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2,7-Dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol as a Host for Volatile and Odorous Guest Molecules

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Abstract: The title compound **1** forms two different classes of lattice inclusion compound: helical tubulates where the guests are contained in parallel canals, and ellipsoidal clathrates with each guest enclosed in a discrete cavity. Formation of these lattice types can be predicted since they are dependent on the size and shape of the guest molecule. This paper presents a preliminary investigation on the ability of **1** to act as a host for low boiling or odorous guests. The preparation and crystal structure of the helical tubulate $(\mathbf{1})_3\cdot(CBr_2F_2)$ and the ellipsoidal clathrate $(\mathbf{1})_4\cdot(CS_2)$ are described. Since the cavity of the ellipsoidal clathrate class is a cage formed by two interpenetrating sublattices this family of inclusion compounds has considerable potential as a chemical storage system.

2,7-Dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol **1** is a member of a family of alicyclic diols termed the helical tubulands.[1] These compounds crystallise as conglomerates[2] in the trigonal space group $P3_121$ (or enantiomorph $P3_221$) with a helical hydrogen bonded structure and forming a lattice containing parallel canals. In many cases these canals have a substantial cross-sectional area allowing the host lattice to enclose guest molecules.[3-5]

Diol **1** is unusual amongst this family of hosts in also forming a second type of lattice inclusion compound which we term the ellipsoidal clathrate type. Here the host lattice contains both diol enantiomers and is achiral in tetragonal space group $I4_1/acd$. The host arrangement now comprises a superlattice constructed from two interpenetrating sublattices which are inversion related. The guests occupy ellipsoidal shaped cavities between the sublattices.[6]

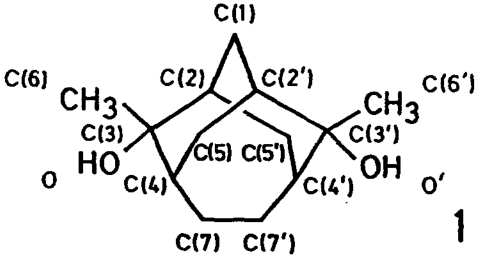

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Figure 1. Structure of the host diol **1** and the crystallographic numbering system used.

When diol **1** is obtained guest free its crystal structure shows that it has packing problems. It has a layer arrangement with three independent diol molecules in the asymmetric unit. Two of these have incomplete hydrogen bonding between the hydroxy groups and, furthermore, one diol molecule is disordered with a minor component of 17.6% occupancy which has a different hydrogen bonding arrangement.[7]

In contrast, both types of inclusion lattice exhibit full hydrogen bonding (one donor and one acceptor per hydroxy group). We have postulated that the guest plays a pivotal role in the choice of lattice type.[6] First of all, a small guest molecule will stabilise the tetragonal ellipsoidal clathrate structure over the guest free structure. Presumably it causes an increase in the packing density and van der Waals interactions between the two independent sublattices. However, when the guest exceeds a certain size or shape the trigonal helical tubulate structure is observed. Presumably the larger guest would now separate the sublattices sufficiently to reduce intermolecular attractions at this location, and it may also press them too close elsewhere in the structure.[8] Above this critical limit the helical tubulate structure results until, in turn, the guest is too large to fit in the canal whereupon the guest free diol is obtained.[6] Support for these ideas is provided by experimental evidence, for example the change in structural type observed along a series of related guests[9]:

CH_2Cl_2 (ellipsoidal clathrate)	$CHCl_3$ (ellipsoidal clathrate *and* helical tubulate)	CCl_4 (helical tubulate)
C_6H_5Cl (ellipsoidal clathrate)	C_6H_5Br (ellipsoidal clathrate *and* helical tubulate)	C_6H_5I (helical tubulate)

Since the size and shape of the guest determine the type of inclusion lattice produced, the diol **1** is therefore of special interest as a host for small guest molecules. These will be trapped in an ellipsoidal cavity between two interpenetrating sublattices of the host providing a stable environment for the combination. Thus diol **1** has considerable potential for entrapment and storage of small or volatile guests.[10] This paper describes preliminary work in demonstrating the validity of these concepts.

