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The Structure of a Disaccharide: 2,2′,3,3′,4,4′-Hexa-*O*-acetyl-*β*-D-glucopyranose 1,6′:6,1′-Dianhydride

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Abstract

This peracetylated cyclic disaccharide ($C_{24}H_{32}O_{16}$, M_r = 576·5) crystallizes in the triclinic space group $P1$ [a = 8·667 (1), b = 10·812 (1), c = 18·624 (2) Å, α = 92·42 (1), β = 105·85 (1), γ = 118·30 (1)°; V = 1447·2 Å^3, d_m = 1·30, d_c = 1·32 Mg m^{-3}, Z = 2] with two independent molecules in the asymmetric unit. R = 0·097, R_w = 0·089 for 5286 reflexions. There are some differences in conformation between the two independent molecules. In both cases, there exists a pseudo axis of symmetry. The internal cyclization yields unusual conformations for the six-membered rings. In one molecule they have roughly a boat conformation while in the other they have a twist-boat conformation. The ten-membered rings do not have a *BCB*-type conformation, as found for most substituted cyclodecanes. In the asymmetric unit, the two molecules are related by a pseudo center of symmetry.

Introduction

In the course of the polycondensation of (1→6)-*β*-D-glucan (Gagnaire & Vignon, 1976), an internal cyclization side-reaction yielded the corresponding peracetylated disaccharide, 2,2′,3,3′,4,4′-hexa-*O*-acetyldi-*β*-D-glucopyranose 1,6′:6,1′-dianhydride (Fig. 1).

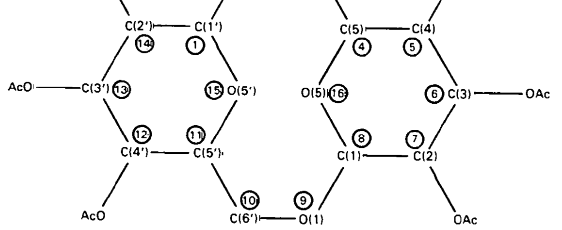

Fig. 1. 2,2′,3,3′,4,4′-Hexa-*O*-acetyldi-*β*-D-glucopyranose 1,6′:6,1′-dianhydride. The circled numbers refer to the tricyclo[9.3.1.1^{4,8}] hexadecane system.

Preliminary conformation studies taking into account the results from ^{1}H and ^{13}C NMR spectroscopy (Bassieux, Gagnaire & Vignon, 1977) and those obtained through molecular-mechanics calculations (Gagnaire, Tran & Vignon, 1976) predicted a 2,9,15,16-tetraoxatricyclo[9.3.1.1^{4,8}]hexadecane backbone structure, with a strained conformation in which the D-glucopyranose rings do not adopt the most stable (chair) form.

Therefore it was of interest to determine the crystal structure of this compound in order to state precisely the 'non-chair' conformations of the six-membered rings; this provides valuable information for NMR spectroscopy. To our knowledge, it is the first crystallographic study of oligosaccharides with a *β*(1→6) glycosidic linkage. Because the crystallization leads to two independent molecules in the asymmetric unit, it is one of the largest oligosaccharide structures solved by the X-ray method.

Independent empirical calculations have revealed three possible backbone conformations (Gagnaire, Pérez & Tran, 1980). Two of these conformations correspond to the two different molecules of the asymmetric unit in the crystal.

Another compound with a similar backbone has been obtained by condensation of two molecules of 6,8-dioxabicyclo[3.2.1]octan-7-one (Okada, Sumitomo & Tajima, 1977). Its crystallographic structure has not yet been published but the structure deduced from NMR data seems to be different from the conformations found here.

Experimental

Small flattened crystals were obtained by slow evaporation from ethanol solution. Preliminary unit-cell dimensions and the space group, $P1$ or $P\bar{1}$, with two molecules per unit cell, were determined from precession photographs. Because the compound is optically active, the space group is assumed to be $P1$, which was confirmed by the statistical tests.

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Cell parameters were refined by a least-squares fitting of the angular positions of 24 reflexions and are reported in the *Abstract* with other crystal data.

The intensities of 5286 independent reflexions ($3° < \theta < 70°$) were collected on the automatic Siemens four-circle diffractometer of the Institute Laue–Langevin (Grenoble) using Ni-filtered Cu $K\alpha$ radiation by the five-point method (Troughton, 1969). Three standard reflexions ($\bar{2}50$, $\bar{4}09$, 384) were periodically recorded and showed a time-dependent decay which amounted to about 18% at the end of the recording. The data were corrected for Lorentz and polarization factors and time-dependent decay, but not for absorption.

Structure determination

Attempts to solve the structure by direct methods using *MULTAN* (Germain, Main & Woolfson, 1970) with three symbolic reflexions and 499 E values $> 1\cdot60$ all gave trivial phase sets with all phases equal to zero.

