Conformations of Methyl D-*glycero*-β-D-*gulo*-Heptopyranoside in the Solid State

F. MO,[a] Ø. BERG,[a] A. GAASDAL[a] and M. A. E. SALLAM[b]

[a] Institutt for røntgenteknikk, Universitetet i Trondheim-NTH, N-7034 Trondheim-NTH, Norway and [b] Chemistry Department, Faculty of Science, Alexandria University, Alexandria, Egypt.

The title compound, $C_8H_{16}O_7$, crystallizes in space group $P2_1$; $a=8.202(2)$, $b=9.895(4)$, $c=12.737(4)$, $\beta=100.15(4)$, $Z=4$. Counter data were collected to a limit in $\sin\theta/\lambda\sim0.756$ Å^{-1}, corrections included coincidence loss and absorption. Structure solution was by a tangent-refinement method. Full-matrix least-squares refinement based on 3656 F_o yielded $R=0.038$ and $R_w=0.035$, R was 0.030 with 2401 F_o within the Cu$K\alpha$ sphere. Two distinct molecules, A and B, in the asymmetric unit differ mainly in the arrangement of the glycero tail group, the terminal bond $C(7)-O(7)$ being oriented *gauche-trans* in one, *gauche-gauche* in the other. Details in the conformation of the $^4C_1(D)$ rings and relative stabilities of the tail-group orientation are discussed and related to other known D-*glycero*-D-*gulo*-heptopyranose structures. For pyranose rings with O(4) axial the favoured orientation of $C(6)-O(6)$ in a glycero tail is *trans-gauche*. When the tail is hydroxymethyl the preferred orientation of this bond appears to be *gauche-trans*. Structure parameters in the acetal moiety compare well with the mean values for other methyl β-D-pyranosides, the bond lengths are also in close agreement with quantum-chemical calculations. All O atoms except those in the rings contribute to H bonding, the majority both as donors and acceptors. There is no direct H bond between molecules A and B in the asymmetric unit.

D-*glycero*-D-*gulo*-Heptose is a homomorph of D-gulose and the two compounds are closely related chemically.[1,2] The structural analogy of the heptose with D-gulose is manifested by nearly identical NMR spectra in the anomeric region; a similar relationship holds for methyl D-*glycero*-D-*gulo*-heptopyranoside and methyl D-*gulo*-pyranoside.[2] The D-*glycero*-D-*gulo*-heptose and methyl D-*glycero*-D-*gulo*-heptoside have been used as model com-

pounds for the corresponding hexoses in studies of chemical reactions and equilibria,[3,4] as they are more readily prepared and purified than their lower homomorphs.

The configuration of D-*glycero*-D-*gulo*-hepto-pyranoside is enantiomeric to that of the L-*gulo*-pyranosyl group present in L-guluronic acid, one of the monomer constituents of alginic acid polysaccharide in brown algae. The D-aldo-heptose moiety was studied recently in two related compounds.[5,6] This makes it feasible to analyze in some detail the gulopyranose ring structure and the conformational freedom of the glycero tail group. In general, detailed studies of mono- and oligomers of the uronic acid constituents, their derivatives and enantiomers may provide knowledge of relevance to the structure and properties of the parent polyuronides, such as chain conformation and the binding of divalent cations.

Methyl D-*glycero*-D-*gulo*-heptopyranoside can be obtained from D-*glycero*-D-*gulo*-heptose by direct Fischer glycosidation with methanol and hydrogen chloride.[1,4] For the present study it was prepared by the Fischer method using methanol and strongly acidic ion exchange resin (Amberlite IR-120(H$^+$)).[7] The α and β anomers were separated from the glycosidation mixture as described previously.[8] The β glycoside was crystallized from ethanol and its crystal structure is reported here. The α anomer forms orthorhombic crystals from ethanol-2-propanol.

EXPERIMENTAL

Single crystals of methyl D-*glycero*-β-D-*gulo*-heptopyranoside (MeβGG) were prismatic with pairs of

Table 1. Crystal data, methyl D-*glycero*-β-D-*gulo*-heptopyranoside, $C_8H_{16}O_7$.