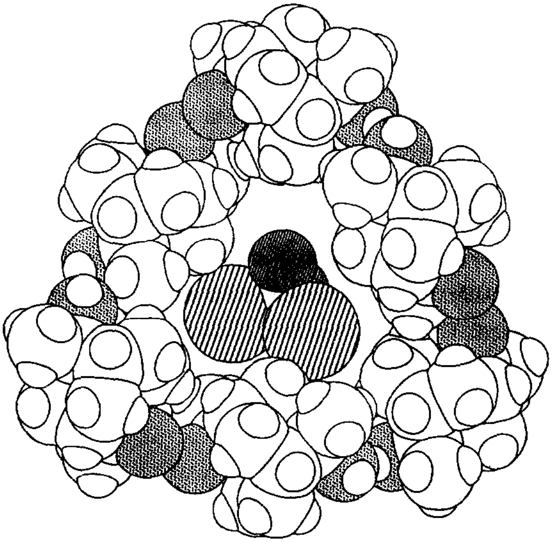

Figure 2. A section across one canal only of the helical tubulate inclusion compound $(\mathbf{1})_3\cdot(CBr_2F_2)$ showing the three-lobed cross-section of the canal with the dibromodifluoromethane guest situated along one face of the canal. The two bromine atoms locate towards two of the lobes with the fluorine atoms situated near the centre of the canal.

The first guest investigated was a volatile polyhaloalkane. Needle crystals obtained by slow evaporation of a solution of diol **1** in warm dibromodifluoromethane (b.p. 22-23 °C) were suitable for structural investigation by single crystal X-ray methods. Numerical details of the solution and refinement of this structure are presented in Table 1. The crystallographic numbering system for **1** is shown in Figure 1. Bond lengths and angles are shown in Table 2, and atomic positional parameters for the structure are given in Table 3 (see Experimental).

As anticipated from the size and shape of the guest species, the material obtained from this experiment had the helical tubulate lattice and was found to have the composition $(1)_3{\cdot}(CBr_2F_2)$. Figure 2 shows a slice across one canal only of this structure with the guest located along one wall of the trefoil-shaped canal. Crystals of this inclusion compound were relatively unstable and most had turned opaque after standing for several days at the ambient temperature (which was roughly equal to the b.p. value of the guest).

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

Formula, formula mass	$(C_{13}H_{22}O_2)_3{\cdot}(CBr_2F_2)$, 840.8	$(C_{13}H_{22}O_2)_4{\cdot}(CS_2)$, 917.4
Crystal description	{100}{001}	{100}{010}(00-1)(1-12)
Space group	$P3_221$	$I4_1/acd$ (Origin at $\bar{1}$)
a, b/ Å	13.240(1)	23.031(2)
c/ Å	6.906(1)	18.773(3)
V/ Å^3	1048.5(2)	9958(2)
Temp./ °C	21(1)	21(1)
Z	1	8
$D_{calc.}$/ g cm^{-3}	1.33	1.22
Radiation, λ/ Å	CuKα, 1.5418	CuKα, 1.5418
μ / cm^{-1}	28.7	13.43
Crystal dimensions/ mm	0.12 x 0.12 x 0.36	0.16 x 0.16 x 0.34
Scan mode	$\theta/2\theta$	$\theta/2\theta$
$2\theta_{max.}$/ °	140	120
ω scan angle	0.60 + 0.15tan θ	0.60 + 0.15tan θ
No. of intensity measurements	3957	4049
Criterion for observed reflection	$I/\sigma(I) > 3$	$I/\sigma(I) > 3$
No. of independent obsd. reflections	972	1258
No. of reflections (m) and variables (n) in final refinement	972, 99	1258, 169
$R = \Sigma^m\lvert\Delta F\rvert/\Sigma^m\lvert F_o\rvert$	0.073	0.046
$R_w = [\Sigma^m w\lvert\Delta F\rvert^2/\Sigma^m w\lvert F_o\rvert^2]^{1/2}$	0.091	0.054
$s = [\Sigma^m w\lvert\Delta F\rvert^2/(m-n)]^{1/2}$	4.00	2.36
Crystal decay	1 to 0.80	none
Max., min. transmission coefficients	0.79, 0.53	0.83, 0.74
Largest peak in final diff. map/ e Å^{-3}	0.82	0.28
R for (multiple) measurements	0.022 (2630)	0.016 (1085)