The solution was eventually arrived at as follows: a plausible model of the molecule, calculated by energy minimization, was oriented in the unit cell by packing considerations; the coordinates so obtained were introduced into the *SF* subprogram of *MULTAN*, and 100 phases were passed to the *FASTAN* subprogram (it was hoped that the triclinic nature of the crystal would eliminate the origin problem). The set of 499 phases calculated by *FASTAN*, expanding the starting set of 100 phases and using 2500 phase relationships, revealed 76 out of the 80 non-hydrogen atoms to be determined. The recycling of this structural fragment gave the remaining four atoms. Since the introduced model was the third predicted conformation (see *Introduction*), the solution of the structure appears to be of the 'random-approach' type (Baggio, Woolfson, Declercq & Germain, 1978).*

The initial failure of the phase generation can be explained as follows: when the structure is referred to the origin defined by *CONVERGE*, it happens that the 57 highest reflexions in the convergence map among which the initial set of phases are chosen have phases equal to zero. Under this circumstance, the true solution is contained in the trivial solution (in which the origin and the initial set of phases are zero) and there is no obvious means of generating a non-zero phase.

The structure was refined using the program *XFLSN* (Busing & Levy, 1964) with O and C atoms anisotropic. Based on all the reflexions, the final $R_w = 0\cdot089$, $R = 0\cdot097$ $\{R_w = [\sum w(F_o - F_c)^2/\sum wF_o^2]^{1/2}$, $R = \sum (F_o - F_c)/\sum |F_o|\}$.*

Results and discussion

In the following discussion, the two experimentally observed conformations are designated A and B. For each one, the two six-membered rings are indis-

Table 1. *Molecule A: final atomic coordinates and equivalent isotropic thermal parameters* ($\times 10^4$) *for the heavy atoms*

The estimated standard deviations are given in parentheses.

$$B_{eq} = 8\pi^2(U_1 U_2 U_3)^{2/3}.$$

	x	y	z	B_{eq} (Å^2)
C(1)	−2255 (12)	−8068 (10)	140 (5)	4·33
C(2)	−4307 (11)	−8997 (9)	−43 (4)	3·68
C(3)	−5258 (11)	−8099 (9)	−102 (4)	3·98
C(4)	−4441 (12)	−7075 (9)	668 (5)	4·10
C(5)	−2311 (15)	−6205 (11)	945 (5)	4·77
C(6)	−1350 (14)	−6177 (10)	1778 (5)	4·66
O(1)	−1478 (8)	−8731 (7)	630 (3)	4·30
O(2)	−5026 (9)	−9872 (6)	−799 (3)	4·25
O(3)	−7179 (0)	−9037 (0)	−193 (0)	4·31
O(4)	−5128 (10)	−6089 (7)	488 (3)	4·83
O(5)	−1551 (9)	−6623 (7)	437 (3)	4·70
C(1′)	−470 (12)	−7655 (10)	2463 (5)	4·24
C(2′)	−1309 (12)	−9204 (10)	2612 (4)	4·17
C(3′)	−31 (12)	−9779 (9)	2605 (5)	4·21
C(4′)	123 (12)	−9784 (10)	1813 (5)	4·34
C(5′)	1172 (13)	−8235 (11)	1710 (5)	4·76
C(6′)	534 (13)	−7997 (12)	886 (5)	4·62
O(1′)	−1906 (8)	−7619 (6)	1886 (3)	4·06
O(2′)	−1365 (8)	−9037 (7)	3386 (3)	4·57
O(3′)	−982 (9)	−11241 (7)	2703 (4)	5·17
O(4′)	1372 (9)	−10325 (8)	1778 (4)	5·16
O(5′)	1109 (8)	−7238 (7)	2251 (4)	4·64
CA(2)	−6091 (16)	−11275 (12)	−898 (6)	5·91
CM(2)	−6727 (23)	−11995 (14)	−1755 (7)	7·59
OA(2)	−6453 (16)	−11899 (10)	−412 (5)	8·79
CA(3)	−8456 (13)	−9456 (10)	−917 (5)	4·67
CM(3)	−10459 (14)	−10419 (11)	−946 (6)	5·97
OA(3)	−8007 (11)	−9049 (9)	−1457 (4)	6·20
CA(4)	−5116 (14)	−5314 (12)	1100 (7)	5·57
CM(4)	−5703 (20)	−4215 (14)	835 (8)	6·97
OA(4)	−4678 (12)	−5506 (9)	1736 (4)	6·32
CA(2′)	−3015 (16)	−9584 (14)	3479 (7)	6·42
CM(2′)	−2874 (18)	−9185 (16)	4296 (6)	6·83
OA(2′)	−4441 (13)	−10266 (17)	2965 (6)	9·96
CA(3′)	−3 (18)	−11674 (12)	3229 (6)	5·53
CM(3′)	−1235 (19)	−13166 (12)	3329 (7)	7·11
OA(3′)	1669 (13)	−10899 (9)	3542 (5)	6·87
CA(4′)	612 (16)	−11626 (12)	1304 (6)	5·26
CM(4′)	2102 (18)	−11975 (15)	1318 (7)	7·05
OA(4′)	−1007 (15)	−12368 (12)	968 (7)	8·73

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* In addition, it was found after the submission of this paper that the plane of the reflexions $h + k + l = 0$ had been inadvertently missed in the data collection. Whether this fact caused the initial failure or, on the contrary, allowed the solution of the structure is, of course, not known.

