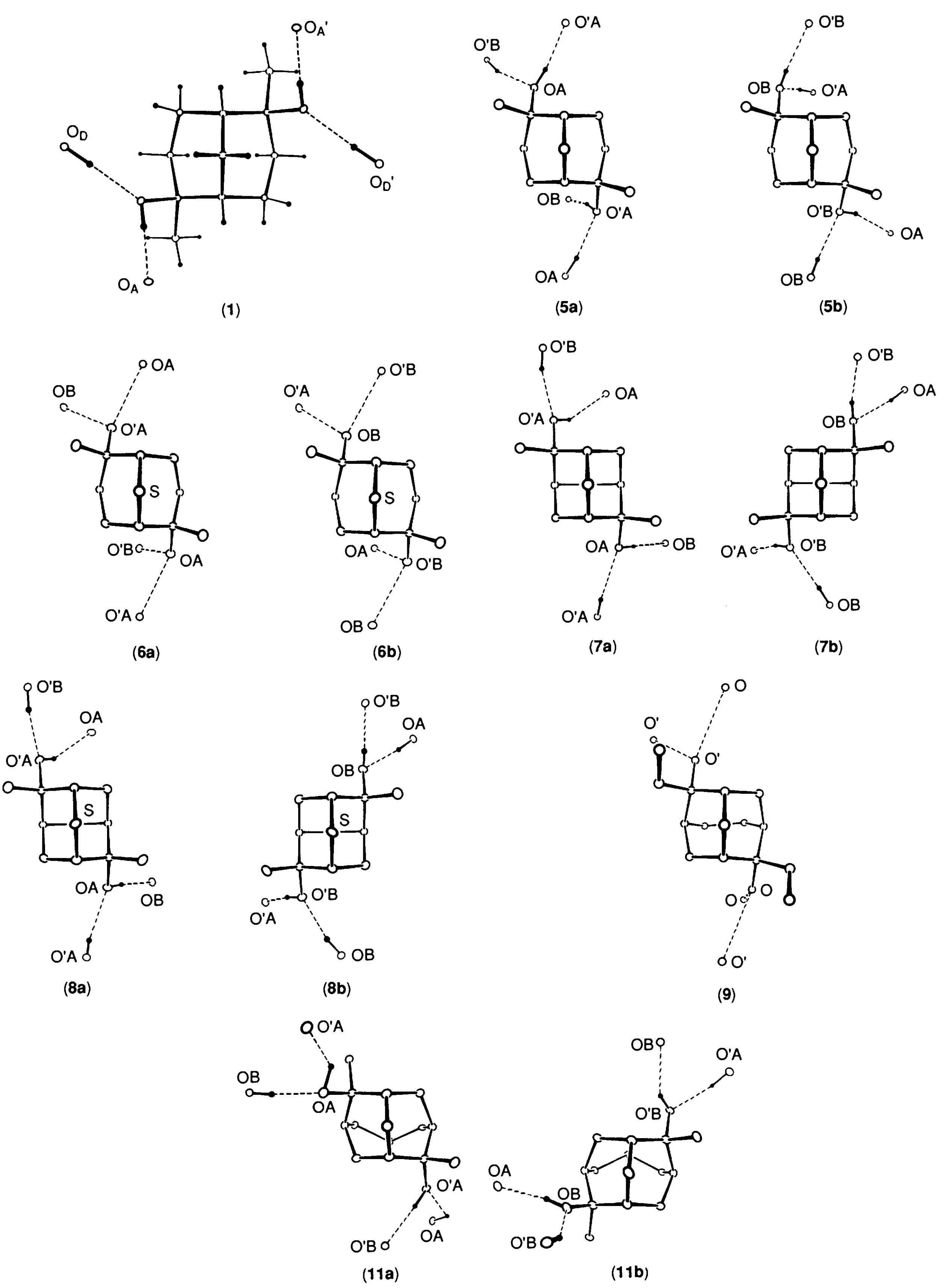
* An alternative statement of the definition of these molecular axes is that epimerisation of both hydroxy groups [as between (**1**) and (**5**)] is equivalent to interchange of *X* and *Y*. Thus *X* for (**1**) corresponds to *Y* for diols (**5**)–(**9**).



(1) **(5a)** **(5b)** **(6a)** **(6b)** **(7a)** **(7b)** **(8a)** **(8b)** **(9)** **(11a)** **(11b)**

Figure 2. Comparative representations of the eleven independent diol molecules in the crystal structures of (**5**)–(**9**) and (**11**), projected along the pseudo-twofold axes. Hydrogen atoms bonded to carbon are omitted, while the hydrogen bonds connecting to each diol molecule are included. The directions of the hydrogen bonds relative to the diol are compared with those of diol (**1**). Subscripts D and A for (**1**) refer to the donor and acceptor hydrogen bonds from adjacent molecules. In all of these diagrams the molecular *Y* axis, as defined in the text, is vertical.

Table 2. Interbond angles for **(5)**–**(9)** and **(11)**.[a]

	(5)	**(6)**	**(7)**	**(8)**	**(9)**	**(11)**
C(2)–C(1)/S–C(2′)	109.0(2)	94.8(1)	109.8(1)	96.1(1)	109.2(4)	108.4(5)
	109.0(2)	94.5(1)	109.7(1)	95.7(1)		108.5(5)
C(1)/S–C(2)–C(3)	110.6(2)	110.8(2)	110.5(1)	111.0(2)	111.7(4)	109.0(5)
	111.0(2)	110.9(2)	110.4(1)	110.5(2)		109.6(5)
C(1)/S–C(2′)–C(3′)	110.7(2)	110.4(2)	110.5(1)	111.0(2)	111.1(4)	112.5(5)
	110.5(2)	110.2(2)	110.2(1)	110.6(2)		111.1(6)
C(1)/S–C(2)–C(5′)	108.2(2)	108.6(2)	108.5(1)	108.6(2)	108.0(4)	108.7(6)
	107.3(2)	108.6(2)	108.5(1)	109.4(2)		109.1(5)
C(1)/S–C(2′)–C(5)	108.1(2)	108.8(2)	108.0(1)	109.0(2)	106.5(4)	108.0(5)
	108.6(2)	109.0(2)	108.5(1)	109.0(2)		106.7(5)
C(3)–C(2)–C(5′)	115.6(2)	116.7(3)	110.1(1)	111.4(2)	113.6(4)	116.0(6)
	115.5(2)	117.2(3)	110.4(1)	111.9(2)		117.3(6)
C(3′)–C(2′)–C(5)	115.6(2)	117.1(3)	110.6(1)	111.9(2)	115.4(4)	116.4(5)
	115.4(2)	117.9(3)	110.3(1)	111.7(2)		119.5(6)
C(2)–C(3)–C(4)	112.5(2)	113.9(3)	107.6(1)	108.8(2)	111.9(4)	114.1(6)
	112.5(2)	113.5(3)	107.4(1)	108.3(2)		114.5(6)
C(2′)–C(3′)–C(4′)	112.2(2)	113.4(3)	107.6(1)	108.6(2)	112.4(4)	113.6(5)
	112.4(2)	113.2(3)	107.7(1)	108.8(2)		114.1(5)
C(2)–C(3)–O	109.3(2)	108.4(3)	107.1(1)	105.5(2)	108.4(4)	106.4(5)
	110.8(2)	107.6(3)	110.0(1)	108.0(2)		103.6(5)
C(2′)–C(3′)–O′	110.2(2)	105.5(3)	110.6(1)	108.9(2)	107.5(3)	112.3(5)
	107.2(2)	107.9(3)	106.6(1)	104.7(2)		111.7(5)
C(4)–C(3)–O	106.0(2)	106.0(3)	109.0(1)	108.8(2)	109.5(4)	103.7(5)
	106.1(2)	106.5(2)	106.3(1)	105.6(2)		107.5(5)
C(4′)–C(3′)–O′	108.5(2)	107.3(3)	110.1(1)	109.7(2)	108.5(4)	108.7(5)
	108.0(2)	106.6(3)	110.4(1)	109.7(2)		107.6(5)
C(3)–C(4)–C(5)	115.0(2)	116.2(3)	110.4(1)	112.6(2)	111.8(4)	112.9(6)
	114.1(2)	118.0(3)	110.7(1)	112.7(2)		111.7(6)
C(3′)–C(4′)–C(5′)	114.5(2)	117.4(3)	110.6(1)	112.5(2)	110.1(4)	111.1(6)
	115.2(2)	115.7(3)	110.4(1)	112.3(2)		109.3(6)
C(4)–C(5)–C(2′)	114.2(2)	116.2(3)	110.0(1)	110.3(2)	114.5(3)	118.5(5)
	113.8(2)	115.8(3)	109.8(1)	110.8(2)		117.4(6)
C(4′)–C(5′)–C(2)	113.8(2)	116.3(3)	109.7(1)	111.3(2)	115.1(3)	119.5(6)
	114.2(2)	115.5(3)	109.5(1)	110.7(2)		119.4(5)
C(4)–C(3)–C(6)	110.9(2)	110.9(3)	113.1(1)	113.0(2)	107.6(4)	115.1(6)
	110.8(2)	110.5(3)	113.0(1)	113.4(2)		112.3(6)
C(4′)–C(3′)–C(6′)	110.8(2)	110.6(3)	113.2(1)	113.4(2)	108.3(4)	106.4(5)
	110.3(2)	110.9(3)	113.0(1)	113.3(2)		107.3(6)
C(2)–C(3)–C(6)	110.5(2)	110.3(3)	112.8(1)	112.9(2)	113.4(4)	110.2(6)
	110.0(2)	110.5(3)	112.7(1)	112.9(2)		112.0(6)
C(2′)–C(3′)–C(6′)	110.1(2)	111.4(3)	112.7(1)	112.6(2)	112.4(4)	109.1(6)
	110.8(2)	112.4(3)	112.5(1)	113.3(2)		110.0(6)
O–C(3)–C(6)	107.4(2)	107.0(3)	107.0(1)	107.4(2)	105.7(4)	106.5(5)
	106.5(2)	108.0(3)	107.4(1)	108.3(2)		106.0(5)
O′–C(3′)–C(6′)	104.8(2)	108.2(3)	102.7(1)	103.4(2)	107.6(4)	106.3(5)
	108.1(2)	105.5(3)	106.4(1)	106.7(2)		105.8(5)
C(4)–C(1′)/S–C(4′)			110.2(1)	110.1(2)		
			110.1(1)	109.7(2)		
C(3)–C(4)–C(1′)/S			109.6(1)	110.0(2)		
			109.8(1)	110.3(2)		
C(3′)–C(4′)–C(1′)/S			109.9(1)	109.9(2)		
			110.2(1)	110.2(2)		
C(5)–C(4)–C(1′)/S			108.9(1)	108.5(2)		
			108.6(1)	108.7(2)		
C(5′)–C(4′)–C(1′)/S			108.1(1)	108.3(2)		
			108.3(1)	108.5(2)		
C(3)–C(4)–C(7)/C(8)					116.7(4)	117.9(6)
						117.8(6)
C(3′)–C(4′)–C(7′)/C(8′)					116.4(4)	117.1(6)
						117.6(6)
C(5)–C(4)–C(7)/C(8)					110.2(4)	112.7(6)
						113.1(6)
C(5′)–C(4′)–C(7′)/C(8′)					111.3(4)	113.7(6)
						113.4(6)
C(4)–C(8)–C(8′)					119.0(4)	
C(4′)–C(8′)–C(8)					119.9(4)	
C(3)–C(6)–C(7)					117.7(5)	
C(3′)–C(6′)–C(7′)					116.9(4)	
C(4)–C(7)–C(8)						118.1(7)
						120.7(8)
C(4′)–C(7′)–C(8)						122.6(7)
						123.2(8)
C(7)–C(8)–C(7′)						119.3(8)
						116.9(8)