$a(\text{Å})$	8.202(2)	Space group	$P2_1$
b	9.895(4)	$\lambda(\text{Å})$	0.71069
c	12.737(4)	Z	4
$\beta(°)$	100.15(3)	$D_x(\text{Mgm}^{-3})$	1.464
$V(\text{Å}^3)$	1017.5	$\mu(\text{mm}^{-1})$	0.121[a]
F.W.	224.21	Size (mm^3)	$\sim 0.60 \times 0.48 \times 0.18$

[a] Mass absorption coefficients taken from *International Tables for X-Ray Crystallography* (1974).

prism faces (011), (01$\bar{1}$), and (001), and base planes (10$\bar{1}$).

Cell dimensions (Table 1) were determined from the setting angles of 19 reflexions. Measurements before, during and after the data collection showed no parameter changes exceeding 2σ. Intensities were measured with Nb-filtered Mo$K\alpha$ radiation on a computer-controlled diffractometer to a limit in $\sin\theta/\lambda = s \sim 0.756$ Å^{-1} ($2\theta_{max} = 65°$). The scan mode was $\omega/2\theta$ at 1° min^{-1} in 2θ, basic scan width was 1.44° and backgrounds were measured for 20 s at each end of the scan. Intensities below $2\theta = 9.5°$ were measured semi-manually with reduced low-angle scans to minimize errors caused by the NbK absorption edge. A set of 4092 reflexions ($hk\pm l$) was collected not including systematic extinctions. Three standard reflexions were monitored every 80 reflexions. The intensities were scaled according to the average standard curve and corrected for coincidence loss and absorption at data reduction time. The experimental recovery constant with this crystal was 4.2×10^{-8} counts^{-1}, absorption factors were in the range 1.019 to 1.064.

Weighted averages (w) of F^2 and $\sigma(F^2)$ were calculated for 223 equivalent pairs $0k\pm l$; $\sigma(F_i^2) = \sigma(I_i)$ (Lp)$^{-1}$ (scale) where $\sigma^2(I_i) = \sigma^2_{i\,count} + (SI_{i\,net})^2$ and $i = 1, 2$. Assuming a normal distribution of the weighted mean of the differences $\Delta_i = |F_i^2 - F_w^2|$ the parameter S was determined as 0.02 following a frequency test of $z = \Delta_w/\sigma_w$. Of 3869 unique reflexions, one was deleted because the NbK edge interfered with the peak itself. 212 reflexions were given zero weight: 209 with $F^2 < \sigma(F^2)$, one due to very uneven backgrounds and two because counting rates were beyond the range for coincidence-loss correction.

The crystallographic calculations were carried out with programs both of local origin and from the X-RAY 76 system.[9] Molecular drawings were made with ORTEP.[10]

STRUCTURE DETERMINATION AND REFINEMENT

The structure was solved by a local phasing program.[11] The E map of the best phase model showed the 30 non-H atoms of two distinct molecules, A and B, in the asymmetric unit. Full-matrix least-squares refinement of positional and isotropic, later anisotropic, thermal parameters based on the 2401 F_o within the Cu$K\alpha$ sphere ($s \le 0.65$ Å^{-1}) gave $R = 0.072$. The H atoms were located in ΔF maps calculated at two successive stages; in the second map at $R = 0.032$, positions of those in the methyl group of molecule A still were tentative because of diffuse and low (0.1 − 0.2 eÅ^{-3}) maxima. 398 variables were refined in two blocks. With the Cu-sphere data convergence was obtained at $R = 0.030$. In the final full-matrix least-squares refinement based on all 3656 F_o the coordinates of the methyl H atoms in A had to be constrained. At the end of this refinement R was 0.038 and $R_w = 0.035$ with weights $w = \sigma^{-2}(F_o)$. Average and maximum parameter shifts in the last cycle were 0.02 and 0.14 σ, respectively. The goodness-of-fit, $\{\sum w(|F_o| - K|F_c|)^2/(M-N)\}^{\frac{1}{2}}$ where $M =$ number of observations and $N =$ number of variables, was 1.97.

With one exception all the largest maxima, 0.15 − 0.29 eÅ^{-3}, in the final ΔF map correspond to deformation density in C − C and some C − O bonds. A peak (X) of density 0.29 eÅ^{-3} near O(16), also present in the preceding ΔF maps, could be taken to indicate a subsidiary H position. The distance O(16) − X and angle C(16) − O(16) − X were 0.84 Å and 113°, respectively, planes C(16) − O(16) − X and C(16) − O(16) − H(O16) defining a dihedral angle $\sim 167°$. Atom O(16) participates in two H bonds, one as a donor and one as an acceptor. If X represented an alternate H position, one would expect that there were at least one H bond of the type O(16) − X···O to compensate for the destabilization caused by the absence of H(O16). No such bond could be identified from the interatomic distances, however. The interpretation of peak X thus remains ambiguous and it was not included as an H atom in the refinement. The map showed no other maxima above density 0.15 eÅ^{-3}. Positional parameters

Table 2. Final atomic coordinates. The values are $\times 10^4$ for C, O and $\times 10^3$ for H. The y coordinate of O(5) was fixed to specify the origin. The coordinates of H(C81), H(C82) and H(C83) were fixed during the last cycles of refinement. E.s.d.'s in parentheses.