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 35692 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Molecule B: final atomic coordinates and equivalent isotropic thermal parameters* (×10⁴) *for the heavy atoms*

The estimated standard deviations are given in parentheses.

$$B_{eq} = 8\pi^2 (U_1 U_2 U_3)^{2/3}.$$

	x	y	z	B_{eq} (Å²)
C(1)	−7804 (13)	−7164 (11)	−3853 (5)	4·81
C(2)	−7140 (14)	−5756 (11)	−4183 (5)	4·83
C(3)	−7254 (13)	−6134 (11)	−5006 (5)	4·85
C(4)	−6278 (13)	−7018 (10)	−4987 (5)	4·54
C(5)	−7611 (12)	−8494 (10)	−4907 (5)	4·34
C(6)	−6774 (14)	−9443 (11)	−4669 (5)	4·88
O(1)	−6219 (9)	−6957 (7)	−3283 (3)	4·45
O(2)	−8458 (10)	−5288 (8)	−4215 (4)	5·80
O(3)	−6190 (11)	−4787 (8)	−5203 (4)	6·19
O(4)	−6141 (9)	−7225 (7)	−5732 (3)	4·87
O(5)	−8643 (8)	−8434 (7)	−4409 (4)	4·97
C(1′)	−4849 (12)	−9553 (10)	−3532 (4)	4·13
C(2′)	−2715 (12)	−8842 (10)	−3112 (5)	4·35
C(3′)	−2135 (11)	−7954 (9)	−2340 (4)	3·91
C(4′)	−3304 (14)	−7246 (10)	−2388 (5)	4·40
C(5′)	−5288 (13)	−8377 (10)	−2501 (5)	4·48
C(6′)	−6706 (16)	−7908 (13)	−2760 (6)	5·48
O(1′)	−5043 (8)	−8653 (6)	−4035 (3)	4·20
O(2′)	−2345 (10)	−10010 (8)	−2929 (4)	5·12
O(3′)	−185 (8)	−6864 (7)	−2169 (3)	4·56
O(4′)	−2751 (10)	−6382 (7)	−1644 (3)	4·76
O(5′)	−5827 (8)	−9690 (7)	−3015 (3)	4·72
CA(2)	−7761 (29)	−3995 (22)	−3786 (9)	8·40
CM(2)	−9417 (22)	−3746 (18)	−3852 (9)	8·20
OA(2)	−6579 (19)	−3751 (18)	−3198 (9)	12·56
CA(3)	−7103 (23)	−4345 (14)	−5760 (7)	6·66
CM(3)	−5680 (28)	−2948 (17)	−5916 (10)	9·59
OA(3)	−8702 (16)	−5021 (10)	−6070 (5)	7·95
CA(4)	−4462 (15)	−6494 (14)	−5797 (6)	6·21
CM(4)	−4527 (17)	−6833 (16)	−6602 (6)	6·76
OA(4)	−3097 (12)	−5678 (14)	−5277 (5)	9·23
CA(2′)	−2254 (16)	−10781 (13)	−3489 (7)	5·98
CM(2′)	−1798 (20)	−11860 (15)	−3243 (8)	7·09
OA(2′)	−2607 (14)	−10545 (10)	−4118 (5)	7·65
CA(3′)	975 (14)	−6539 (11)	−1441 (5)	4·90
CM(3′)	2922 (14)	−5384 (11)	−1372 (6)	5·82
OA(3′)	441 (10)	−7095 (9)	−939 (4)	5·76
CA(4′)	−1851 (18)	−4922 (12)	−1546 (7)	6·23
CM(4′)	−1282 (20)	−4214 (12)	−748 (7)	6·95
OA(4′)	−1487 (17)	−4340 (9)	−2067 (5)	8·52

tinguishable, so the unprimed or primed labelling is therefore arbitrary. The final atomic coordinates, thermal parameters, and standard deviations of non-hydrogen atoms and the calculated H positions are listed in Tables 1, 2 and 3 for molecules *A* and *B*.

For the non-hydrogen atoms of the pyranose rings, the averages of the standard deviations for the distances and angles are respectively 0·014 Å and 0·8° for the two conformations. These values are 0·016 Å and 1·1° for *A*, 0·019 Å and 1·2° for *B* for acetate-group atoms. Thus the two conformations are similarly defined. This rather low accuracy is attributed to the high thermal motion (especially for the acetate group) and the large number of parameters being refined. Figs. 2 and 3 show stereoscopic views of backbone conformations *A* and *B* respectively (*ORTEP*, Johnson, 1965).