Table 2 (*continued*)

	(5)	(6)	(7)	(8)	(9)	(11)
C(3)–O–HO	114(2)	121(1) 105(1)	111(1)	109(1)	98(2) 99(2)	80(3)
	111(3)	117(2) 118(2)	110(1)	105(1)		115(3)
C(3′)–O′–HO′	103(3)	133(2) 120(2)	114(1)	117(1)	105(2) 137(2)	107(4)
	111(3)	120(2) 104(2)	109(1)	114(1)		102(3)

[a] The successive entries for structures (**5**)–(**8**) and (**11**) refer to the independent molecules A and B respectively.

Table 3. Macro dimensions (distances/Å, angles/°, and torsional angles/°) of the molecules (**1**)–(**4**), (**5**)–(**9**) and (**11**).[a]

	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)	(11)
O···O′	5.60	5.55	5.53	5.68	5.29	5.30	5.48	5.51	5.40	5.70
			5.53		5.24	5.32	5.42	5.42		5.73
C(3)···C(3′)	3.71	3.71	3.66	3.82	3.69	3.73	3.61	3.66	3.68	3.78
			3.67		3.69	3.74	3.61	3.65		3.75
C(4)···C(4′)	3.14	3.04	3.05	3.35	3.13	3.12	2.51	2.50	3.03	3.35
			3.06		3.12	3.12	2.51	2.50		3.37
C(6)···C(6′)	5.75	5.88	5.79	5.88	6.00	6.00	5.86	5.87	6.00	6.00
			5.80		6.00	6.04	5.85	5.87		5.94
C(3′)···C(3)–O	126.1	122.3	124.8	123.0	115.9, 119.8	118.7, 115.8	121.2, 125.8	121.5, 125.5	119.1, 119.3	122.7, 125.5
			124.7, 124.6		118.5, 114.8	116.4, 119.2	121.3, 122.6	120.8, 122.0		124.0, 125.6
O–C(3)···C(3′)–O′[b]	73.5	94.3	78.9	97.2	79.8	78.2	90.6	87.0	88.3	102.1
					80.1	76.7	89.8	86.2		109.3

[a] The successive entries for structures (**5**)–(**8**) and (**11**) refer to the independent molecules A and B respectively. [b] These are absolute values of the torsional angles: the sign depends on the enantiomer.

Table 4. Comparison of C(4)–C(4′) distances/Å in alicyclic diols.

Bridge F	Bridge A	Compound	Distance(s)
CH_2	CH_2	(**7**)	2.51, 2.51
CH_2	S	(**8**)	2.50, 2.49
CH_2CH_2	CH_2	(**2**)	3.04
CH_2CH_2	CH_2	(**3**)	3.05, 3.06
CH_2CH_2	CH_2	(**9**)	3.03
—	CH_2	(**1**)	3.14
—	CH_2	(**5**)	3.13; 3.12
—	S	(**6**)	3.12; 3.12
$CH_2CH_2CH_2$	CH_2	(**4**)	3.35
$CH_2CH_2CH_2$	CH_2	(**11**)	3.35, 3.37

(**11**) the direction of each hydrogen bond is best assessed relative to the direction of its C–O bond and the molecule: there are no abnormalities.

Although this analysis of the hydrogen-bond connections between each diol and its surroundings is relatively crude, it can be stated there is no indication that the new diols present any impediment to hydrogen bonding in the manner of the helical tubuland structure. However it is also clear that there is variability of direction of hydrogen bonding, and no impediment to alternative hydrogen-bonded structure types.

We note (Table 5) that the hydrogen bonds in (**9**) are generally longer than in the other structures: this may be a consequence of the ethyl substituents, but in (**10**) where there are also ethyl substituents, the O ··· O distances are 2.73 and 2.67 Å.

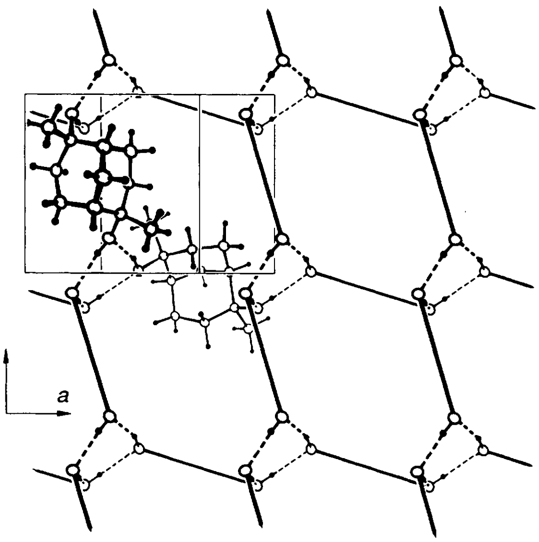


Figure 3. Diagrammatic representation of the chains of diol molecules (represented as full lines) and four-membered cycles of hydrogen bonds (broken lines) in one layer for (**5**) and (**6**), with inclusion of one of each of the two diol molecules in the asymmetric unit. Oxygen atoms are drawn as large open circles and the hydrogen atoms as small filled circles. In (**5**) molecules labelled A continue in the *b* direction, and in (**6**) molecules labelled B run in the *b* direction.

The crystal densities for the layered crystal structures reported here range 1.17–1.24 g cm^{-3} for diols without sulphur, and 1.26–1.34 g cm^{-3} for diols with sulphur. In general, the densities of the layered structures are higher than those for the (empty) helical tubuland lattices of (**1**)–(**4**). (**1**) and (**5**) are double epimers, but the density of (**1**) (1.02 g cm^{-3}) is significantly lower than that of (**5**) (1.17 g cm^{-3}); similarly for (**4**) and (**11**) which are single epimers there is a marked difference in densities (0.97 and 1.19 g cm^{-3}, respectively). The higher density for the layer-type structure persists when (**9**) (density 1.22 g

Table 5. Dimensions of hydrogen bonding cycles in (**5**)–(**9**) and (**11**).

O(1)•••O(2)
•   •
•   •
•   •
O(4)•••O(3)

	(**5**)	(**6**)	(**7**)	(**8**)	(**9**)	(**11**)
O(1)	OA	OA	OA	OA	O	OA
O(2)	O′B	O′A^{c}	OB	OB	O^{h}	OB
O(3)	OB^{a}	OB^{d}	O′B^{e}	O′B^{e}	O′^{i}	O′B^{k}
O(4)	O′A^{b}	O′B	O′A^{f}	O′A^{g}	O′^{j}	O′A^{l}
Bond distances/Å						
O(1)•••O(2)	2.773(2)	2.735(3)	2.848(2)	2.827(3)	3.126(7)	2.840(6)
O(2)•••O(3)	2.734(2)	2.759(3)	2.730(2)	2.891(3)	2.994(4)	2.904(6)
O(3)•••O(4)	2.771(3)	2.784(3)	2.784(2)	2.710(3)	2.959(7)	2.942(7)
O(4)•••O(1)	2.746(2)	2.773(4)	2.866(2)	2.779(3)	2.994(4)	2.887(7)
Bond angles/°						
O(4)•••O(1)•••O(2)	88.98(7)	90.60(1)	90.84(4)	90.56(8)	83.1(1)	78.8(1)
O(1)•••O(2)•••O(3)	85.89(7)	86.6(1)	80.77(4)	81.06(8)	83.1(1)	95.3(1)
O(2)•••O(3)•••O(4)	89.25(7)	89.9(1)	95.12(5)	95.50(8)	86.0(1)	76.9(1)
O(3)•••O(4)•••O(1)	85.70(7)	85.3(1)	79.54(4)	78.79(7)	86.0(1)	93.5(1)
Deviations Å from the planes of best fit through $(\text{–OH})_4$ and lengths Å of O••• O diagonals						
(**5**)	−0.29	0.29	−0.29	0.29	3.75	3.87
(**6**)	0.25	−0.26	0.25	−0.25	3.77	3.92
(**7**)	−0.33	0.35	−0.36	0.34	3.62	4.07
(**8**)	−0.33	0.35	−0.36	0.34	3.60	4.06
(**9**)	−0.45	0.45	−0.48	0.48	4.06	4.06
(**10**)	0.45	−0.45	0.41	−0.41	3.62	3.62
(**11**)	−0.38	0.38	−0.37	0.37	4.25	3.64

a	$-1 + x, y, z$
b	$x, -1 + y, z$
c	$x - 1, y, z$
d	$x, y + 1, z$
e	$1/2 - x, -1/2 + y, z$
f	$-1/2 + x, y, 1\,1/2 - z$
g	$-1/2 + x, y, 1/2 - z$
h	$1 - x, y, 1/2 - z$
i	$1/2 - x, 1/2 + y, 1/2 - z$
j	$1/2 + x, 1/2 + y, z$
k	$1 - x, 1/2 + y, 1\,1/2 - z$
l	$x, 1/2 - y, 1/2 + z$