Atom	x	y	z	Atom	x	y	z
C(1)	5202(2)	2805(2)	1681(1)	C(11)	7613(2)	9616(2)	4009(1)
C(2)	4201(2)	2118(2)	713(1)	C(12)	6643(2)	8625(2)	3226(1)
C(3)	5316(2)	1228(2)	162(1)	C(13)	7818(2)	7575(2)	2894(1)
C(4)	6857(2)	1982(2)	−32(1)	C(14)	9309(2)	8234(2)	2512(1)
C(5)	7677(2)	2726(2)	969(1)	C(15)	10075(2)	9313(2)	3300(1)
C(6)	9090(2)	3658(2)	803(1)	C(16)	11357(2)	10206(2)	2907(1)
C(7)	9928(2)	4291(2)	1844(1)	C(17)	12207(2)	11173(2)	3755(1)
C(8)	4981(3)	4281(2)	3113(2)	C(18)	7384(3)	11550(3)	5049(2)
O(1)	4194(1)	3706(1)	2109(1)	O(11)	6560(1)	10620(1)	4262(1)
O(2)	2928(1)	1293(1)	1001(1)	O(12)	5404(1)	7955(1)	3680(1)
O(3)	5858(1)	87(1)	823(1)	O(13)	8497(2)	6733(1)	3765(1)
O(4)	6313(2)	2920(1)	−882(1)	O(14)	8844(1)	8769(1)	1454(1)
O(5)	6491(1)	3570	1355(1)	O(15)	8823(1)	10245(1)	3492(1)
O(6)	10266(1)	2858(1)	371(1)	O(16)	12555(1)	9382(1)	2529(1)
O(7)	11216(2)	5193(2)	1705(1)	O(17)	13121(2)	10472(2)	4651(1)
H(C1)	568(2)	215(2)	224(1)	H(C11)	812(2)	923(2)	473(1)
H(C2)	375(2)	278(2)	26(1)	H(C12)	614(2)	918(2)	264(1)
H(C3)	469(2)	94(2)	−51(1)	H(C13)	716(2)	703(2)	229(1)
H(C4)	764(2)	131(2)	−20(1)	H(C14)	1016(2)	755(2)	250(1)
H(C5)	805(2)	203(2)	149(1)	H(C15)	1054(2)	890(2)	396(1)
H(C6)	869(2)	438(2)	33(1)	H(C16)	1080(2)	1076(2)	231(1)
H(C71)	923(2)	481(2)	216(1)	H(C171)	1134(2)	1165(2)	401(1)
H(C72)	1049(2)	355(2)	239(1)	H(C172)	1292(2)	1177(2)	345(1)
H(C81)	607	435	314	H(C181)	654(4)	1214(4)	532(2)
H(C82)	468	379	365	H(C182)	807(4)	1104(3)	570(2)
H(C83)	441	514	315	H(C183)	810(4)	1196(3)	478(2)
H(O2)	213(2)	178(2)	87(2)	H(O12)	449(3)	834(3)	340(2)
H(O3)	513(3)	−49(2)	71(1)	H(O13)	776(3)	643(3)	401(2)
H(O4)	688(3)	287(3)	−118(2)	H(O14)	819(3)	927(2)	142(2)
H(O6)	1035(3)	313(3)	−19(2)	H(O16)	1291(3)	988(2)	205(2)
H(O7)	1207(3)	472(3)	170(2)	H(O17)	1396(3)	1031(3)	456(1)

are given in Table 2. Tables of thermal parameters and structure factors are available on request. Scattering factors were those of Doyle and Turner[12] except for H.[13] No corrections for anomalous dispersion were applied.