Table 3. *Calculated atomic coordinates of the hydrogen atoms* (×10³)

	x	y	z
Molecule *A*			
H(1)	−195	−813	−38
H(2)	−462	−966	37
H(3)	−510	−753	−56
H(4)	−494	−764	109
H(5)	−194	−511	92
H(6)1	14	−559	192
H(6)2	−173	−569	216
H(1′)	−9	−693	298
H(2′)	−268	−990	221
H(3′)	131	−914	304
H(4′)	−122	−1040	137
H(5′)	261	−794	185
H(6′)1	94	−847	50
H(6′)2	105	−687	89
Molecule *B*			
H(1)	−880	−724	−359
H(2)	−575	−494	−384
H(3)	−867	−672	−539
H(4)	−494	−653	−454
H(5)	−863	−903	−547
H(6)1	−772	−1036	−450
H(6)2	−649	−982	−514
H(1′)	−537	−1060	−386
H(2′)	−193	−822	−346
H(3′)	−229	−861	−191
H(4′)	−321	−662	−283
H(5′)	−532	−865	−195
H(6′)1	−674	−734	−228
H(6′)2	−807	−882	−305

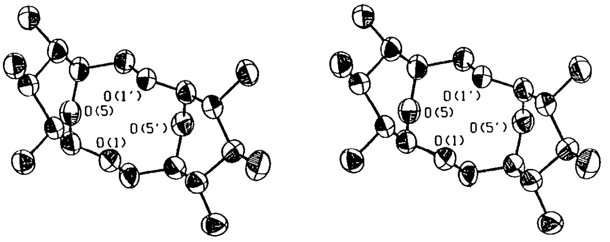

Fig. 2. Molecule *A*: stereoscopic view of the backbone conformation.

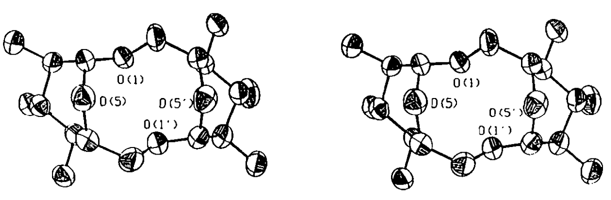

Fig. 3. Molecule *B*: stereoscopic view of the backbone conformation.

Bond distances and angles

For each kind of bond length, the two conformations have very similar mean values. The C—C ring bond lengths average 1·530 Å. The four exocyclic C(5)—C(6) bonds are not shorter than the C—C ring bond average, as emphasized by Ham & Williams (1970) and Takeda, Yasuoka & Kasai (1977). The exocyclic C(i)—O(i) (i = 2,3,4,5) bond lengths average 1·457 Å. This value is slightly different from the mean value (1·426 Å) reported by Arnott & Scott (1972), but is very close to that in β-cellotriose undecaacetate (Pérez & Brisse, 1977). The O(1)—C(6) bond-length values are very comparable to C(i)—O(i). As part of the anomeric effect, C(1)—O(1) and C(1)—O(5) bond-length averages are found to be shorter (1·411 and 1·409 Å respectively), as predicted by *ab initio* calculations on relevant model compounds (Jeffrey, Pople & Radom, 1972, 1974; Jeffrey, Pople, Binkley & Vishveshwara, 1978).

In pyranose rings, the mean values of bond angles are larger for molecule *A*. The internal C—C—C ring angles average 109·6 to 108·5° for *A* and *B* respectively. The endocyclic C—C—O angle averages to 112·8 for *A*, and 110·7° for *B*. It is of particular interest to note that endocyclic C—O—C angles are very large. The averages are 121·0 and 117·7° for *A* and *B* respectively. These values are significantly larger (especially for conformation *A*) than those usually found in strainless pyranose rings (about 113°). Therefore, it must be stressed that the six-membered rings are strained; such a strain is essentially located about the endocyclic C—O—C bond angles. In both molecules, the exocyclic C—C—O angles exhibit a large range of variation (102·1 to 110·1°, mean value 106·4°), as found in other oligosaccharides. All data about bond lengths and angles are depicted in Figs. 4 and 5. [The e.s.d.'s in parentheses have been calculated with a modified program of Ahmed, Hall, Pippy & Huber (1969).]

Molecular conformation

Conformations are mainly characterized by their dihedral angles. The values of the torsion angles along the backbone are reported in Table 4. The signs of these angles have been defined according to the IUPAC–IUB Commission on Biochemical Nomenclature (1970). This set of data allows for a discussion and a comparison of the six- and ten-membered ring forms of molecules *A* and *B*. For all the reported values, differences of about 10° should not be considered significant.

Six-membered rings

None of the four pyranose rings has a dihedral-angles sequence like (−60, +60, −60, +60, −60, +60°)* which characterizes the chair form. Thus, these rings do not have the most stable form and con-

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* All the sequences refer to torsion angles C(1)—C(2)—C(3)—C(4), C(2)—C(3)—C(4)—C(5), C(3)—C(4)—C(5)—O(5), C(4)—C(5)—O(5)—O(1), C(5)—O(5)—C(1)—C(2), O(5)—C(1)—C(2)—C(3).