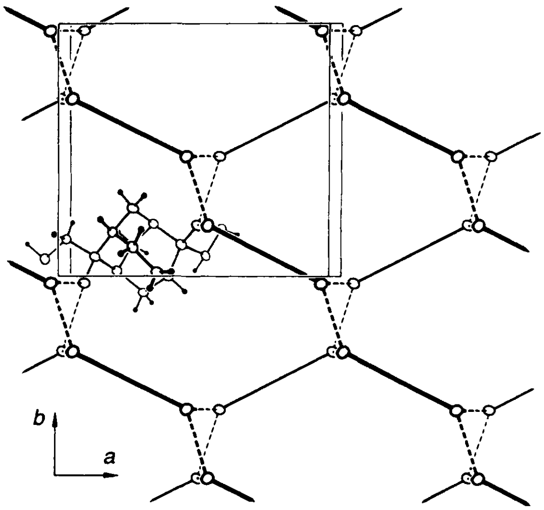


Figure 4. Diagrammatic representation of one layer of the crystal structure of (**9**), with one diol molecule shown in full and others represented as full lines. The four-membered cycles of hydrogen bonds are drawn as broken lines, without the hydroxy hydrogen atoms which are disordered across twofold axes.

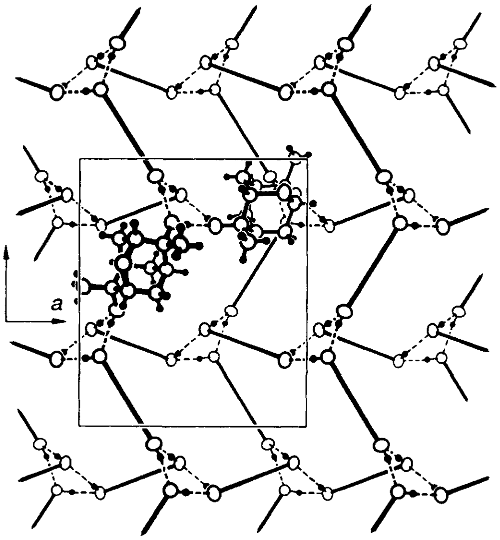


Figure 5. Diagrammatic representation of the partially woven diol molecules in the layer structure of (**7**) and (**8**), with inclusion of one of each of the two diol molecules in the asymmetric unit. Oxygen atoms are drawn as large open circles and the hydrogen atoms as small filled circles.

cm^{-3}) is compared with its methyl homologue (**2**) (density 1.01 g cm^{-3}), but the densities of (**10**) and its dimethyl homologue (**3**) are almost the same (1.19 and 1.22 g cm^{-3}, respectively). However, in the case of (**3**), much of the helical canal is obstructed by the bulky propyl linkage, thus increasing its density. The m.p.s of the crystals of (**5**)–(**8**) range from 188 to 202 °C, similar to the value of 191 °C for (**1**); (**9**)–(**11**) melt at temperatures as low as 150 °C.

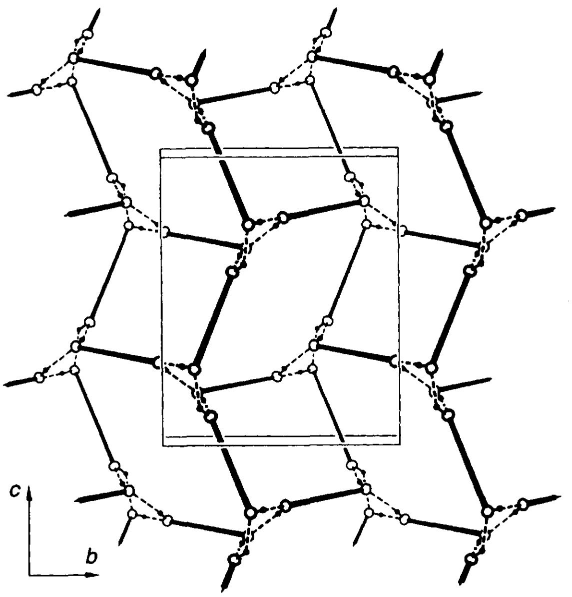


Figure 6. Diagrammatic representation of the partially woven diol molecules in the layer structure of (**11**). Oxygen atoms are drawn as large open circles and the hydrogen atoms as small filled circles.

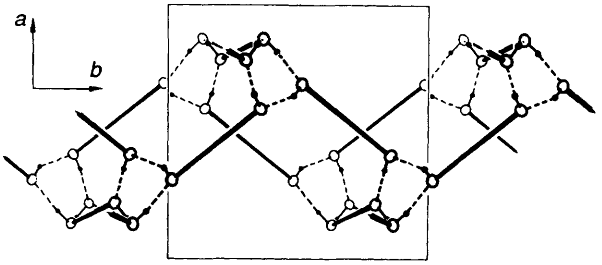


Figure 7. Side view of the undulating layer in (**11**), using the same diagrammatic representation as Figure 6, showing how the chains in the *c*-direction are alternately above and below the chains in the *b*-direction.

Discussion

Although the diol stereochemistry for (**11**) precludes its crystallisation in the helical tubuland lattice, it was expected that (**5**)–(**10**) could have adopted that interesting host structure. In particular it was expected that (**5**), the double epimer of (**1**), would crystallise as a helical tubuland since a very similar pair of doubly epimeric diols, (**2**) and (**3**), are both crystalline helical tubulands, and the dimensions and shape of (**5**) are hardly different from those of (**2**).

It is now clear that whereas some members of the general class of alicyclic diol molecules form the helical tubuland crystal lattice, there is a sub-class of diols that crystallise instead in another general structure type composed of layers. The characteristic structural properties of these layers are: maximised hydrogen bonding of diol molecules within the layers, an absence of inter-layer hydrogen bonding, and the occurrence of cycles of four hydrogen bonds within the layers. It is also apparent that despite these similarities the layered structure has some variability, with rather similar diol molecules occurring in different arrangements within the layers, and with varying relationships between the layers.

We can conclude also that the dimensions of the diol molecules do not have a *direct* influence on the structure type adopted in the crystals, and neither is there any clear relationship between the geometry of the diol molecule and the directions of the hydrogen bonds it engages. Further prescription of diol molecular properties which favour the helical tubuland structure type is difficult, although we can postulate that contracted diols such as the adamantane derivatives (**7**) and (**8**) do not present hydroxy groups suitable for the helical tubuland structure.

Spontaneous resolution of the diols, as occurs on crystallisation in the helical tubuland structure, does not occur in the layered structures.

Experimental

Except where stated otherwise, ^{13}C NMR spectra (25.1 MHz) were recorded with a JEOL FX-100 spectrometer, and the substitution of carbon atoms was determined by off-resonance decoupling. Most ^1H NMR spectra were recorded using the same instrument (100 MHz), but a few spectra were run on a Bruker CXP-300 (300 MHz). All NMR spectra are recorded relative to $SiMe_4$. M.p.s were obtained with a Kofler instrument and are uncorrected.

endo-2,endo-6-*Dihydroxy*-2,6-*dimethylbicyclo*[3.3.1]*nonane* (**5**).—A solution of methyl magnesium iodide was prepared in the customary manner from magnesium turnings (3.89 g, 0.16 mol) and iodomethane (22.72 g, 0.16 mol) in dry diethyl ether (150 cm^3). Powdered bicyclo[3.3.1]nonane-2,6-dione[11] (**12**) (10.64 g, 0.07 mol) was dissolved in dry benzene (200 cm^3) and the solution was added to the vigorously stirred (mechanical stirrer) Grignard reagent. When the addition was complete, the reaction was refluxed and stirred overnight, and then allowed to cool to room temperature. The reaction was worked up by addition of water and separation of the organic layer. Continuous extraction of the aqueous phase for 4 days with ethyl acetate removed the rest of the product. The combined organic extracts were dried (Na_2SO_4), filtered, and the solvent evaporated to give a white solid.[12] This was recrystallised from ethyl acetate to give the diol (**5**) (6.28 g, 48%), m.p. 190–192 °C (Found: C, 71.85; H, 10.75. $C_{11}H_{20}O_2$ requires C, 71.70; H, 10.94%); ν_{max} (paraffin mull) 3 400s, 1 145s, 1 125s, 1 035m, 995m, 970m, and 925s cm^{-1}; δ_H [$(CD_3)_2SO$] 1.17 (s, 6 H), 1.2–2.2 (m, 12 H), and 4.13 (s, 2 H, exchanged with D_2O); δ_C[$(CD_3)_2SO$] 23.8 (t), 29.2 (q), 30.1 (t), 35.8 (t), 39.2 (d), and 70.5 (s). Crystals for X-ray study were obtained by recrystallisation from tetrahydrofuran (THF).