RESULTS AND DISCUSSION

The molecular structure. Both molecules A and B of MeβGG are distorted $^4C_1$ chairs. Fig. 1 shows the molecular conformation and labelling of atoms. The OH groups at C(3) and C(4) of gulopyranosidic rings are involved in 1,3-diaxial contacts with H atoms. The repulsion induces a flattening of this part of the ring, in MeβGG the endocyclic torsion angles

(Table 3) about the bonds C(2)−C(3) and C(3)−C(4) are in the range 47.6−51.2°. Opposing torsion angles about C(5)−O(5) and O(5)−C(1) are increased over normal values as predicted by Bucourt and Hainaut.[14] Asymmetric distortions of the same type and magnitude are found in two closely related gulopyranose derivatives: D-*glycero*-β-D-*gulo*-heptopyranose or βGG[5] and methyl D-*glycero*-α-D-*gulo*-heptopyranoside calcium chloride hydrate or MeαGGS.[6] The axial O(1) in MeαGGS effects additional flattening of this ring, in particular about the C(1)−C(2) bond, *cf.* Table 3. Puckering parameters according to Cremer and Pople[15] are also given in this table. The magnitude of the distortion, θ, ranges from 6 to 9° in all four rings.
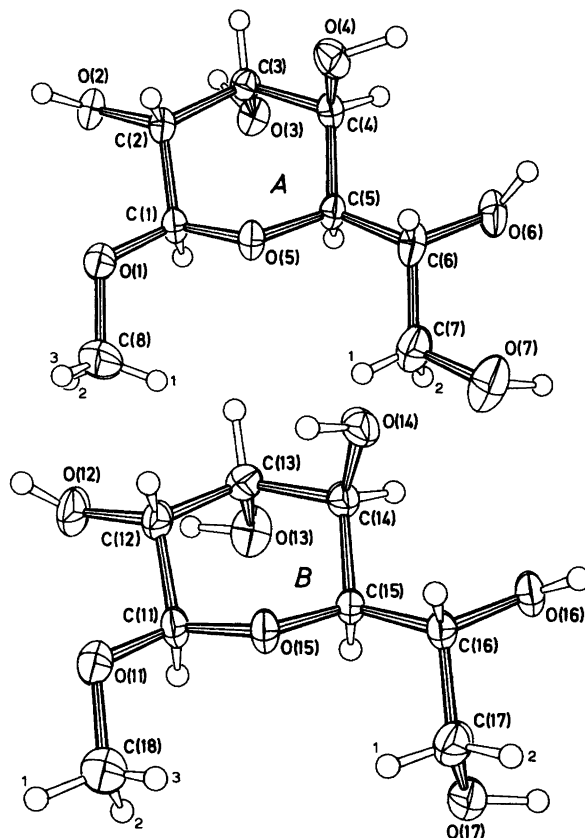
Fig. 1. Structure and atomic labelling of molecules *A* and *B*. Sequential numbering of H atoms is given only where necessary. Thermal ellipsoids of the C and O atoms correspond to a 50 % probability.

Rings *A* and *B* of MeβGG differ mainly in the orientation of the glycero tail at C(5). The conformations of C(6)−O(6) and C(7)−O(7) are *trans-gauche*[16] (*t* − *g*) and *gauche-trans* (*g* − *t*), respectively, in ring *A*, *t* − *g* and *g* − *g* in *B*. The *t* − *g*, *g* − *g* sequence is also adopted by βGG; in MeαGGS, however, both these C − O bonds are *g* − *g*. The relative stabilities of the three possible noneclipsing conformations of C(6) − O(6) in pyranose rings depend largely on the configuration of the ring and the tail group. In rings with O(4) axial, a *g* − *g* orientation should be the least favourable due to the close contact O(4)···O(6). With a D-*glycero* tail as in the present case, the *g* − *t* orientation would also be destabilized because it involves a similar short contact O(4)···C(7). The favoured *t* − *g* orientation is observed in all structures of Table 3 except MeαGGS. The increase in energy associated with

the *g* − *g* orientation in the latter structure must be more than offset by the stability gained by O(6) complexing to both Ca and Cl. The *g* − *g* conformation is also present in 1,2,3,4,6-penta-*O*-acetyl α-D-gulopyranose[17] which appears to be the only other relevant gulopyranose derivative studied to date by X-ray diffraction. The scarcity of known gulopyranose structures precludes any statistically valid conclusion as to the relative frequency of C(6) − O(6) orientations in the general case. A more reliable estimate can be obtained from the larger sample of known galactopyranose structures in which O(4) is also axial. In 16 monogalactose rings the conformations *g* − *t*, *t* − *g* and *g* − *g* are distributed as 10:5:1, this ratio is 6:1:1 in 8 galactose-containing di- or trisaccharides. In the two structures with C(6) − O(6) *g* − *g*, O(4) and O(6) are either engaged in an intramolecular O(4) − H(O4)···O(6)

Table 3. Puckering parameters according to Cremer and Pople[15] and torsion angles (°) for some D-*glycero*-D-*gulo*-heptopyranose rings.[a] Signs of torsion angles follow the convention of Klyne and Prelog,[24] e.s.d.'s for rings *A* and *B* are in the range 0.1 – 0.2°.