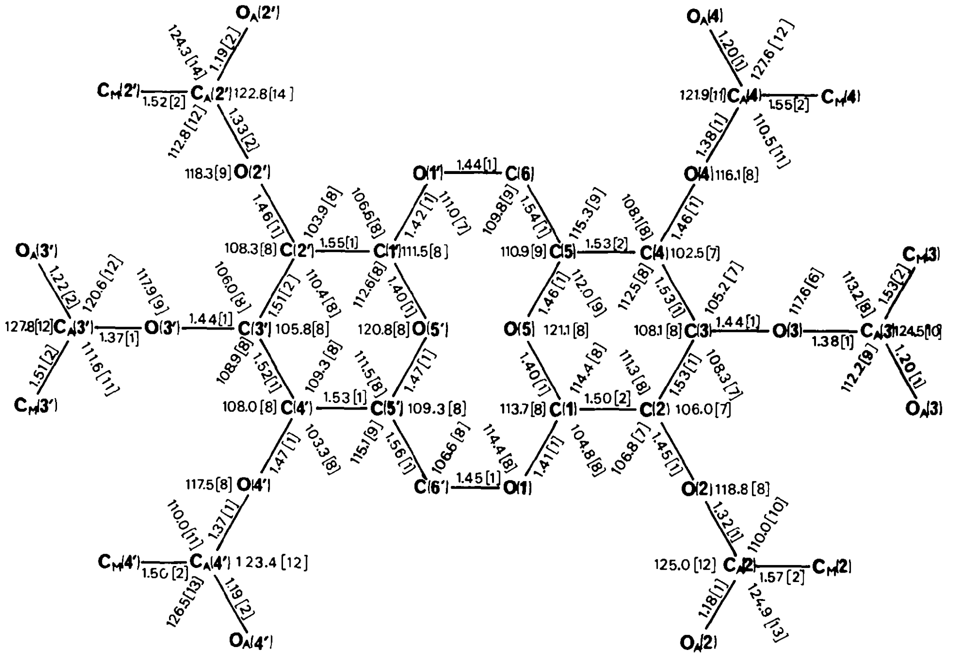

Fig. 4. Molecule *A*: bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

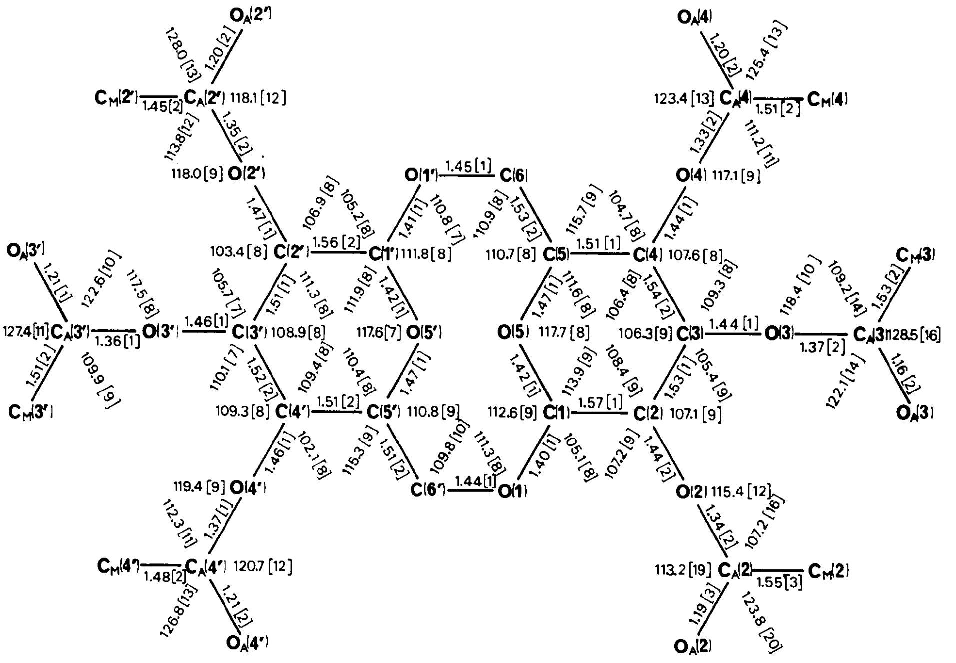

Fig. 5. Molecule *B*: bond distances (Å) and angles (°) with e.s.d.'s in parentheses.

formations involving forms of higher energy must be considered. The flexible conformations (boat and twist-boat forms) present an energy difference of about 23 kJ mol^{-1} in comparison with the chair forms and can be used as reasonable models to describe the observed crystalline forms. Interconversion forms between flexible and chair conformations have to be discarded; they involve a much higher energy level of about 42 kJ mol^{-1}. The crystalline conformation *A* presents the two sequences (−60, +52, −4, −44, +36, +18°) and (−61, +68, −21, −35, +42, +9°). For *B*, the sequences are (−49, +76, −37, −26, +52, −11°) and (−36, +69, −38, −24, +57, −23°).

In cyclohexane, the boat and twist-boat forms are characterized by theoretical sequences of torsion angles such as (−60, +60, 0, −60, +60, 0°) and (−33, +71, −33, −33, +71, −33°) respectively. Thus for the pyranose rings of conformation *A*, the corresponding form is the boat and for those of conformation *B* the corresponding form is the twist-boat.

Ten-membered rings

From electron diffraction data collected at 403 K for cyclodecane, Hilderbrandt, Wieser & Montgomery (1973) showed that the boat–chair–boat (*BCB*) form with C_{2h} symmetry is a good model for this ten-membered ring. This conformation predicted by Dale (1963) is in good agreement with most crystallographic results for substituted cyclodecanes compiled by Dunitz (1968). In this form, because of the intra-annular H atoms, there appears a deformation of the diamond lattice. Hilderbrandt *et al.* have also studied the twelve conformations depicted by Hendrickson (1967); in addition to the *BCB* form, three other forms (*TBCC*, *TBC*, *BCC*) have rather stable conformations and could also exist.