Concentration of the mother liquors from the recrystallisation gave a second crop of solid. Examination by ^{13}C NMR spectroscopy showed this to be a mixture of the two diols (**5**) and (**13**) (*ca.* 1:2).

endo-2-*Hydroxy*-2-*methyl*-6-*methylenebicyclo*[3.3.1]*nonane* (**15**).—6-Methylenebicyclo[3.3.1]nonane-2-one (**14**) was prepared (52%) from the dione (**12**) as previously described.[13] A solution of (**14**) (3.00 g, 0.02 mol) in dry ether (20 cm^3) was added over a few minutes to a stirred solution of methylmagnesium iodide (0.03 mol) in ether (20 cm^3). The reaction was refluxed for 3 h, stirred at room temperature overnight and worked up in the standard manner with 0.5 mol dm^{-3} HCl and ether. Trituration of the crude solid product with a small volume of pentane, followed by filtration, gave the alcohol (**15**) (2.34 g, 71%), m.p. 70–71 °C; ν_{max}(paraffin mull) 3 340s, 3 075w, 1 645m, 1 115s, 985m, 910m, and 875s cm^{-1}; δ_H(CCl_4) 1.30 (s, 3 H), 1.4–2.0 (m, 8 H), 2.1–2.6 (m, 4 H), 2.95 (s, 1 H, exchanged with D_2O), and 4.55 (br s, 2 H); δ_C($CDCl_3$) 25.6 (t), 28.6 (q), 30.3 (t), 30.6 (t), 32.8 (t), 35.8 (t), 37.2 (d), 39.4 (d), 72.8 (s), 107.3(t), and 152.4(s).

endo-2,exo-6-*Dihydroxy*-2,6-*dimethylbicyclo*[3.3.1]*nonane* (**13**).—A solution of the alcohol (**15**) (2.20 g, 13.2 mmol) in freshly distilled THF (20 cm^3) was added to a stirred slurry of mercuric acetate (4.46 g, 0.014 mol) in water (15 cm^3) and redistilled THF (15 cm^3). After being stirred for 30 min, the reaction was worked up following the method described as method A for the preparation of diol **(6)** to yield the diol **(13)** (0.64 g, 26%), m.p. 166–167 °C (from ethyl acetate). ν_{max}(paraffin mull) 3 400s, 1 120s, 1 025m, 985m, 960m, 910m, and 890m cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.06 (s, 3 H), 1.18 (s, 3 H), 1.2–2.2 (m, 12 H), 3.89 (s, 1 H, exchanged with D_2O), and 4.13 (s, 1 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 22.6 (t), 25.6 (t), 28.1 (t), 29.6 (q), 29.7 (q), 35.3 (t), 35.8 (t), 39.4 (d), 39.7 (d), 70.4 (s), and 71.2 (s).

2,6-*Dimethylene*-9-*thiabicyclo*[3.3.1]*nonane* **(17)**.—9-Thiabicyclo[3.3.1]nonane-2,6-dione[14] **(16)** (3.57 g, 0.021 mol) was added to a stirred solution of methylenetriphenylphosphorane (0.045 mol) in dry dimethyl sulphoxide (DMSO) under dry nitrogen, as in the Corey method[15] for the Wittig reaction. After being heated for 2 h at 80 °C, the cooled mixture was worked up in the usual manner with water and pentane. The crude product was eluted with pentane through a short column of alumina to remove traces of triphenylphosphine oxide and the solvent removed by distillation to give an oil. Microdistillation gave the diene[16] **(17)** (1.64 g, 47%), b.p. 230–234 °C (Found: C, 72.3; H, 8.3. $C_{10}H_{14}S$ requires C, 72.23; H, 8.49%); ν_{max}(film) 3 070m, 2 980m, 2 930s, 2 850m, 1 780w, 1 630s, 1 465s, 1 440s, 1 270w, 1 240m, 1 195w, 1 145w, 1 055m, 970m, 935m, 890s, and 865m cm^{-1}; $\delta_H(CDCl_3)$ 2.07–2.15 (m, 2 H), 2.27– 2.40 (m, 2 H), 2.46–2.55 (m, 2 H), 2.66–2.79 (m, 2 H), 3.47 (t, *J* 4 Hz, 2 H), and 4.72–4.76 (m, 4 H); $\delta_C(CDCl_3)$ 30.5 (t), 34.7 (t), 41.1 (d), 108.2 (t), and 148.1 (s).

endo-2,endo-6-*Dihydroxy*-2,6-*dimethyl*-9-*thiabicyclo*[3.3.1]-*nonane* **(6)**.—*Method A*. Mercuric acetate (5.32 g, 0.017 mol) was dissolved in freshly distilled THF (40 cm^3) and water (40 cm^3), and stirred at room temperature. A solution of 2,6-dimethylene-9-thiabicyclo[3.3.1]nonane **(17)** (1.39 g, 8.35 mmol) in distilled THF (10 cm^3) was then added. The yellow colour was discharged after *ca.* 3 min, but the reaction was stirred for a total of 2 h. Sodium hydroxide solution (3 mol dm^{-3}; 45 cm^3) was added, followed by sodium borohydride solution (0.5 mol dm^{-3} in 3 mol dm^{-3} NaOH; 45 cm^3), and the reaction mixture was stirred for 2 h. Solvent was evaporated and the solution was extracted with ethyl acetate (5 × 100 cm^3). The combined extracts were washed with water (2 × 100 cm^3), brine (100 cm^3), and dried (Na_2SO_4). Removal of solvent from the filtrate furnished a grey-white residue which was recrystallised from ethyl acetate to give the diol **(6)** (1.13 g, 66%), m.p. 201–203 °C (Found; C, 59.15; H, 9.2. $C_{10}H_{18}O_2S$ requires C, 59.37; H, 8.97%); ν_{max}(paraffin mull) 3 310s, 1 095s, 1 050m, 990m, 970m, 960m, 935m, 905s, 875m, and 860m cm^{-1}; $\delta_H[CD_3)_2SO]$ 1.39 (s, 6 H), 1.47–1.54 (m, 2 H), 1.80–1.92 (m, 2 H), 1.99–2.10 (m, 2 H), 2.26–2.28 (m, 2 H), 2.37–2.50 (m, 2 H), and 4.55 (s, 2 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 27.3 (t), 30.0 (q), 35.9 (t), 43.1 (d), and 70.2 (s). Material crystallised from ethyl acetate was used for X-ray analysis.

Method B. A solution of 9-thiabicyclo[3.3.1]nonane-2,6-dione **(16)** (1.00 g, 5.88 mmol) in dry THF (50 cm^3) was added to a vigorously stirred solution of methylmagnesium iodide (0.021 mol) in ether (20 cm^3), and the resulting mixture was refluxed overnight. The cooled reaction was poured into a beaker containing crushed ice (50 g) and saturated NH_4Cl (25 cm^3). After stirring for 10 min, the organic phase was separated and the aqueous phase extracted with ethyl acetate (4 × 100 cm^3). The combined organic extracts were washed with water (2 × 50 cm^3), brine (50 cm^3) and dried (Na_2SO_4). Concentration of the filtrate to low volume caused precipitation of a white solid which was filtered and washed with cold ether to yield the diol **(6)** (0.52 g, 44%), m.p. 201.5–203 °C. This material had IR and ^{13}C NMR spectra identical with the material prepared by Method A. The filtrate and washings were evaporated to dryness to yield further solid the ^{13}C NMR spectrum of which indicated that it comprised a mixture of diol **(6)**, and *exo*-2,*endo*-6-dihydroxy-2,6-dimethyl-9-thiabicyclo[3.3.1]nonane **(18)**: $\delta_C[(CD_3)_2SO]$ 24.4 (t), 28.8 (t), 29.2 (q), 30.0 (q), 35.1 (t), 35.4 (t), 42.9 (d), 45.9 (d), 67.9 (s), and 70.6 (s).

2,6-*Dihydroxy*-2,6-*dimethyltricyclo*[3.3.1.1^{3,7}]*decane* **(7)**.—The bis(enamine) of dione **(12)** was bridged with di-iodomethane to produce tricyclo[3.3.1.1^{3,7}]decane-2,6-dione **(19)** following the procedure of Janku and Landa.[17] A solution of **(19)** (1.00 g, 6.09 mmol) in dry ether (15 cm^3) was added dropwise to a stirred solution of methylmagnesium iodide (17 mmol) in ether (25 cm^3), and then refluxed for 1.5 h. The reaction was worked up in the standard manner using 5 mol dm^{-3} HCl and chloroform to yield the crude product which was recrystallised from benzene to afford the diol **(7)** (0.46 g, 39%), m.p. 198.5–199 °C (lit.,[17] 67%, m.p. 195.5–196 °C) (Found: C, 73.1; H, 10.4. $C_{12}H_{20}O_2$ requires C, 73.43; H, 10.27%); ν_{max}(paraffin mull) 3 460w, 3 330s, 1 120s, 1 095m, 1 030m, 995s, 950m, 915w, and 895m cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.19 (s, 6 H), 1.3–1.6 (m, 6 H), 1.70 (br s, 2 H), 1.90 (br s, 2 H), 2.0–2.3 (m, 2 H), and 4.00 (s, 2 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 26.6 (q), 26.9 (t), 29.0 (t), 31.0 (t), 37.6 (d), 37.9 (d), and 70.7 (s). Small cubic blocks that crystallised from ethyl acetate were used for X-ray analysis.

2,6-*Dihydroxytricyclo*[3.3.1.1^{3,7}]*decane* **(20)**.—A solution of dione **(19)** (0.40 g, 2.44 mmol) in dry ether (60 cm^3) was reacted with lithium aluminium hydride under routine conditions, and the crude product was recrystallised twice from ethyl acetate to give the diol **(20)** (0.31 g, 76%), m.p. 336–338 °C (sealed capillary) (lit.[17] 94%, m.p. 344 °C) (Found: C, 71.45; H, 9.7. $C_{10}H_{16}O_2$ requires C, 71.39; H, 9.59%); ν_{max}(paraffin mull) 3 280s, 1 105w, 1 075w, 1 035s, 970m, and 935w cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.29 (d, 2 H), 1.55–1.80 (m, 8 H), 2.1 (d, 2 H), 3.57 (br s, 2 H), and 4.49 (d, 2 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 24.4 (t), 29.7 (t), 33.1 (d), 33.7 (d), 34.6 (t), and 72.4 (d). Crystals suitable for X-ray analysis could not be prepared. Tapering needles were formed from all solvents. The least irregular were obtained from ethyl acetate.

