Conclusion

La structure cristalline du tétraphénylborate de tributylammonium monohydrate présente une interaction complexe $N^+-H\cdots W\begin{matrix}<H\cdots\pi\\<H\cdots\pi\end{matrix}$ dans laquelle une molécule d'eau sert de liaison entre le cation ammonium et l'anion. Cette molécule d'eau est fortement fixée par deux liaisons hydrogène dans lesquelles les orbitales électroniques π des deux cycles phényle qui l'enserrent jouent le rôle de site accepteur de liaison H. Cette interaction est suffisamment forte pour entraîner une déformation de l'angle valentiel dont l'atome de bore est au sommet et un pincement des noyaux aromatiques qui tendent à se rapprocher.

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The Crystal and Molecular Structure of a Trisaccharide, β-Cellotriose Undecaacetate: 1,2,3,6-Tetra-*O*-acetyl-4-*O*-[2,3,6-tri-*O*-acetyl-4-*O*-(2,3,4,6-tetra-*O*-acetyl-β-D-glucopyranosyl)-β-D-glucopyranosyl]-β-D-glucopyranose

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(*Received* 10 *September* 1976; *accepted* 10 *February* 1977)

The crystal structure of β-cellotriose undecaacetate, $C_{40}O_{27}H_{54}$, has been solved by direct methods from 3391 independent reflexions and refined by a least-squares block-diagonal approximation to a final R value of 0·091. The crystal data are: $a = 5{\cdot}675$ (3), $b = 37{\cdot}216$ (10), $c = 11{\cdot}709$ (5) Å, $\beta = 94{\cdot}78$ (10)°, space group $P2_1$, $Z = 2$. The three β-D-glucose (1 → 4)-linked residues have the $^4C_1$ pyranose conformation. The conformation of the glycosidic linkage is characterized by the torsion angles (φ, ψ), which take the values $\varphi = 24°$, $\psi = -20°$ between the non-reducing residues and $\varphi = 46°$, $\psi = 12°$ between the reducing and the middle residues. The primary acetate substituent at C(6) of the reducing residue is in the *gt* conformation. However, the conformation is *gg* for the other primary acetates in the non-reducing residues. The molecules are all extended in the same direction, which is nearly parallel to **b**.

Introduction

An approach to the determination of the conformational features of a polymer may lie in the systematic study of crystal structures of related small molecules or oligomers. The studies of the crystalline conformation of oligomethylene derivatives related to the poly(oligomethylene terephthalates): $[O-(CH_2)_p-O-CO-C_6H_4-CO]_n$, with $p = 2$, 3 and 6 (Pérez & Brisse, 1976*a*,*b*, 1977*a*), have indicated that the solid-state conformation of the polymer could be close to that of the model compound. The present study aims at the same type of investigation in the area of oligosaccharides and their chemically related polysaccharides.

The crystal structure of β-cellobiose octaacetate was reported previously (Leung, Chanzy, Pérez & Marchessault, 1976). A conformational study taking into account the information derived from the above-mentioned dimer pointed out the restricted range of available data (Marchessault & Sundararajan, 1975). The purpose of the determination of the structure of β-cellotriose undecaacetate is to try to establish the most likely conformation of the anhydroglucose triacetate repeating unit present in cellulose triacetate and in related acetate oligosaccharides.

Experimental

Samples of β-cellotriose undecaacetate were obtained from D. Horton (Ohio State University, Columbus, Ohio). They were examined by NMR to confirm that only the β-anomer was present. The samples, dissolved in hot ethanol containing about 5% water, were allowed to evaporate very slowly. After about two weeks, long needles suitable for X-ray study were obtained.

Weissenberg and precession photographs indicated that the crystals were monoclinic, space group $P2_1$ (systematic absences $0k0$, $k \neq 2n$). The unit-cell dimensions were obtained as part of the alignment process on an automatic diffractometer by a least-squares fit to the setting of 12 well centred reflexions. These and other relevant crystallographic data are presented in Table 1.

Intensity data were collected on a Picker FACS-I diffractometer with a graphite monochromator, within one quadrant of the sphere limited by $2\theta \leq 120°$. The θ–2θ scan technique was used with a 2θ scan rate of 1° min^{-1} at a minimum scan width of 1·5° (2θ). Background counts of 20 s were taken at each end of the scan range. The intensities of three reference reflexions measured every 30 reflexions decreased by about 5% of their initial value over the duration of the data collection. The data were corrected for Lorentz and polarization effects. The data reduction was performed with the programs of Ahmed, Hall, Pippy & Huber (1966). 3446 independent reflexions were measured, of which 471 were assigned zero weight as the net count of each was less than $1{\cdot}96\sigma(I)$, where $\sigma(I)$ is the standard deviation estimated from counting statistics by a relation described by Pérez & Brisse (1976*a*). No absorption correction was applied. The X-ray scattering factors were obtained from Cromer & Waber (1965) for C and O atoms, and from Stewart, Davidson & Simpson (1965) for H.