The 1,3,6,8-tetraoxacyclodecane structure is analogous to the ten-membered ring studied. Its X-ray crystal structure (Bassi, Scordamaglia & Fiore, 1975) shows rather a *BCB* conformation. In this case, the diamond-lattice deformation is slightly weaker than that observed in substituted cyclodecanes; the replacement of four C atoms by O atoms eliminates repulsion between intra-annular H atoms. Because this conformation is compared to the *BCB* form, the C_{2h} symmetry is still a valid approximation although the positions assumed by the four O atoms formally cancel this symmetry.

For 2,9,15,16-tetraoxatricyclo[9.3.1.1^{4,8}]hexadecane-3,10-dione, Okada *et al.* (1977) propose a *BCB*-type conformation for the ten-membered ring. But for this compound, such a conformation requires a cyclization involving a pair of different enantiomers. In our case, a *BCB* form is not allowed because the cyclization occurs with two *identical* enantiomers. The cyclization of two pyranose rings simultaneously is impossible. As listed in Table 4, to every torsion-angle value corresponds a nearly equal value on the reverse side of the ten-membered ring. Thus these rings present new conformations with approximate C_{2v} symmetry. They exist in two slightly different conformations.

Table 4. *Torsion angles* (°)

E.s.d.'s are less than 2°.

	Conformation *A*		Conformation *B*	
	Unprimed residue	Primed residue	Unprimed residue	Primed residue
Endocyclic torsion angles about the six-membered rings				
C(1)–C(2)–C(3)–C(4)	−60·2	−61·2	−49·2	−35·7
C(2)–C(3)–C(4)–C(5)	51·9	67·8	75·8	69·1
C(3)–C(4)–C(5)–O(5)	−3·7	−21·4	−37·0	−38·5
C(4)–C(5)–O(5)–C(1)	−43·6	−35·2	−25·5	−24·1
C(5)–O(5)–C(1)–C(2)	36·0	41·9	52·1	57·0
O(5)–C(1)–C(2)–C(3)	18·0	8·6	−10·8	−23·2
Exocyclic torsion angles about the six-membered rings				
O(5)–C(1)–C(2)–O(2)	133·2	124·6	104·4	89·0
O(1)–C(1)–C(2)–C(3)	143·2	131·2	112·8	98·3
O(1)–C(1)–C(2)–O(2)	−101·5	−112·8	−131·9	−149·5
C(1)–C(2)–C(3)–O(3)	−173·7	−176·7	−165·1	−154·1
O(2)–C(2)–C(3)–C(4)	−175·9	−174·4	−164·5	−150·2
O(2)–C(2)–C(3)–O(3)	70·6	70·1	79·5	91·5
C(2)–C(3)–C(4)–O(4)	167·9	179·6	−172·5	−179·9
O(3)–C(3)–C(4)–C(5)	167·4	−178·7	−170·9	−175·4
O(3)–C(3)–C(4)–O(4)	−76·7	−66·9	−59·2	−64·5
C(3)–C(4)–C(5)–C(6)	−131·7	−146·6	−164·7	−165·1
O(4)–C(4)–C(5)–O(5)	−116·2	−136·2	−150·7	−154·1
O(4)–C(4)–C(5)–C(6)	115·7	98·6	81·6	79·3

	Conformation *A*	Conformation *B*
Torsion angles about the ten-membered rings (°)		
O(1)–C(1)–O(5)–C(5)	−84·4	−67·4
C(1)–O(5)–C(5)–C(6)	86·8	104·8
O(5)–C(5)–C(6)–O(1′)	−70·7	−81·8
C(5)–C(6)–O(1′)–C(1′)	149·9	144·1
C(6)–O(1′)–C(1′)–O(5′)	−64·5	−82·5
O(1′)–C(1′)–O(5′)–C(5′)	−77·8	−60·6
C(1′)–O(5′)–C(5′)–O(6′)	93·2	105·0
O(5′)–C(5′)–C(6′)–O(1)	−79·3	−89·6
C(5′)–C(6′)–O(1)–C(1)	147·0	144·4
C(6′)–O(1)–C(1)–O(5)	−54·1	−75·2
C(4)–C(5)–C(6)–O(1′)	57·9	46·3
C(6′)–O(1)–C(1)–C(2)	−179·7	160·3
C(4′)–C(5′)–C(6′)–O(1)	47·1	36·8
C(6)–O(1′)–C(1′)–C(2′)	172·2	155·9
Torsion angles about the glucoside bonds, as usually defined		
φ C(6′)–O(1)–C(1)–H(1)	65·5	44·7
C(6)–O(1′)–C(1′)–H(1′)	55·2	38·6
ψ C(5)–C(6)–O(1′)–C(1′)	149·9	144·1
C(5′)–C(6′)–O(1)–C(1)	147·0	144·4
Ω H(5)–C(5)–C(6)–O(1′)	174·8	163·6
H(5′)–C(5′)–C(6′)–O(1)	165·5	154·9

Backbone conformation

For both conformations, the pseudo C_2 symmetry of the ten-membered ring is still valid for the whole backbone. For the ten-membered rings, the difference between analogous torsion angles averages 7·0° for *A* and 4·5° for *B* (maximum values: 10·5 and 7·8° respectively). For the pyranose rings, with reference to endo- and exocyclic torsion angles of unprimed and primed rings, the difference between analogous angles averages 9·7 and 7·8° for *A* and *B* respectively.