2,6-*Diethyl*-2,6-*dihydroxytricyclo*[3.3.1.1^{3,7}]*decane* **(21)**.—A solution of dione **(19)** (0.23 g, 1.40 mmol) in dry ether (10 cm^3) was added slowly at 0 °C to a solution of ethyl-lithium generated from lithium (0.10 g, 14.6 mmol) and bromoethane (0.80 g, 7.3 mmol) in dry ether (5 cm^3) under argon. The reaction was maintained at 0 °C overnight and then allowed to warm to room temperature. Water (15 cm^3) was added cautiously, precipitating some of the product. After being stirred for 1 h the reaction was thoroughly extracted with ethyl acetate, and the combined extracts dried ($MgSO_4$). The filtrate was concentrated to a volume of 10 cm^3 and cooled. Filtration gave the diol **(21)** (0.30 g, 96%), m.p. 212 °C (lit.[17] 88%, m.p. 211–212 °C) (Found: C, 74.8; H, 11.05. $C_{14}H_{24}O_2$ requires, C, 74.95; H, 10.78%); ν_{max}(paraffin mull) 3 400s, 1 140m, 1 120m, 1 045m, 980s, and 940s cm^{-1}; $\delta_H[(CD_3)_2SO]$ 0.78 (t, 6 H), 1.36–1.66 (m, 12 H) including 1.57 (q), 1.9 (br s, 2 H), 2.1 (d, 2 H), and 3.71 (s, 2 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 6.6 (q), 27.0 (t), 28.5 (t), 29.3 (t), 30.0 (t), 35.0 (d), 35.5 (d), and 71.9 (s). Crystals suitable for X-ray analysis could not be prepared. Close inspection of the small octahedral crystals formed from ethyl acetate revealed that they were distorted, indicative of twinning disorder. Dendritic crystals were obtained from other solvents attempted.

4,8-*Dimethylene*-2-*thiatricyclo*[3.3.1.1^{3,7}]*decane* **(23)**.—The bis(enamine) of dione **(12)** was bridged with sulphur dichloride to produce 2-thiatricyclo[3.3.1.1^{3,7}]decane-4,8-dione (**22**) following the procedure of Stetter.[18] Dione (**22**) (0.73 g, 4.0 mmol) was added as a powder to a solution of methylenetriphenylphosphorane (9.2 mmol) in Me_2SO under dry nitrogen, following a similar procedure to that used for (**17**). The crude waxy solid was sublimed to yield the diene (**23**) (0.48 g, 67%), m.p. 111–112 °C (Found: C, 73.8; H, 8.05; S, 17.8. $C_{11}H_{14}S$ requires C, 74.10; H, 7.92; S, 17.98%); ν_{max}(paraffin mull) 3 070w, 1 645m, and 900s cm^{-1}; $\delta_H(CDCl_3)$ 2.00 (m, 2 H), 2.31 (m, 2 H), 2.55 (m, 2 H), 2.73 (m, 2 H), 3.44 (m, 2 H), 4.71 (d, 2 H), and 4.74 (d, 2 H); $\delta_C(CDCl_3)$ 37.6 (d), 40.0 (t), 41.8 (d), 43.9 (t), 103.3 (t), and 152.3 (s).

anti-4,anti-8-*Dihydroxy*-4,8-*dimethyl*-2-*thiatricyclo*-[3.3.1.1^{3,7}]*decane* (**8**).—Diene (**23**) (0.10 g, 0.56 mmol) in freshly distilled THF (2 cm^3) was added to a stirred solution of mercuric acetate (0.36 g, 1.12 mmol) in freshly distilled THF (6 cm^3) and water (6 cm^3). The yellow colour faded rapidly over the first 10 min, then more slowly to colourless (45 min). After a further 20 min the reaction was worked up following a similar procedure to that described for (**6**) (method A), except that the extraction solvent used was ether. (Longer reaction times led to a serious reduction in yield and the formation of many byproducts). Evaporation of solvent gave a gum which was triturated with a little light petroleum and filtered. This removed a minor impurity and *ca.* 25% unchanged diene. The crude product was recrystallised from dichloromethane to yield the diol (**8**) (0.07 g, 58%), m.p. 188–190 °C (slight decomp.) (Found: C, 61.25; H, 8.8; S, 14.8. $C_{11}H_{18}O_2S$ requires C, 61.64; H, 8.47; S, 14.98%); ν_{max}(paraffin mull) 3 470w, 3 330s, 1 095s, and 990m cm^{-1}; $\delta_H(CDCl_3)$ 1.45 (s, 2 H, exchanged with D_2O), 1.63 (s, 6 H), 1.69–1.77 (m, 2 H), 2.10 (m, 2 H), 2.28 (m, 2 H), 2.41 (m, 2 H), and 2.61 (m, 2 H); $\delta_C(CDCl_3)$ 26.7 (t), 27.8 (q), 32.7 (t), 37.6 (d), 42.2 (d), and 72.2 (s). Cubic block crystals from ethyl acetate were used for X-ray analysis.

syn-2,*syn*-7-*Dihydroxy*-2,7-*diethyltricyclo*[4.3.1.1^{3,8}]*undecane* (**9**).—Dione (**24**)[2,19] (0.15 g, 0.84 mmol) in dry ether (10 cm^3) was added dropwise to a stirred solution of ethyl lithium (2.5 mmol) in ether (20 cm^3) under argon, following the conditions described for (**21**) except that the extraction solvent was ether. The crude product was recrystallised from ether–light petroleum to give the diol (**9**) (0.14 g, 70%), m.p. 150.0–150.5 °C (Found: C, 75.70; H, 11.17. $C_{15}H_{26}O_2$ requires C, 75.58; H, 10.99%); ν_{max}(paraffin mull) 3 490s, 1 320w, 1 190w, 1 130s, 1 110s, 1 080w, 975s, 945s, and 895m cm^{-1}; $\delta_H(CDCl_3)$ 0.88 (t, 6 H), 1.23 (br s, 2 H, exchanged with D_2O), and 1.3–2.1 (m, 18 H); $\delta_C(CDCl_3)$ 7.7 (q), 27.6 (t), 31.0 (t), 31.9 (t), 33.0 (t), 35.9 (d), 41.7 (d), and 76.2 (s). Small blocks from ethyl acetate were used for X-ray analysis.

2,7-*Diethylidenetricyclo*[4.3.1.1^{3,8}]*undecane* (**25**).—A solution of ethylidenetriphenylphosphorane (12.9 mmol) in dry Me_2SO (30 cm^3) under dry nitrogen was prepared according to the Corey procedure[15] for the Wittig reaction. Tricyclo-[4.3.1.1^{3,8}]undecane-2,7-dione[2,19] (**24**) (1.00 g, 5.62 mmol) was added as a powder. A similar procedure to the preparation of (**17**) was followed, except that the solvent used for extraction was diethyl ether. The diene (**25**) (0.44 g, 39%) was obtained as a viscous liquid, b.p. *ca.* 240 °C/1 atm (Found: C, 89.2; H, 11.2. $C_{15}H_{22}$ requires C, 89.04; H, 10.96%); ν_{max}(film) 3 030w, 1 660w, 1 445s, 1 375m, 1 030w, 975w, 940w, 820s, and 680w cm^{-1}; $\delta_H(CDCl_3)$ 1.24 (m, 2 H), 1.35–3.2 (m, 18 H) includes 1.58 (d, *ca.* 6 H), and 5.22 (q, 2 H); $\delta_C(CDCl_3)$ was complex (indicating a mixture of geometrical isomers).

anti,anti-*Bisepoxide of* 2,7-*Diethylidenetricyclo*[4.3.1.1^{3,8}]*undecane* (**26**).—A solution of diene (**25**) (0.17 g, 0.86 mmol) in dichloromethane (4 cm^3) was vigorously stirred with aqueous sodium hydrogen carbonate (1 mol dm^{-3}; 4 cm^3). *m*-Chloroperbenzoic acid (0.5 g; 80–90% purity) in dichloromethane (4 cm^3) was added dropwise. Conversion into the monoepoxide was rapid, but the bisepoxide only formed slowly, as indicated by TLC. After an hour of stirring at room temperature, excess peracid was destroyed by addition of a small quantity of aqueous sodium sulphide. The dichloromethane layer was separated, and the aqueous layer extracted with further dichloromethane. The combined organic extracts were washed (aqueous sodium hydrogen carbonate, then water) and dried ($MgSO_4$). Evaporation of solvent from the filtrate gave the crude product which was purified by column chromatography (alumina, $CHCl_3$) and then vacuum sublimation at 70 °C to give the bisepoxide (**26**) (0.15 g, 77%). m.p. 72.5–73.0 °C (Found: C, 76.7; H, 9.85. $C_{15}H_{22}O_2$ requires C, 76.88; H, 9.46%); ν_{max}(film) 2 930s, 2 860s, 1 455s, 1 380m, 1 015w, 980m, 950w, 925w, 885s, 850w, and 760w cm^{-1}; $\delta_H(CDCl_3)$ 1.32 (d, 3 H), 1.33 (d, 3 H), 1.45–1.60 (m, 2 H), 1.70–1.79 (m, 6 H), 1.85–2.20 (m, 6 H), and 2.89 (m, 2 H); $\delta_C(CDCl_3)$ was complex (indicating a mixture of geometrical isomers).

anti-2,anti-7-*Dihydroxy*-2,7-*diethyltricyclo*[4.3.1.1^{3,8}]*undecane* (**10**).—Excess lithium aluminium hydride was added to a solution of bisepoxide (**26**) (0.13 g, 0.56 mmol) in dry ether (25 cm^3) and dry THF (1 cm^3), and the mixture heated under reflux overnight. The cooled reaction was worked up by cautious addition of damp ether, then water, separation of the ether layer, and extraction of the aqueous phase with ether. After being dried ($MgSO_4$) and filtered, the combined ethereal extracts were evaporated to give the crude product which was recrystallised from ether to give the diol (**10**) (0.09 g, 62%), m.p. 180.5–181.0 °C (Found: C, 75.65; H, 11.2. $C_{15}H_{26}O_2$ requires C, 75.58; H, 10.99%); ν_{max}(paraffin mull) 3 400s, 1 205w, 1 100w, 1 080m, 1 040w, 965s, 920w, and 900w cm^{-1}; $\delta_H(CDCl_3)$ 0.93 (t, 6 H), 1.19 (s, 2 H, exchanged with D_2O), 1.36 (m, 2 H), 1.45–1.72 (m, 8 H) [includes 1.57 (q)], 1.8–1.9 (m, 4 H), 1.96 (m, 2 H), and 2.10–2.20 (m, 2 H); $\delta_C(CDCl_3)$ 6.7 (CH_3) 27.57 (CH_2), 27.64 (CH_2), 30.8 (CH_2), 31.1 (CH_2), 37.5 (CH), 41.7 (CH), and 76.4 (C), (spectra measured at 125.8 MHz using DEPT; Bruker AM-500 instrument). The diol crystallised as small blocks from a variety of solvents. Material for X-ray analysis was crystallised from diethyl ether. Complete refinement of this structure was not possible due to disorder [see the Crystallography section].