Table 1. *Crystal data*

$C_{40}O_{27}H_{54}$, $M_r = 966{\cdot}8$, $F(000) = 1020$, $a = 5{\cdot}675$ (3), $b = 37{\cdot}216$ (10), $c = 11{\cdot}709$ (5) Å, $\beta = 94{\cdot}78$ (4)°, $V = 2464{\cdot}3$ Å^3, monoclinic, $P2_1$, $d_o = 1{\cdot}28$, $d_c = 1{\cdot}303$ g cm^{-3}, $Z = 2$, μ(Cu $K\alpha$) = 9·9 cm^{-1}, λ(Cu $K\bar{\alpha}$) = 1·54178 Å.

Structure determination and refinement

A first set, E_A, of normalized structure factors was calculated for randomly positioned *atoms*. Then a second set, E_B, was calculated according to Main (1976) with the assumption that the *groups of atoms* were in random positions and orientation. This was performed with the equation

$$|E|^2 = Ke^{2Bs^2}|F|^2/\varepsilon \Sigma g^2(s),$$

where g is the spherically averaged molecular scattering factor calculated by the relation (Debye, 1915):

$$g^2(s) = \sum_i \sum_j f_i(s) f_j(s) \sin(4\pi s r_{ij})/4\pi s r_{ij},$$

where r_{ij} is the distance between atoms i and j. This computation was performed with the molecular geometry of β-cellotriose undecaacetate as partially provided by the crystal structure of β-cellobiose octaacetate (Leung *et al.*, 1976). The two sets of E's were then used as inputs in the *SIGMA*2 and *CONVERGE* routines of *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974), with all E's down to 1·65. In this manner there were approximately four E's per non-hydrogen atom to be found. In the case of set E_A the development of 1024 sets of phases was required, while set E_B necessitated only 32. The *FASTAN* procedure was applied on the E_B data set only and among the 32 different solutions provided by this computation, only one appeared to be self-consistent. The various indicators which led to the best set of phases and to the solution of the structure are shown in Table 2.

The resulting E map revealed 33 non-hydrogen atoms. A recycling procedure making use of the most reliable phases failed to yield more than five additional non-hydrogen atoms. Similarly, a new generation of phases initiated with the phases given by the known 33 atoms allowed the location of very few of the remaining atoms. It was then noticed that the $h0\bar{l}$ reflexions had been accidentally omitted at the data-reduction stage. When these were included the R value at this stage was 0·35. The complete molecule, with the exception of the $OA(6'')$ and $CM(6'')$ atoms of the $C(6'')$ acetate group, was obtained after a succession of Fourier or difference

Table 2. *Figures of merit (FOM) of the best set of phases and extreme values*

	Absolute FOM	Ψ_0* ($\times 10^3$)	Residual	Combined FOM	Mean phase error (°)
Best set of phases	1·2607	198·7	20·4	2·00	25·5
Maximum value	1·3755	420·2	30·4		89·8
Minimum value	1·1355	198·7	20·4		25·5
Published phases	1·2281	195·0	18·6		21·9
Published phases refined by *FASTAN*	1·2699	193·7	18·7		20·7

* $\Psi_0 = \sum_H |\sum_{H'} E_{H'} E_{H-H'}|$ for all H's with $E_H = 0$, or nearly 0.

Fourier maps.* Similarly to what was observed in the case of β-cellobiose octaacetate, the C(6) acetate group belonging to the reducing end of the oligosaccharide was very poorly defined, *i.e.* the isotropic temperature factors of the C(6″), O(6″) and C*A*(6″) atoms were very high: 8, 12 and 16 Å^2 respectively. At the end of the refinement any attempt to localize the remaining O*A*(6″) and C*M*(6″) atoms on difference Fourier maps failed. However, 'columns' of residual electron density centred on the likely position of these two missing atoms were revealed. As the determination of a precise molecular geometry of the acetate groups was not our prime interest, and because an approximately reliable knowledge of the relative orientation of this acetate group could, nevertheless, be derived from the location of the C*A*(6″) carbon atom, no other refinement approach was tried. Taking into account the resonance within the acetate group, the rotation about the O(6″)–C*A*(6″) bond was ignored, and a conformation was assumed in which the four atoms of the acetate group were kept coplanar. Most of the non-methyl H atoms were located from difference Fourier maps. The positions of the others and all the methyl H atoms were calculated. The latter were computed on the basis that, in an acetate group, one of the methyl H atoms and the O atom are in a *gauche* conformation. The main steps of the refinement of the structure are summarized in Table 3. In the last stages of the refinement 12 reflexions probably suffering from extinction were removed. At the end of the refinement the average shift/e.s.d. of the coordinates was less than 0·6 and the final R value was 0·091.† A final electron density map showed some residual density within 0·7 and −0·6 e Å^{-3}, located, as previously mentioned, around the C(6″) acetate group.