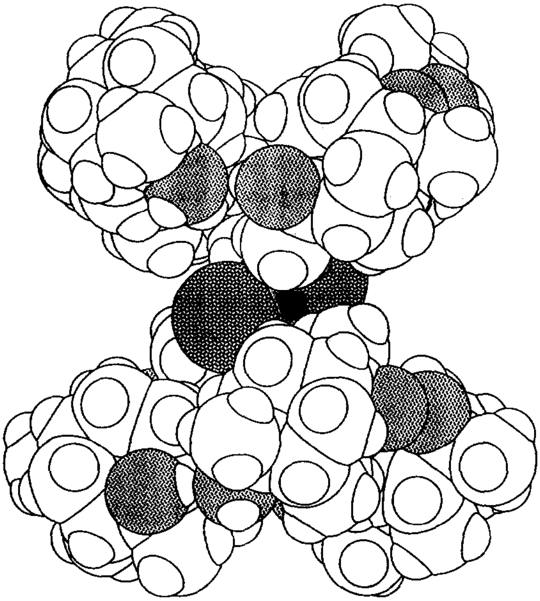

Figure 3. Arrangement of the major orientation of the carbon disulfide guest in structure $(\mathbf{1})_4\cdot(CS_2)$ viewed along *b*. The molecule occupies an ellipsoidal shaped cavity created from two adjacent cyclic quartets of the diol. In this view, with the *c* axis vertical, the top quartet of diols is from one sublattice and the bottom quartet from the other. Thus the guest is wedged between the two interpenetrating sublattices.

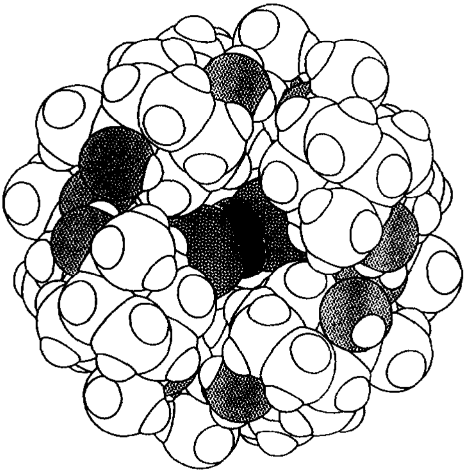

Figure 4. Projection view parallel to *c* in the structure $(\mathbf{1})_4\cdot(CS_2)$ showing the major orientation of the carbon disulfide guest in its ellipsoidal cavity between the two cyclic quartets of diol molecules. Successive cavities are orthogonal and linked by small windows through which the guest can be seen in this figure.

The second guest investigated was both volatile and odorous. Crystals of the inclusion compound produced on cooling a warm solution of diol **1** in carbon disulfide (b.p. 46 °C) were studied by X-ray methods. Numerical details of the solution and refinement of this structure are presented in Table 1. Bond lengths and angles for the structure are given in Table 4, and atomic positional parameters are shown in Table 5 (see Experimental).

The much smaller linear guest results this time in formation of the alternative ellipsoidal clathrate structure with composition $(\mathbf{1})_4\cdot(CS_2)$. As discussed later, refinement of this structure revealed three alternate orientations of the guest CS_2 molecule (occupancies 0.49, 0.44 and 0.07). Figures 3 and 4 illustrate the major orientation of the guest in this structure. In these Figures the upper and lower groups of diol molecules belong to the two independent and interpenetrating sublattices and it can be seen that the guest is sandwiched between these.

The best known examples of guest molecules enclosed between independent and interpenetrating sublattices are the *p*-hydroquinone clathrates whose structures were uncovered through the classical work of Powell.[8,11] This host was able to form stable combinations with a large range of small and volatile substances.

Similarly, in this study, the compound $(\mathbf{1})_4\cdot(CS_2)$ exhibited considerably greater stability than the CBr_2F_2 compound where the open tubular structure can allow loss of volatile guests. These exploratory results suggest that the ellipsoidal clathrate lattice formed by diol **1** will prove to be a versatile agent for molecular imprisonment of small, volatile, reactive, noxious or odorous guest molecules. Further work towards these ends is in progress.