syn-2,-syn-7-*Dihydroxytricyclo*[4.3.1.1^{3,8}]*undecane* (**27**).—Tricyclo[4.3.1.1^{3,8}]undecane-2,7-dione[2,19] (**24**) (0.20 g, 1.12 mmol) in dry ether (15 cm^3) was reduced using excess lithium aluminium hydride, and the reaction worked up in the customary manner. The crude product was recrystallised from ethyl acetate to afford the diol (**27**) (0.17 g, 83%), m.p. 216 °C (Found: C, 72.3; H, 10.35. $C_{11}H_{18}O_2$ requires C, 72.49; H, 9.96%); ν_{max}(paraffin mull) 3 350s, 1 210w, 1 050s, 1 025s, 935w, 920w, and 870w cm^{-1}; $\delta_H[(CD_3)_2SO]$ 1.1–1.3 (m, 2 H), 1.3–1.7 (m, 8 H), 1.7–2.1 (m, 4 H), 3.65 (br s, 2 H), and 4.37 (d, 2 H, exchanged with D_2O); $\delta_C[(CD_3)_2SO]$ 23.5 (t), 29.1 (t), 34.1 (d), 34.7 (t), 37.6 (d), and 73.1 (d). The diol crystallised as blocks from most of the solvents attempted. However, all crystals examined were found to suffer from twinning disorder.

8-*Methylenetricyclo*[5.3.1.1^{3,9}]*dodecan*-2-*one* (**29**).—Tricyclo[5.3.1.1^{3,9}]dodecane-2,8-dione[2] (**28**) (1.5 g, 7.80 mmol) was added as a powder to a stirred solution of methylenetriphenylphosphorane (13.3 mmol) in Me_2SO under dry N_2, following the procedure described for (**17**) except that the extraction solvent used was ether. Column chromatography of the crude product (alumina/pentane) first yielded 2,8-dimethylenetricyclo[5.3.1.1^{3,9}]dodecane (0.54 g, 37%), and then enone (**29**) (0.64

g, 43%), m.p. 193 °C (Found: C, 81.75; H, 9.7. $C_{13}H_{18}O$ requires C, 82.06; H, 9.54%); ν_{max}(paraffin mull) 3 060w, 1 690s, 1 630m, 1 075m, 1 015m, and 895s cm^{-1}; δ_H($CDCl_3$) 1.35–1.45 (m, 1 H), 1.55–1.70 (m, 3 H), 1.70–2.20 (m, 8 H), 2.50 (m, 1 H), 2.64 (m, 1 H), 2.72 (br s, 1 H), 2.89 (m, 1 H), 4.77 (d, 1 H), and 5.02 (d, 1 H); δ_C($CDCl_3$) 21.2 (CH_2), 21.3 (CH_2), 34.0 (CH_2), 35.7 (CH_2), 36.0 (CH_2), 36.23 (CH), 36.28 (CH), 42.9 (CH), 43.4 (CH), 112.7 (CH_2), 151.8 (C), 221.9 (C), plus one peak (CH_2) unresolved. (Spectra measured at 125.8 MHz using DEPT; Bruker AM-500 instrument).

syn-2-*Hydroxy*-2-*methyl*-8-*methylenetricyclo*[5.3.1.1^{3,9}]*dodecane* (**30**).—A solution of enone (**29**) (0.48 g, 2.51 mmol) in dry ether (10 cm^3) was added to a stirred solution of methylmagnesium iodide (5 mmol) in ether (25 cm^3). After 1 h at room temperature and then 20 min at reflux, the reaction was worked up in the usual manner. Evaporation of solvent from the dried ether extracts gave the alcohol (**30**) (0.38 g, 73%) as a waxy solid, m.p. 95 °C (slight decomp.) (Found: C, 81.55; H, 11.05. $C_{14}H_{22}O$ requires C, 81.50; H, 10.75%); ν_{max}(paraffin mull) 3 440s, 3 070w, 1 635w, 1 140m, 1 105m, 1 005w, 945w, and 890s cm^{-1}; δ_H($CDCl_3$) 1.3–1.7 (m, 10 H) including 1.40 (s, 3 H) and 1.6 (s, *ca.* 1 H, exchanged with D_2O), 1.8–2.1 (m, 8 H), 2.40 (m, 1 H), 2.75 (m, 1 H), 4.56 (d, 1 H), and 4.86 (d, 1 H); δ_C 21.5 (t), 26.2 (t), 31.5 (t), 32.7 (t), 33.6 (q), 33.9 (t), 34.5 (d), 36.6 (d), 39.0 (d), 39.1 (d), 39.3 (t), 72.8 (s), 109.7 (t), and 155.2 (s).

syn-2,anti-8-*Dihydroxy*-2,8-*dimethyltricyclo*[5.3.1.1^{3,9}]*dodecane* (**11**).—A mixture of the alcohol (**30**) (0.28 g, 1.36 mmol) in dichloromethane (6 cm^3) and aqueous sodium hydrogen carbonate (0.5 mol dm^{-3}; 3 cm^3) was stirred vigorously at 0 °C. *m*-Chloroperbenzoic acid (0.34 g) in dichloromethane (6 cm^3) was added dropwise and then stirring was continued for 1 h at room temperature. The reaction was worked up following the procedure used for (**26**). The crude epoxide product was dissolved in dry ether (10 cm^3), stirred with excess lithium aluminium hydride for 12 h at room temperature, and worked up in the customary manner. Purification of the crude product was effected by recrystallisation from benzene to give the diol (**11**) (0.20 g, 64%), m.p. 156.5–157 °C. (The material slowly decomposed to a yellow gum on prolonged standing.) (Found: C, 76.1; H, 11.1. $C_{14}H_{24}O_2$ requires C, 74.95; H, 10.78%); ν_{max}(paraffin mull) 3 480s, 1 095s, 1 070m, 1 025m, 1 000m, 935w, 905s, and 870m cm^{-1}; δ_H($CDCl_3$) 1.17–1.27 (m, 2 H), 1.33 (s, 3 H), 1.38 (s, 3 H), 1.40–1.77 (m, 8 H), 1.90–2.17 (m, 7 H), and 2.28 (m, 1 H); δ_C($CDCl_3$) 22.9 (t), 25.2 (t), 28.1 (t), 28.1 (q), 30.2 (t), 31.5 (t), 31.8 (t), 34.3 (q), 38.7 (d), 39.1 (d), 39.5 (d), 39.6 (d), 75.0 (s), and 75.6 (s). Small cubic blocks from ethyl acetate were used for X-ray analysis.

Crystallography.—Crystals of (**5**) suitable for diffraction studies were obtained from THF, while those for (**6**)–(**9**) and (**11**) were grown from ethyl acetate. Diol (**10**) was crystallised from diethyl ether.

Diffraction for all seven compounds were recorded using an Enraf-Nonius CAD4 diffractometer. Table 6 contains details of the crystals used, the diffractometry conditions, the lattice dimensions, space groups and intensity data collection and final residuals. The procedures used for the collection and reduction of the intensity data have been described.[20] Extinction corrections were made by the method of Larson.[21] Weights, $w = 1/\sigma^2(F_0)$, were assigned to individual reflections with $\sigma(F_0)$ being derived from $\sigma(I_0) = [\sigma^2(I_0) + (0.04I_0)^2]^{\frac{1}{2}}$.

The structures of (**5**)–(**9**) and (**11**) were solved by direct methods using the program MULTAN. For (**5**) this was only accomplished after changing from space group $P2/c$ to the non-centrosymmetric equivalent, Pc. In (**5**)–(**8**) and (**11**) there are two molecules, labelled A and B, in the asymmetric unit. (**9**) contains a single molecule in the asymmetric unit. The atom labelling scheme is given in (**II**), with the prime indicating approximate twofold symmetry. This atom labelling is the same as that used previously for diols (**1**)–(**4**) where the prime indicated exact twofold symmetry. All hydrogen atoms were labelled according to the atom to which they were bonded.

The crystal of (**10**) studied had space group *Fddd* (second setting) with one half a formula unit per asymmetric unit of the crystal cell. Structure solution (MULTAN) and subsequent anisotropic refinement with inferred H atom positions rapidly converged to a poor value of $R = 0.14$ and the resulting structure had unsatisfactory bond lengths and thermal parameters. A disordered structure was suspected. The structure is a hydrogen-bonded network, and the molecule has a twofold axis which at first appearance coincides with a crystallographic twofold axis parallel to the *c* axis. However it appears that crystal packing forces, dominated as they are by the hydrogen bonding, are insufficient to force an exact coincidence of the crystal and molecular twofold axes and disorder results as suggested by the high thermal motion of the carbon atoms of the $-CH_2-CH_2-$ bridge. Constrained refinement (program RAELS[22]) of such a disordered model did not improve the refinement and subsequent difference maps suggested the presence of substantial amounts of 2,7-diethyl-*anti*-2,*syn*-7-dihydroxytricyclo[4.3.1.1^{3,8}]undecane (**31**) as an impurity. Within the constraints of the hydrogen bonding which fixes the positions of the OH groups of the molecule, it is possible for a molecule of (**31**) to occupy the same location as a molecule of (**10**). This is because, in (**10**), the interchange of the $-CH_2-CH_2-$ bridge with one of the $-CH_2-$ bridges not on the twofold axis (and leaving all other atoms unchanged) produces (**31**) with the opposite chirality. (**31**) is a likely by-product of the preparation of (**10**) and it appears that recrystallisation as a purification technique did not work in this instance. (**31**) does not have a twofold symmetry axis and disorder is implicit for this molecule. It would appear that two orientations of (**10**) and two orientations of (**31**) of unequal occupancies are required to describe fully the electron density and it was not possible to refine such a complicated superposition of molecules. The study of a crystal from further attempts at purification produced no better results. However, the hydrogen bonding network locating O atoms at 0.248, 0.162, 0.154 and its equivalents with O–H···O distances of 2.73 and 2.67 Å is essentially correct.