	(A)	(B)	(C)	(D)
q_2(Å)	0.082	0.089	0.061	0.058
q_3(Å)	0.560	0.574	0.564	0.538
ϕ_2(°)[b]	17.1	26.5	338.9	325.3
θ(°)	8.3	8.9	6.2	6.2
Q(Å)	0.566	0.581	0.568	0.541
Endocyclic				
O(5)C(1)C(2)C(3)	57.4	59.2	54.2	51.8
C(1)C(2)C(3)C(4)	−49.6	−51.2	−49.9	−48.0
C(2)C(3)C(4)C(5)	47.6	47.9	51.5	49.2
C(3)C(4)C(5)O(5)	−53.3	−52.9	−57.6	−55.8
C(4)C(5)O(5)C(1)	64.0	65.0	64.3	62.4
C(5)O(5)C(1)C(2)	−65.8	−67.8	−62.2	−58.7
Exocyclic				
O(1)C(1)C(2)O(2)	−65.2	−62.7	−66.4	49.6
O(2)C(2)C(3)O(3)	−52.6	−55.4	−53.8	−50.1
O(3)C(3)C(4)O(4)	167.0	162.1	171.9	166.7
O(4)C(4)C(5)C(6)	−54.4	−45.4	−54.3	−54.9
C(5)O(5)C(1)O(1)	175.8	173.8	−178.1	61.9
O(5)C(1)O(1)C(8)	−69.4	−66.2	−	66.0
O(5)C(5)C(6)O(6)	−177.4	−171.1	−173.3	−64.8
C(4)C(5)C(6)O(6)	−56.2	−51.2	−53.2	59.6
O(5)C(5)C(6)C(7)	62.7	65.8	67.5	174.4
C(4)C(5)C(6)C(7)	−176.1	−174.3	−172.4	−61.2
O(6)C(6)C(7)O(7)	63.1	−60.3	−60.5	−49.6
C(5)C(6)C(7)O(7)	−178.3	62.6	59.4	75.1

[a] References: (A) MeβGG ring *A*. (B) MeβGG ring *B*. (C) βGG.[5] (D) MeαGGS.[6]   [b] Atomic sequence: O(5)C(1)· · ·C(5).

bond (*N*-acetyl α-D-galactosamine[18]) or intermolecular H bonding (planteose[19]) including a weaker intramolecular O(6)−H(O6)···O(4) interaction.

Bond lengths and angles. These parameters are listed with their e.s.d.'s in Tables 4 and 5. Mean values and ranges of endocyclic C−C bonds are 1.523 and 0.010 in ring *A*, 1.527 and 0.019 Å in *B*. *A* and *B* have means of 1.428 and 1.426 Å, both with range about 0.017 Å, in exocyclic C−O bonds not involving O(1). The averages of bond lengths in the acetal moiety C(5)−O(5)−C(1)−O(1)−C(8) are in sequence: 1.433[1.433]−1.424[1.428]−1.392 [1.383]−1.442[1.427] Å. Compared with the mean values [in brackets] for eight methyl β-D-pyranosides[20] both bonds at O(1) in MeβGG are longer by about 0.010 Å. Except for a deviation of 0.008 Å in C(1)−O(1), the experimental bond lengths are

in very good agreement with quantum-chemical calculations of C−O bond-length variations in the model compound dimethoxymethane.[20] Averages of the bond angles at O(5), C(1) and O(1) in MeβGG are respectively: 112.0[111.4], 107.6[107.9], 113.0[113.4]°. Values in brackets are corresponding averages for eight methyl β-D-pyranosides.[20]

The mean value of endocyclic C−C−X angles (X=C, O) is 110.5° in ring *A*, and 109.9° in *B*, with fairly large spreads, 2.9 and 4.3°, respectively. C−H bond lengths in both rings excluding those in the methyl groups vary from 0.91 to 1.06, the mean is 0.97 Å. The range of methyl C−H bonds is 0.83−1.05, mean 0.94 Å, and O−H bonds from the refinement range from 0.65 to 0.87 with mean 0.79 Å. A summary of valency angles involving H is given in Table 6.