Table 5. *Mean values of bond lengths* (Å), *bond angles* (°) *and torsion angles* (°) *in the acetate groups*

C(*i*)–O(*i*)	1·45 (1)	C(*i*)–O(*i*)–CA(*i*)	117·7 (9)
O(*i*)–CA(*i*)	1·36 (2)	O(*i*)–CA(*i*)–OA(*i*)	120·5 (13)
OA(*i*)–CA(*i*)	1·20 (2)	O(*i*)–CA(*i*)–CM(*i*)	110·9 (11)
CA(*i*)–CM(*i*)	1·52 (2)	OA(*i*)–CA(*i*)–CM(*i*)	126·3 (13)

C(*i*)–O(*i*)–CA(*i*)–OA(*i*)	6
C(*i*)–O(*i*)–CA(*i*)–CM(*i*)	177

The *gluco* configuration of the pyranose ring has O(4)–C(4)–C(5)–O(5) values of −116·3 and −136·1° for *A* and −150·7 and −154·1° for *B* [180° for a ${}^4C_1$ (D) ring]. These hexapyranose rings show one of the two preferred conformations of the *gluco* configuration, *gauche–gauche* (the other being *gauche–trans*). The O(5)–C(5)–C(6)–O(1′) $[\varphi^{O(5)}]$ and C(4)–C(5)–C(6)–O(1′) $[\varphi^{C(4)}]$ torsion angles are −70·6, −79·2° and 57·9, 47·1° for *A*, −81·8, −89·6° and 46·5, 36·6° for *B* and are significantly different from those recorded in a survey of *gluco*-configuration crystal structures by Pérez & Marchessault (1980) (mean values −66·5 and 65·0°).

Acetate groups

As reported in Table 5, the mean values of the acetate-group angles and torsion angles are consistent with those found in other carbohydrates. H(*i*)–C(*i*)–O(*i*)–CA(*i*) averages 18° in form *A*, but 39° in form *B*.

Packing and pseudosymmetry

The packing of the molecules in the unit cell is shown in Fig. 7. There are no very short intermolecular contacts and no particular molecular associations between two molecules. As reported in Table 6, the more significant intermolecular contacts are evenly distributed among the acetate-group atoms of molecules *A* and *B* and their translations; the molecules are held together by van der Waals forces only.

From Figs. 6 and 7 it is clear that the two molecules *A* and *B* of the asymmetric unit are roughly related by pseudo centers of symmetry, one of which is located at

Table 6. *Intermolecular distances* (Å)

First atom	Type	Second atom	Type	Translation for second atom			
CM(2)	*B*	OA(4)	*B*	−1	0	0	3·19 (1)
CM(2)	*A*	OA(2)	*B*	0	−1	0	3·29 (3)
CM(3)	*A*	OA(3′)	*B*	−1	0	0	3·30 (2)
CM(4′)	*A*	OA(2′)	*A*	1	0	0	3·32 (1)
CM(2′)	*A*	OA(2′)	*B*	0	0	1	3·35 (2)
CM(3′)	*A*	OA(4)	*A*	0	−1	0	3·39 (1)
OA(3)	*A*	C(6′)	*B*	0	0	0	3·02 (1)
CA(3)	*A*	OA(3′)	*B*	−1	0	0	3·12 (2)
CM(2′)	*A*	CM(3)	*B*	0	−1	1	3·55 (2)

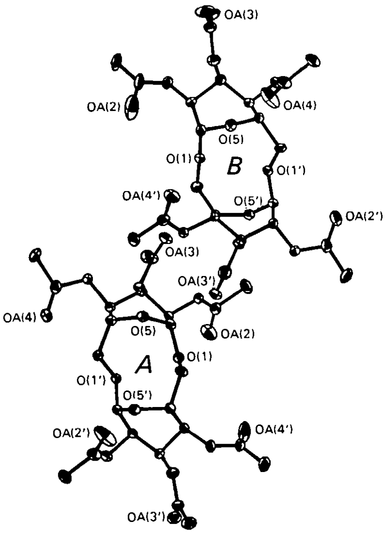

Fig. 6. A projection of the two molecules in the asymmetric unit.

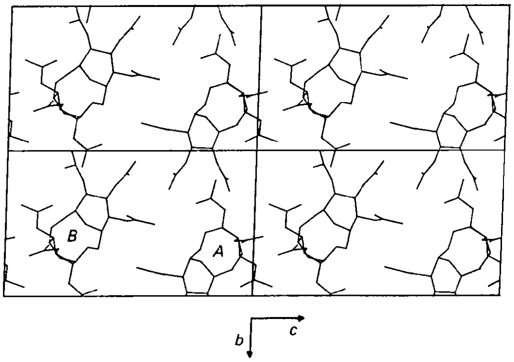

Fig. 7. Molecular packing of the two molecules.