EXPERIMENTAL

Preparation of Inclusion Compounds of 1

Solutions of 2,7-dimethyltricyclo[4.3.1.1^{3,8}]undecane-*syn*-2,*syn*-7-diol **1** (prepared as described previously[12]) in warm dibromodifluoromethane or carbon disulfide were allowed to cool to room temperature and undergo slow evaporation of solvent. The crystalline material produced was filtered and checked for solvent inclusion by IR (paraffin mull) spectroscopy. Suitable single crystals were then examined by X-ray crystallography.

Solution and Refinement of the Structure $(1)_3\cdot(CBr_2F_2)$

Data were recorded using an Enraf-Nonius CAD4 X-ray diffractrometer in $\theta/2\theta$ scan mode. Data collection and processing procedures have been described.[13] Corrections were made for absorption[14] and for decomposition of the crystal.

The initial positional parameters for the diol were taken from a previously determined structure with a different guest.[15] A difference Fourier synthesis computed at this stage showed one large peak. This was the appropriate distance from a symmetry related counterpart to represent the two bromine atoms of the guest molecule. A suitable position for the central carbon atom was also seen on the map, along with possible positions for the fluorine atoms. A rigid group representing the CBr_2F_2 molecule was overlaid on these peaks. This model was refined using the program RAELS.[16] The atoms of the host diol were refined anisotropically and the position and orientation of the rigid group was refined. A single 12 parameter TL group (where T is the translational tensor and L is the librational tensor) was used to define the thermal motion of the guest. Refinement showed that the incorrect enantiomer had been selected. When the coordinates of the atoms were transformed to $-x,-y,-z$ and the space group was changed to $P3_221$, there was an improvement in the R factor. The occupancy of the guest molecule was refined and converged to about 0.16. It was therefore set at 0.1667 (representing one molecule of CBr_2F_2 per unit cell). In the final refinement, the atoms of the guest molecule were refined individually, with slack constraints ensuring that the geometry remained reasonable. Reflection weights used for refinement were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual was defined as $R_w=(\Sigma w\Delta^2/\Sigma wF_o{}^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[17] Methyl and methylene hydrogen atoms were included in calculated positions with isotropic temperature factors set equal to those of the atoms to which they were bonded. The hydroxy hydrogen position was taken from a difference Fourier and its position was refined. The final residual was 0.073. The R factor for the other enantiomer was 0.075. When the guest was omitted $R = 0.199$ (and for data with $\sin\theta/\lambda < 0.1$, R rose from 0.042 to 0.538). The largest peak in the final difference map was 0.82 e Å^{-3}. A DEC Alpha AXP workstation was used for calculations.

Table 2. Bond Lengths (Å) and Angles (°) in Structure $(\mathbf{1})_3{\cdot}(CF_2Br_2)$.

O-C(3)	1.445(6)	C(2)-C(1)-C(2)^a	108.3(6)	C(3)-O-HO	107(3)
C(1)-C(2)	1.514(9)	C(1)-C(2)-C(3)	110.8(4)	Br(1)-C-Br(2)	109.2(15)
C(2)-C(3)	1.539(6)	C(1)-C(2)-C(5)^a	109.2(3)	Br(1)-C-F(1)	109.4(10)
C(3)-C(4)	1.548(6)	C(3)-C(2)-C(5)^a	114.4(4)	Br(1)-C-F(2)	111.5(10)
C(4)-C(5)	1.527(7)	C(2)-C(3)-O	107.0(4)	Br(2)-C-F(1)	109.4(6)
C(3)-C(6)	1.520(7)	C(2)-C(3)-C(4)	110.8(4)	Br(2)-C-F(2)	109.1(6)
O-HO	1.04(7)	C(2)-C(3)-C(6)	110.6(4)	F(1)-C-F(2)	108.3(17)
C-Br(1)	1.890(7)	O -C(3)-C(4)	112.0(4)		
C-Br(2)	1.881(9)	O -C(3)-C(6)	105.5(4)		
C(2)-C(5)^a	1.531(8)	C(4)-C(3)-C(6)	110.7(4)		
C-F(1)	1.327(17)	C(3)-C(4)-C(5)	112.2(4)		
C-F(2)	1.340(19)	C(4)-C(5)-C(2)^a	114.7(4)		

Equivalent Position Indicator: a $-x, -x+y, -1/3-z$

Table 3. Fractional Coordinates for the Non-CH Atoms of Structure $(\mathbf{1})_3{\cdot}(CF_2Br_2)$.