Table 4. Bond lengths (Å) with standard deviations.

	Ring A	Ring B
C(1)−C(2)	1.517(2)	1.519(2)
C(2)−C(3)	1.527(2)	1.527(2)
C(3)−C(4)	1.525(2)	1.538(2)
C(4)−C(5)	1.523(2)	1.524(2)
C(5)−O(5)	1.433(2)	1.432(2)
C(1)−O(5)	1.420(2)	1.427(2)
C(1)−O(1)	1.391(2)	1.392(2)
C(8)−O(1)	1.444(2)	1.439(3)
C(2)−O(2)	1.424(2)	1.419(2)
C(3)−O(3)	1.431(2)	1.421(2)
C(4)−O(4)	1.435(2)	1.435(2)
C(6)−O(6)	1.430(2)	1.425(2)
C(7)−O(7)	1.418(2)	1.429(2)
C(5)−C(6)	1.525(2)	1.524(2)
C(6)−C(7)	1.517(2)	1.518(2)

The crystal structure. Packing of the molecules is shown in Fig. 2 where *A*- and *B*-rings are distinguished by unprimed and primed numbers, respectively. The exposed parts of both molecules are involved in normal nonpolar interactions, atoms C(2), C(8), O(3), O(7) and C(17), C(18), O(13) being particularly well embedded. Short distances are: *C(16)···O(2)$_7$ 3.132, C(8)···O(17)$_9$ 3.219, C(8)···H(O7)$_3$ 2.76, O(12)···H(C181)$_8$ 2.35 and O(3)···H(C12)$_2$ 2.45 Å, with H positions from the refinement.

All O atoms except O(5) and O(15) in the rings participate in an extensive 3-dimensional network of H bonds, with most of the atoms both as donor and acceptor. The H-bonding system is indicated

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*The subscript$_7$ denotes molecule at $1+x$, $1+y$, z. The symmetry code is explained in Table 6.

Table 5. Valency angles (°) with standard deviations.

	Ring A	Ring B		
O(5)C(1)C(2)	109.0(1)	107.8(1)		
C(1)C(2)C(3)	110.5(1)	109.7(1)		
C(2)C(3)C(4)	111.9(1)	112.1(1)		
C(3)C(4)C(5)	110.9(1)	110.3(1)		
C(4)C(5)O(5)	110.0(1)	109.8(1)		
C(5)O(5)C(1)	112.0(1)	112.0(1)		
O(5)C(1)O(1)	107.3(1)	107.8(1)		
C(2)C(1)O(1)	109.4(1)	109.8(1)		
C(1)C(2)O(2)	111.3(1)	111.4(1)		
C(3)C(2)O(2)	108.3(1)	109.1(1)		
C(2)C(3)O(3)	109.5(1)	111.2(1)		
C(4)C(3)O(3)	107.6(1)	105.8(1)		
C(3)C(4)O(4)	106.4(1)	111.0(1)		
C(5)C(4)O(4)	110.6(1)	111.7(1)		
C(4)C(5)C(6)	114.2(1)	114.7(1)		
O(5)C(5)C(6)	105.9(1)	103.9(1)		
C(5)C(6)C(7)	111.5(1)	112.9(1)		
C(5)C(6)O(6)	107.4(1)	109.7(1)		
C(7)C(6)O(6)	109.4(1)	110.1(1)		
C(6)C(7)O(7)	112.5(2)	111.9(2)		
C(1)O(1)C(8)	113.3(1)	112.6(1)		

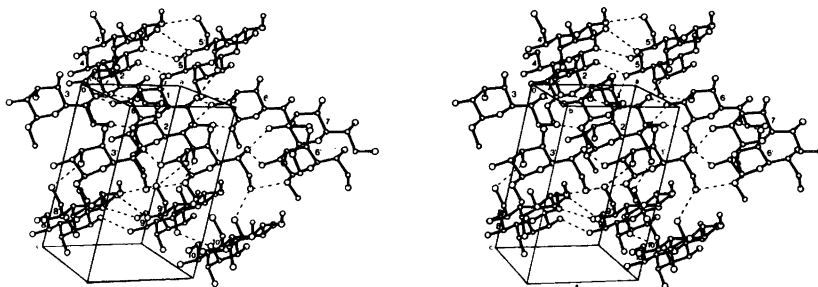| Angles involving H Type[a]	Number	Range	Mean	σ_{ave}
XCH	44	103.5−115.6	109.0	1.0
COH	10	101.8−112.4	107.1	1.8
OCH (Methyl)	6	104.2−111.3	108.7	−
HCH	8	103.1−115.8	110.4	−

[a] X = C,O.