Structure (**9**) was refined using full matrix methods. All other structures [except (**10**)] were refined by block diagonal least squares. In each case, the non-hydrogen atoms were refined with anisotropic thermal parameters. The procedure adopted for the treatment of hydrogen atoms in the refinement of each structure is given below.

Refinement of (**5**). Alkyl hydrogen atoms were included in calculated positions and were not refined. Hydroxy hydrogen atoms were located in a difference map and their positions were refined. The temperature factors of all hydrogen atoms were maintained at the isotropic equivalent of those of the atom to which they were bonded.

Refinement of (**7**). Hydrogen atoms were included in calculated positions with methyl hydrogen atoms assuming a staggered configuration. The positions of all hydrogen atoms were varied but their isotropic temperature factors were held equivalent to those of the atom to which they were bonded.

Refinement of (**6**), (**8**), (**9**), *and* (**11**). Hydrogen atoms were included in the positions at which they occurred on a difference map. They were not refined. Their temperature factors were held at the isotropic equivalent of the atoms to which they were bonded. In (**6**) and (**9**) the hydroxy hydrogen atoms were disordered and each was included in two positions of equal

Table 6. Crystallographic details for (**5**)–(**11**).

	(**5**)	(**6**)	(**7**)	(**8**)	(**9**)	(**10**)	(**11**)
Formula	$C_{11}H_{20}O_2$	$C_{10}H_{18}O_2S$	$C_{12}H_{20}O_2$	$C_{11}H_{18}O_2S$	$C_{15}H_{26}O_2$	$C_{15}H_{26}O_2$	$C_{14}H_{24}O_2$
M	184.3	202.3	196.17	214.3	238.4	238.4	224.3
F(000)	408	880	1 728	1 856	1 056	2 112	992
Crystal description	(001)(20–3)(–101) (010)(0–12)	{10–2}(001)(02–7) (0–2–5)		{001}{102}{010}	{001}{112}{100} {1–12}{–1–11}	{001}{11–3}	{100}{110} {1–12}{01–1}
Space group	*Pc*	*P*2$_1$/*c*	*Pbca*	*Pbca*	*C*2/*c*	*Fddd*	*P*2$_1$/*c*
a/Å	7.286 2(9)	7.278(3)	11.826 5(9)	11.905(1)	11.466(2)	10.516 6(7)	12.473(2)
b/Å	7.280 9(4)	7.281(2)	13.727 1(9)	13.700(2)	10.472(1)	11.643 1(9)	13.058(1)
c/Å	19.910(2)	40.42(1)	25.936(2)	26.069(2)	21.614(3)	43.642(3)	15.449(3)
β/°	99.170(6)	97.39(2)	90	90	91.400(6)	90	92.13(9)
V/Å^3	1 042.7(2)	2 124(1)	4 210.5(5)	4 251.8(9)	2 594.4(5)	5 343.7(6)	2 514.4(7)
T/°C	21(1)	21(1)	21(1)	21(1)	21(1)	21(1)	21(1)
Z	4	8	16	16	8	16	8
D_{calc}/g cm^{-3}	1.17	1.26	1.24	1.34	1.22	1.19	1.19
λ/Å	Cu–K_α, 1.5418	Mo–K_α, 0.710 69	Cu–K_α, 1.5418	Cu–K_α, 1.5418	Cu–K_α, 1.5418	Cu–K_α, 1.541 8	Cu–K_α, 1.5418
μ/cm^{-1}	5.85	2.60	6.57	24.3	5.75	5.58	5.66
Crystal dimensions	0.14 × 0.24 × 0.35	0.2 × 0.1 × 0.1		0.25 × 0.38 × 0.15	0.21 × 0.20 × 0.11	0.25 × 0.23 × 0.31	0.09 × 0.25 × 0.25
Scan mode	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ	θ/2θ
$2\theta_{max}$/°	140	50	140	140	120	140	120
No. of intens. meas.	3 768	4 408	4 488	4 652	2 102	1 440	4 123
Criterion for obsd. reflections	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No of independent obsd. reflections	1 969	2 402	3 495	2 815	1 244	473	2 161
No of refl. (*m*), variables (*n*) in final refinement	1 969, 245	2 402, 235	3 495, 374	2 815, 254	1 244, 154		2 161, 290
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_o\rvert$	0.032	0.047	0.042	0.040	0.067		0.085
$R_w = [\Sigma^m w\lvert\Delta F\rvert^2/\Sigma^m w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.040	0.066	0.066	0.055	0.095		0.102
$s = [\Sigma^m w\lvert\Delta F\rvert^2/(m-n)]^{\frac{1}{2}}$	1.75	2.07	2.49	1.72	2.94		3.10
Crystal decay	1–0.93	1–0.95	none	1 to 0.94	1 to 0.93		1 to 0.95
Max/min. transmission coefficient	0.93, 0.81	0.97, 0.96		0.73, 0.43	0.94, 0.90	0.90, 0.88	0.95, 0.84
Extinction coefficient	6.0 × 10^{-4}	8.6 × 10^{-6}	1.1 × 10^{-6}	8.6 × 10^{-6}	—		
Largest peak in final difference map/*e* Å^{-3}	0.1	0.2	0.3	0.3	0.5		

Table 7. Atomic co-ordinates (with standard deviations in parentheses.)

Atom	*x/a*	*y/b*	*z/c*
endo-2,*endo*-6-Dihydroxy-2,6-dimethylbicyclo[3.3.1]nonane (**5**)			
O(A)	0.0682	0.196 6(2)	0.0497
C(1A)	0.101 8(4)	0.533 8(4)	0.195 1(1)
C(2A)	0.032 1(4)	0.367 1(3)	0.152 2(1)
C(3A)	0.156 6(4)	0.330 3(3)	0.097 4(1)
C(4A)	0.183 7(4)	0.501 8(3)	0.055 7(1)
C(5A)	0.214 7(4)	0.680 0(3)	0.096 7(1)
C(6A)	0.344 3(4)	0.250 4(4)	0.130 1(2)
O(′A)	−0.133 4(3)	0.889 8(2)	0.071 5(1)
C(2′A)	0.084 7(4)	0.704 4(3)	0.149 6(1)
C(3′A)	−0.120 4(4)	0.743 0(3)	0.120 6(1)
C(4′A)	−0.218 7(4)	0.573 5(3)	0.086 2(1)
C(5′A)	−0.175 2(4)	0.394 9(3)	0.125 3(1)
C(6′A)	−0.222 6(5)	0.815 0(4)	0.176 8(2)
O(B)	0.875 0(3)	−0.191 7(2)	−0.063 9(1)
C(1B)	0.492 5(4)	0.017 2(4)	−0.193 4(1)
C(2B)	0.677 0(4)	0.008 9(3)	−0.144 3(1)
C(3B)	0.719 2(4)	−0.189 2(3)	−0.118 3(1)
C(4B)	0.556 9(4)	−0.275 0(3)	−0.089 5(1)
C(5B)	0.366 7(4)	−0.240 7(3)	−0.132 6(2)
C(6B)	0.774 1(5)	−0.308 6(4)	−0.175 5(2)
O(′B)	0.189 3(3)	0.016 7(2)	−0.057 9(1)
C(2′B)	0.334 7(4)	−0.040 9(3)	−0.155 6(1)
C(3′B)	0.313 9(4)	0.097 0(3)	−0.098 8(1)
C(4′B)	0.499 9(4)	0.135 5(3)	−0.052 3(1)
C(5′B)	0.667 9(4)	0.154 3(3)	−0.088 8(1)
C(6′B)	0.227 9(4)	0.275 9(4)	−0.128 6(2)
endo-2-,*endo*-6-Dihydroxy-2,6-dimethyl-9-thiabicyclo[3.3.1]nonane (**6**)			
S(A)	0.711 4(1)	0.465 5(1)	0.477 5(0)
O(A)	0.336 0(3)	0.264 9(3)	0.404 3(1)
O(′A)	1.030 3(3)	0.483 8(4)	0.404 0(1)
C(2A)	0.517 5(5)	0.457 6(5)	0.444 7(1)
C(3A)	0.486 2(4)	0.261 7(5)	0.431 3(1)
C(4A)	0.651 6(5)	0.181 2(5)	0.416 9(1)
C(5A)	0.840 1(5)	0.208 6(5)	0.437 4(1)
C(6A)	0.426 6(6)	0.137 3(6)	0.458 1(1)
C(2′A)	0.882 7(5)	0.401 9(5)	0.450 7(1)
C(3′A)	0.901 3(5)	0.553 5(5)	0.425 0(1)
C(4′A)	0.719 7(5)	0.594 5(5)	0.402 5(1)
C(5′A)	0.544 2(5)	0.607 0(5)	0.419 0(1)
C(6′A)	0.981 7(6)	0.727 9(6)	0.441 5(1)
S(B)	0.087 9(1)	0.004 0(2)	0.271 5(0)
O(B)	0.148 8(3)	−0.339 0(3)	0.350 2(1)
O(′B)	0.360 6(4)	0.355 2(3)	0.338 4(1)
C(2B)	0.180 8(5)	−0.177 6(5)	0.299 7(1)
C(3B)	0.059 7(4)	−0.205 4(5)	0.327 8(1)
C(4B)	0.038 9(5)	−0.030 9(5)	0.348 5(1)
C(5B)	0.007 2(5)	0.150 8(5)	0.330 0(1)
C(6B)	−0.130 4(5)	−0.280 4(6)	0.313 6(1)
C(2′B)	0.128 1(5)	0.185 4(5)	0.302 6(1)
C(3′B)	0.336 8(5)	0.212 1(5)	0.313 0(1)
C(4′B)	0.433 1(5)	0.040 6(5)	0.328 8(1)
C(5′B)	0.385 7(5)	−0.141 7(5)	0.310 0(1)
C(6′B)	0.435 8(6)	0.283 0(6)	0.284 4(1)
2,6-Dihydroxy-2,6-dimethyltricyclo[3.3.1.$1^{3,7}$]decane (**7**)			
O(A)	0.058 3(1)	0.363 7(1)	0.782 3(0)
O(′A)	0.405 0(1)	0.255 4(1)	0.654 1(0)
O(B)	0.170 7(1)	0.437 6(1)	0.871 2(0)
O(′B)	0.408 2(1)	0.766 5(1)	0.911 0(0)
C(1A)	0.114 1(1)	0.371 6(1)	0.639 4(1)
C(2A)	0.063 3(1)	0.337 8(1)	0.690 8(1)
C(3A)	0.103 4(1)	0.403 9(1)	0.735 0(1)
C(4A)	0.233 5(1)	0.398 6(1)	0.736 7(0)
C(5A)	0.283 8(1)	0.432 5(1)	0.685 4(1)
C(6A)	0.058 6(2)	0.507 8(1)	0.730 5(1)
C(1′A)	0.270 5(1)	0.293 6(1)	0.746 8(1)
C(2′A)	0.244 0(1)	0.366 0(1)	0.641 9(1)
C(3′A)	0.282 6(1)	0.260 7(1)	0.651 5(1)
C(4′A)	0.230 3(1)	0.227 2(1)	0.703 0(1)