(–0·366, –0·797, –0·1197). Since the compound is optically active, and the two conformations A and B are slightly different, it cannot be a true center of symmetry. In particular, application of pseudosymmetry transforms atoms O(1), C(6), O(1′), C(6′) of molecule A into C(6′), O(1′), C(6), O(1) of molecule B respectively (interchange O↔C) (see Fig. 6). However the six-membered rings and acetate groups of molecules A and B correspond quite well to each other by the pseudosymmetry.

A good idea of the extent of the pseudosymmetry is given by the distribution of phase values when the origin is located at one of the centers of pseudosymmetry (Fig. 8): 52% of the phases are pseudocentrosymmetric, differing from 0 or π by less than 30°. It is even more striking that out of the 499 reflexions used in *MULTAN*, 79% are pseudocentrosymmetric as defined above.

As a consequence of the high degree of pseudocentrosymmetry, it was interesting to see if the structure could have been solved in $P1$. The same characteristics of the convergence map occur as in $P1$, *i.e.* the 57 strongest reflexions have phases of 0° and it is then impossible to generate automatically a nonzero phase. However, a solution is arrived at by forcing into the initial set the reflexions of high E which have not been used for origin definition. This trick is based on the idea that among the strongest E's there may be a reflexion with a non-zero phase. This remark may be of general value and help to the solution in some cases.

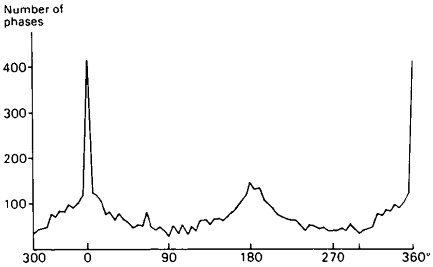

Fig. 8. Distributions of the phases for the 5286 reflexions.

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Changes in the Structure of the 1:2 Complex of *N*-Ethyl-*N*-methylmorpholinium and 7,7,8,8-Tetracyano-*p*-quinodimethane, MEM(TCNQ)$_2$, above Room Temperature. I. Determination of the Structures at 294 and 323 K

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Abstract

Crystals of MEM(TCNQ)$_2$ are triclinic, space group $P\bar{1}$, with a = 7·773 (8), b = 15·292 (15), c = 6·960 (7) Å, α = 112·34 (6), β = 74·59 (6), γ = 111·85 (6)°, U = 702 Å^3 at 294 K, and a = 7·775 (8), b = 15·290 (15), c = 6·979 (7) Å, α = 112·01 (6), β = 75·00 (6), γ = 111·77 (6)°, U = 707 Å^3 at 323 *K*, Z = 1. Intensities were collected with Zr-filtered Mo radiation on an automatic Nonius CAD-3 diffractometer. Anisotropic least-squares refinements decreased $R_w(F)$ to 0·077 for 2471 reflections at 294 K, and to 0·089 for 1877 reflections at 323 K. The reported structures are compared with the structure at 113 K [Bosch & van Bodegom (1977). *Acta Cryst.* B**33**, 3013–3021]. The individual TCNQ group, as well as the types of overlap between successive TCNQ molecules in the dimerized TCNQ stack, hardly changes between 113 and 323 K; both separations between the TCNQ units increase by 0·07 Å. The major change is the increasing disorder of the MEM group with increasing temperature. With the assumption of two preferred orientations the 100% occupancy of the orientation observed at 113 K decreases to 84% at 294 K and 63% at 323 K. This increase in disorder is used to explain the results of electrical-conductivity measurements.

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Introduction

In the study of a series of 1:2 complexes of *N*-substituted morpholinium and TCNQ most attention has been paid to the complex MEM(TCNQ)$_2$ (MEM = *N*-ethyl-*N*-methylmorpholinium). The compound undergoes two phase transitions, of second order at 19 K, and of first order at 340 K. Various physical properties have been measured for the three phases (Huizinga, Kommandeur, Sawatzky, Kopinga & De Jonge, 1978) and have, together with the phase transitions, been interpreted by Sawatzky, Huizinga & Kommandeur (1978). The transition at 19 K has a strong impact on the magnetic properties, whereas the high-temperature phase transition has a drastic effect on the electronic behaviour. As an example, the conductivity measured along the single-crystal needle axis is shown in Fig. 1 for temperatures ranging from 250 to 375 K (Sawatzky, Huizinga & Kommandeur, 1978). A jump of three orders of magnitude occurs at the transition temperature, 342 K on heating and 338 K on cooling. Above the phase transition the conductivity is weakly temperature dependent and lies between 1·5 and 3·0 Ω^{-1} mm^{-1}. In the ranges 250 to 290 K and 320 to 340 K the conductivity $\sigma(T)$ can be described by the function $\sigma(T) = \sigma_o \exp(-E_{\rm ACT}/kT)$, with an activation energy $E_{\rm ACT}$ = 0·35–0·39 eV. Between these ranges an