	x	*y*	*z*		*x*	*y*	*z*
O	0.2415(3)	-0.3997(3)	-0.1311(5)	C(7)	0.0270(5)	-0.4029(6)	-0.0678(8)
C(1)	0.0000	-0.7106(8)	-0.1667	HO	0.2868(53)	-0.3506(56)	-0.0117(95)
C(2)	0.1001(4)	-0.5937(4)	-0.2298(7)	Br(1)	-0.0427(16)	-0.1465(15)	-0.0111(39)
C(3)	0.1477(4)	-0.5087(4)	-0.0577(7)	Br(2)	-0.1427(12)	0.0071(23)	0.1230(49)
C(4)	0.0498(4)	-0.4936(5)	0.0361(7)	F(1)	0.0758(19)	0.0833(22)	0.0225(63)
C(5)	-0.0614(4)	-0.6103(5)	0.0694(7)	F(2)	0.0281(25)	-0.0050(30)	0.2991(48)
C(6)	0.2035(5)	-0.5503(6)	0.0910(9)	C	-0.0081(14)	-0.0068(18)	0.1173(36)

Solution and Refinement of the Structure $(1)_4{\cdot}(CS_2)$

Data were recorded using an Enraf-Nonius CAD4 X-ray diffractometer in $\theta/2\theta$ scan mode. Data collection and processing procedures have been described.[13] Corrections were made for absorption.[14]

For the diol molecule, coordinates from one of the previously determined structures with a different guest molecule[15] were used as input for a structure factor calculation. A difference Fourier revealed the position of the CS_2 molecule, with the carbon atom situated at the 222 site.

Reflection weights used for refinement were $1/\sigma^2(F_o)$, with $\sigma(F_o)$ being derived from $\sigma(I_o) = [\sigma^2(I_o) + (0.04I_o)^2]^{1/2}$. The weighted residual is defined as $R_w=(\Sigma w\Delta^2/\Sigma wF_o^2)^{1/2}$. Atomic scattering factors and anomalous dispersion parameters were from International Tables for X-ray Crystallography.[17] Initial refinement used BLOCKLS, a local version of ORFLS.[18] Refinement was carried out with anisotropic temperature factors for all atoms of the diol. Methyl and methylene hydrogen atoms were included in calculated positions with isotropic temperature factors set equal to those of the atoms to which they were bonded. A difference Fourier calculated at this stage revealed alternate orientions for the CS_2 molecule. The central C atom remained in the same position, but the molecule was rotated from its original position. Refinement was completed using a program (RAELS[16]) with rigid group refinement capabilities. A total of three orientations (with sulfur atoms labelled S, S' and S") were incorporated for the CS_2 molecule. The occupancy of each component was refined, with the total constrained to be one. The final values of the occupancies were 0.49, 0.44 and 0.07 for CS_2, CS'_2 and CS''_2, respectively. The C-S distances were slack constrained to be 1.55 Å, and the S-C-S angle was constrained to be 180°. A 12 parameter TL thermal model was used for the disordered CS_2 group (where T is the translational tensor and L is the librational tensor). The hydroxy hydrogen atoms of the diol were twofold disordered (in keeping with symmetry). Each component was included with half occupancy. Refinement converged with $R = 0.046$. The largest peak in the final difference map was 0.28 e Å^{-3}. A DEC Alpha AXP workstation was used for calculations.

Table 4. Bond Lengths (Å) and Angles (°) in Structure (**1**)$_4$·(CS_2).