Fig. 2. Stereoscopic packing diagram with H bonds shown as dashed lines. Numbering of molecules, with *A* unprimed and *B* primed, is according to symmetry code in Table 6. Orientation of cell is given.

by dashed lines in Fig. 2. Details of the geometry are given in Table 6 where contact distances and angles involving H have been recalculated with H positions shifted to give standard neutron diffraction O–H bond lengths. This type of correction which is significant and can be rationalized both from theory[13,21] and experimental[22] evidence has been applied routinely also in previous X-ray work.[23]

The mutual arrangement of rings *A* and *B* in the asymmetric unit, *i.e.* 1 and 1′, and the translation along *b* generate double layers of molecules with *A* and *B* roughly on top of each other. The tilt between planes defined by atoms C(1), C(2), C(4), C(5) of the two rings is about 16°. The mean ring

planes of successive double layers along *c* have a relative tilt of approximately 56°. Within one layer *A* molecules are connected along *a* through pairs of H bonds: $O(2) \rightarrow O(6)_3$ and $O(7)_3 \rightarrow O(1)$ repeated by translation. Molecules *B* are involved in the analogous system: $O(12) \rightarrow O(16)_3$ and $O(17)_3 \rightarrow O(11)$. There are no H bonds between *A* and *B* molecules within the asymmetric unit, *i.e.* roughly along *b*. H bonds between lower (*B*) and upper (*A*) molecules in the double layer are: $O(14) \rightarrow O(3)_{11}$ and $O(16) \rightarrow O(2)_7$, and between adjacent layers: $O(3) \rightarrow O(4)_4$, $O(6) \rightarrow O(14)_5$ and $O(13) \rightarrow O(17)_9$. The geometry of the contact $O(4) \rightarrow O(16)_5$ suggests that it is a very weak interaction. It has been classified in Table 6 as an intermolecular contact.

Table 6. Geometry of the hydrogen-bonding system.

$D-H \cdots A$	$D \cdots A$ (Å)	$H \cdots A$ (Å)	$(H \cdots A)^a_{corr}$ (Å)	$(\angle D-H \cdots A^a_{corr}$ (°)
$O(2)-H(O2) \cdots O(6)_3$	2.682(2)	1.88(2)	1.71	172
$O(3)-H(O3) \cdots O(4)_4$	2.796(2)	2.01(2)	1.85	161
$O(6)-H(O6) \cdots O(14)_5$	2.711(2)	1.95(3)	1.76	164
$O(7)-H(O7) \cdots O(1)_6$	2.820(2)	2.00(3)	1.87	164
$O(12)-H(O12) \cdots O(16)_3$	2.897(2)	2.05(3)	1.93	168
$O(13)-H(O13) \cdots O(17)_9$	2.886(2)	2.19(3)	2.02	146
$O(14)-H(O14) \cdots O(3)_{11}$	2.766(2)	2.09(2)	1.86	152
$O(16)-H(O16) \cdots O(2)_7$	2.768(2)	1.94(2)	1.83	158
$O(17)-H(O17) \cdots O(11)_6$	2.952(2)	2.26(3)	2.03	157
Intermolecular contact				
$O(4)-H(O4) \cdots O(16)_5$	2.836(2)	2.38(2)	2.19	122

Symmetry code

(1) x, y, z; (2) $x, -1+y, z$; (3) $-1+x, y\ z$; (4) $1-x, -\frac{1}{2}+y, -z$; (5) $2-x, -\frac{1}{2}+y, -z$; (6) $1+x, y, z$; (7) $1+x, 1+y, z$; (8) $1-x, -\frac{1}{2}+y, 1-z$; (9) $2-x, -\frac{1}{2}+y, 1-z$; (10) $2-x, \frac{1}{2}+y, 1-z$; (11) $x, 1+y, z$.

^{a}O–H bond distances were expanded to 0.98 Å[25] in the direction of the bond.

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