Table 7 (*continued*)

Atom	*x/a*	*y/b*	*z/c*
2,6-Dihydroxy-2,6-dimethyltricyclo[3.3.1.$1^{3.7}$]decane (**7**)			
C(5′A)	0.100 2(1)	0.232 6(1)	0.700 7(1)
C(6′A)	0.254 9(2)	0.193 1(1)	0.606 7(1)
C(1B)	0.206 0(1)	0.608 8(1)	0.984 9(1)
C(2B)	0.219 3(1)	0.515 0(1)	0.952 9(1)
C(3B)	0.149 5(1)	0.521 7(1)	0.903 0(1)
C(4B)	0.193 3(1)	0.610 3(1)	0.872 6(1)
C(5B)	0.180 1(1)	0.703 9(1)	0.904 2(1)
C(6B)	0.022 5(1)	0.525 7(1)	0.913 2(1)
C(1′B)	0.318 8(1)	0.596 5(1)	0.859 8(1)
C(2′B)	0.249 3(1)	0.696 3(1)	0.953 8(1)
C(3′B)	0.375 4(1)	0.683 3(1)	0.941 2(1)
C(4′B)	0.387 8(1)	0.589 2(1)	0.909 4(1)
C(5′B)	0.344 8(1)	0.501 1(1)	0.940 4(1)
C(6′B)	0.449 9(2)	0.684 4(1)	0.989 4(1)
anti-4,*anti*-8-Dihydroxy-4,8-dimethyl-2-thiatricyclo[3.3.1.$1^{3.7}$]-decane (**8**)			
S(A)	0.101 4(1)	0.375 5(1)	0.128 3(0)
O(A)	0.055 8(2)	0.361 9(2)	0.281 2(1)
O(′A)	0.404 2(2)	0.249 9(2)	0.155 3(1)
C(2A)	0.056 6(2)	0.333 3(2)	0.191 5(1)
C(3A)	0.099 9(2)	0.401 2(2)	0.233 8(1)
C(4A)	0.228 9(2)	0.395 4(2)	0.235 3(1)
C(5A)	0.284 0(2)	0.431 0(2)	0.184 6(1)
C(6A)	0.056 4(3)	0.504 9(3)	0.228 7(1)
C(1′A)	0.266 1(2)	0.290 6(2)	0.245 2(1)
C(2′A)	0.251 3(2)	0.363 8(2)	0.140 1(1)
C(3′A)	0.283 3(2)	0.256 8(2)	0.150 7(1)
C(4′A)	0.227 5(2)	0.224 6(2)	0.201 7(1)
C(5′A)	0.098 6(3)	0.228 5(2)	0.199 1(1)
C(6′A)	0.256 7(3)	0.190 0(2)	0.106 1(1)
S(B)	0.192 0(1)	0.608 2(1)	0.494 0(0)
O(B)	0.167 1(2)	0.433 0(1)	0.369 4(1)
O(′B)	0.407 7(2)	0.760 8(1)	0.407 5(1)
C(2B)	0.215 3(2)	0.505 0(2)	0.451 1(1)
C(3B)	0.145 5(2)	0.516 7(2)	0.401 6(1)
C(4B)	0.191 1(2)	0.605 5(2)	0.371 8(1)
C(5B)	0.177 5(2)	0.701 2(2)	0.401 3(1)
C(6B)	0.019 7(3)	0.521 9(2)	0.411 8(1)
C(1′B)	0.315 1(2)	0.591 0(2)	0.359 3(1)
C(2′B)	0.248 1(2)	0.700 1(2)	0.450 6(1)
C(3′B)	0.372 9(2)	0.680 4(2)	0.439 2(1)
C(4′B)	0.382 7(2)	0.584 5(2)	0.408 9(1)
C(5′B)	0.340 7(2)	0.495 8(2)	0.439 8(1)
C(6′B)	0.446 4(3)	0.682 9(3)	0.486 9(1)
syn-2,*syn*-7-Dihydroxy-2,7-dimethyltricyclo[4.3.1.$1^{3.8}$]undecane (**9**)			
O	0.478 2(3)	0.200 6(3)	0.178 3(1)
O(′)	0.057 5(3)	−0.027 8(3)	0.189 4(2)
C(1)	0.233 2(4)	0.126 0(4)	0.063 6(2)
C(2)	0.312 5(4)	0.204 7(4)	0.106 1(2)
C(3)	0.414 4(4)	0.123 6(4)	0.133 6(2)
C(4)	0.370 5(4)	0.001 7(4)	0.165 1(2)
C(5)	0.274 5(4)	−0.066 9(4)	0.125 0(2)
C(6)	0.504 3(5)	0.083 1(5)	0.085 2(3)
C(7)	0.557 4(6)	0.183 4(6)	0.048 5(3)
C(8)	0.331 6(5)	0.015 0(5)	0.230 9(2)
C(2′)	0.175 7(4)	0.020 7(4)	0.101 3(2)
C(3′)	0.098 5(4)	0.077 8(4)	0.151 7(2)
C(4′)	0.166 1(4)	0.172 9(4)	0.194 3(2)
C(5′)	0.237 2(4)	0.266 9(4)	0.155 0(2)
C(6′)	−0.008 4(4)	0.145 6(4)	0.124 6(2)
C(7′)	−0.090 6(5)	0.066 6(5)	0.083 1(3)
C(8′)	0.240 6(5)	0.115 0(5)	0.245 8(2)
syn-2,*anti*-8-Dihydroxy-2,8-dimethyltricyclo[5.3.1.$1^{3,9}$]dodecane (**11**)			
O(1A)	0.784 2(4)	0.298 4(4)	0.594 0(2)
O(1′A)	0.865 0(3)	0.132 1(3)	0.261 4(2)
C(1A)	0.906 0(5)	0.152 0(5)	0.503 9(4)
C(2A)	0.939 3(5)	0.265 2(5)	0.509 7(4)
C(3A)	0.837 6(5)	0.332 0(5)	0.516 0(4)

Table 7 (*continued*)

Atom	*x*/*a*	*y*/*b*	*z*/*c*
syn-2,*anti*-8-Dihydroxy-2,8-dimethyltricyclo[5.3.1.$1^{3,9}$]dodecane (**11**)			
C(4A)	0.754 9(5)	0.313 9(5)	0.444 5(4)
C(5A)	0.746 4(6)	0.199 0(5)	0.417 0(4)
C(6A)	0.868 4(6)	0.443 6(5)	0.530 7(4)
C(7A)	0.753 0(6)	0.389 1(5)	0.364 6(4)
C(8A)	0.807 0(6)	0.354 2(5)	0.282 0(4)
C(2′A)	0.847 7(5)	0.134 9(4)	0.418 6(3)
C(3′A)	0.920 4(5)	0.148 0(4)	0.342 0(3)
C(4′A)	0.976 9(4)	0.253 0(5)	0.340 1(4)
C(5′A)	1.011 3(5)	0.289 5(5)	0.434 4(4)
C(6′A)	1.011 8(6)	0.065 1(6)	0.348 2(4)
C(7′A)	0.923 7(5)	0.336 2(5)	0.284 6(4)
O(1B)	0.591 3(3)	0.357 1(3)	0.672 5(3)
O(1′B)	0.310 5(3)	0.015 7(3)	0.719 2(3)
C(1B)	0.455 6(5)	0.259 8(5)	0.785 5(4)
C(2B)	0.415 8(5)	0.326 3(5)	0.711 7(4)
C(3B)	0.491 1(5)	0.317 6(4)	0.636 9(4)
C(4B)	0.511 8(5)	0.205 5(5)	0.606 2(4)
C(5B)	0.517 7(5)	0.128 8(5)	0.684 0(4)
C(6B)	0.458 8(7)	0.387 3(5)	0.563 1(5)
C(7B)	0.444 8(6)	0.165 7(5)	0.529 1(4)
C(8B)	0.345 4(7)	0.102 8(6)	0.542 2(4)
C(2′B)	0.441 6(5)	0.147 6(5)	0.758 6(4)
C(3′B)	0.324 8(6)	0.120 3(5)	0.746 8(4)
C(4′B)	0.261 5(5)	0.189 4(5)	0.680 8(4)
C(5′B)	0.299 7(6)	0.304 2(5)	0.692 7(4)
C(6′B)	0.269 0(6)	0.128 8(6)	0.834 3(4)
C(7′B)	0.254 8(6)	0.154 6(6)	0.585 9(5)

occupancy. In (**9**), disorder of the hydroxy hydrogen atoms was required by space-group symmetry.

Anomalous scattering was included for C, O and S [for (**6**) and (**8**)]. An extinction correction[21] was included in the refinement of (**5**)–(**8**). Full lists of bond lengths, bond angles, hydrogen atom co-ordinates and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC).* Selected atomic parameters are given in Table 7.

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