O-C(3)	1.451(3)	O'-C(3)'	1.451(3)	C(7)-C(7)'	1.523(4)
C(1)-C(2)	1.523(4)	C(1)-C(2)'	1.537(4)	O-HO	0.93(6)
C(2)-C(3)	1.533(4)	C(2)'-C(3)'	1.537(4)	O'-HO'	0.97(6)
C(3)-C(4)	1.541(4)	C(3)'-C(4)'	1.535(4)	O-H'O	0.91(6)
C(4)-C(5)	1.537(4)	C(4)'-C(5)'	1.538(4)	O'-H'O'	0.93(5)
C(3)-C(6)	1.535(4)	C(3)'-C(6)'	1.525(4)	C-S	1.549(1)
C(4)-C(7)	1.523(4)	C(4)'-C(7)'	1.530(4)	C-S'	1.548(1)
C(2)'-C(5)	1.539(4)	C(2)-C(5)'	1.522(4)	C-S"	1.557(8)
C(1)-C(2)-C(3)	111.2(2)	C(1)-C(2)'-C(3)'	110.3(2)	C(2)-C(1)-C(2)'	108.8(2)
C(1)-C(2)-C(5)'	107.8(2)	C(1)-C(2)'-C(5)	107.8(2)	C(3)-O-HO	108(3)
C(3)-C(2)-C(5)'	114.5(2)	C(3)'-C(2)'-C(5)	114.8(2)	C(3)-O-H'O	99(4)
O-C(3)-C(2)	108.2(2)	O'-C(3)'-C(2)'	108.0(2)	C(3)'-O'-HO'	107(3)
O-C(3)-C(4)	108.5(2)	O'-C(3)'-C(4)'	108.6(2)	C(3)'-O'-H'O'	106(4)
O-C(3)-C(6)	107.2(2)	O'-C(3)'-C(6)'	107.0(2)	S-C-S[a]	179.6(1)
C(2)-C(3)-C(4)	112.0(2)	C(2)'-C(3)'-C(4)'	112.1(2)	S'-C-S'[b]	179.7(1)
C(2)-C(3)-C(6)	110.7(2)	C(2)'-C(3)'-C(6)'	110.7(2)	S"-C-S"[c]	180.0(0)
C(4)-C(3)-C(6)	110.1(2)	C(4)'-C(3)'-C(6)'	110.3(2)		
C(3)-C(4)-C(5)	112.2(2)	C(3)'-C(4)'-C(5)'	111.5(2)		
C(3)-C(4)-C(7)	115.6(2)	C(3)'-C(4)'-C(7)'	115.9(2)		
C(5)-C(4)-C(7)	111.1(2)	C(5)'-C(4)'-C(7)'	111.8(2)		
C(4)-C(5)-C(2)'	114.6(2)	C(4)'-C(5)'-C(2)	115.0(2)		
C(4)-C(7)-C(7)'	119.9(2)	C(4)'-C(7)'-C(7)	118.7(2)		

Equivalent Position Indicators: a 1 1/4-*y*, 1 1/4-*x*, 1/4-*z* b 2-*x*, 1/2-*y*, *z* c 3/4+*y*, -3/4+*x*, 1/4-*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.

Acknowledgement. We thank the Australian Research Council for financial support of this work.

Table 5. Fractional Coordinates for the Non-CH Atoms of Structure $(\mathbf{1})_4{\cdot}(CS_2)$.

	x	y	z		x	y	z
O	0.4653(1)	0.0325(1)	0.1826(1)	C(5)'	0.4518(1)	0.1201(1)	0.0741(1)
O'	0.2916(1)	0.1542(1)	0.0580(1)	C(6)'	0.3598(1)	0.1696(1)	-0.0363(2)
C(1)	0.4058(1)	0.0476(1)	-0.0038(2)	C(7)'	0.3747(1)	0.1442(1)	0.1663(2)
C(2)	0.4470(1)	0.0554(1)	0.0590(1)	HO	0.4629(22)	0.0023(29)	0.2157(25)
C(3)	0.4277(1)	0.0187(1)	0.1230(2)	H'O	0.5003(28)	0.0298(25)	0.1603(31)
C(4)	0.3645(1)	0.0315(1)	0.1446(2)	HO'	0.2938(23)	0.1957(26)	0.0662(30)
C(5)	0.3235(1)	0.0334(1)	0.0800(2)	H'O'	0.2668(22)	0.1516(21)	0.0194(29)
C(6)	0.4352(1)	-0.0463(1)	0.1071(2)	S	0.9561(1)	0.2057(1)	0.0941(4)
C(7)	0.3559(1)	0.0844(1)	0.1922(2)	S'	0.9620(3)	0.1946(2)	0.1248(1)
C(2)'	0.3455(1)	0.0704(1)	0.0173(1)	S"	1.0000	0.2500	0.0421(4)
C(3)'	0.3481(1)	0.1359(1)	0.0322(2)	C	1.0000	0.2500	0.1250
C(4)'	0.3939(1)	0.1511(1)	0.0887(2)				

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