* The atoms of the acetate groups have been labelled C*A*, C*M* and O*A*. These abbreviations stand for the carbonyl C, the methyl C and the carbonyl O atom respectively (see Fig. 2).

† Lists of structure factors and thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32526 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Results and discussion

The positional parameters and their standard deviations are presented in Table 4. The standard deviations of the corresponding distances and angles amount to 0·015 Å and 0·8° for nonhydrogen-atom bond distances and angles respectively, when referring to the pyranose rings. These quantities amount to 0·020 Å and 1·5° for bond distances and angles within the different acetate groups.

Thus, the reliability of bond lengths and angles, particularly for the acetate groups, is greatly reduced. This low accuracy, by modern standards, is attributed to the high thermal motion in this structure as well as the relative paucity of the number of reflexions compared with the number of parameters being refined. A stereoscopic view of the β-cellotriose undecaacetate molecule is shown in Fig. 1 (*ORTEP*, Johnson, 1965).

Bond distances and angles

The bond lengths, bond angles and the numbering system of the molecule are depicted in Fig. 2. The numbering of the atoms proceeds from the non-reducing glucose end (unprimed) to the reducing end (double primed).

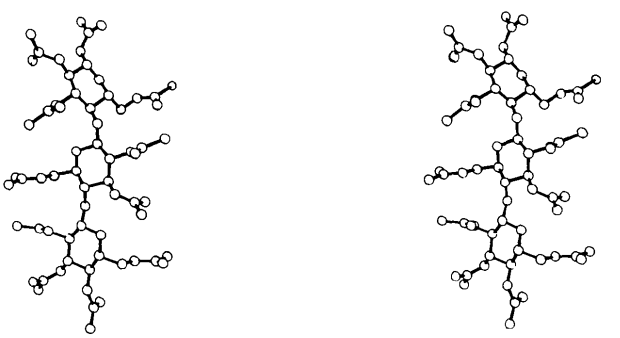

Fig. 1. Stereoscopic view of one β-cellotriose undecaacetate molecule.

Table 3. *Summary of the unweighted block-diagonal least-squares refinement*

$R = \Sigma \Delta F / \Sigma F_o$; $\sigma_F = [\Sigma w \Delta F^2/(m-n)]^{1/2}$; m = number of reflexions; n = number of parameters refined.

Cycle	n	R	σ_F	Comments
1–3	254	0·165	17·2	63 non-hydrogen atoms; isotropic refinement
4–6	569	0·140	13·6	63 non-hydrogen atoms; anisotropic refinement
7–9	569	0·117	11·2	Addition of the four atoms of the C(6″) group in fixed positions
10–12	569	0·108	10·6	Addition of 21 H atoms (not refined)
13–16	653	0·091	9·1	Addition of 33 methyl H atoms in fixed positions; anisotropic refinement of C and O; isotropic refinement of the 21 non-methyl H atoms

Table 4. *Fractional coordinates and their e.s.d.'s*

The coordinates are in fractions of unit cell edges $\times 10^4$ for O and C, and $\times 10^3$ for H. The standard deviations refer to the least significant digit.

	x	*y*	*z*		*x*	*y*	*z*
O(1)	2393 (13)	−108 (2)	6854 (7)	C*A*(2″)	79 (32)	−2709 (4)	9292 (14)
O(2)	3601 (15)	317 (2)	8922 (7)	C*M*(2″)	−1774 (37)	−2898 (5)	9821 (18)
O(3)	4670 (15)	1040 (2)	8255 (8)	C*A*(3″)	−2123 (28)	−1672 (5)	8830 (16)
O(4)	689 (21)	1330 (2)	6858 (9)	C*M*(3″)	−1844 (36)	−1489 (6)	9878 (15)
O(5)	622 (14)	392 (2)	6024 (7)	C*A*(6″)	2081	−2011	2811
O(6)	341 (15)	834 (2)	4216 (7)	C*M*(6″)	2726	−2227	1802
O*A*(2)	7565 (19)	338 (5)	8963 (10)	H(1)	9 (27)	26 (4)	765 (13)
O*A*(3)	2983 (21)	1211 (3)	9805 (10)	H(2)	488 (21)	47 (3)	736 (10)
O*A*(4)	3695 (30)	1594 (4)	6045 (15)	H(3)	112 (32)	83 (5)	844 (15)
O*A*(6)	−2543 (17)	861 (3)	2803 (9)	H(4)	296 (25)	102 (4)	616 (12)
C(1)	1391 (21)	220 (3)	7136 (10)	H(5)	−168 (21)	70 (3)	664 (10)
C(2)	3347 (22)	450 (3)	7759 (11)	H(61)	−275 (27)	77 (4)	465 (13)
C(3)	2547 (24)	843 (4)	7830 (11)	H(62)	−208 (24)	109 (3)	488 (12)
C(4)	1752 (25)	979 (3)	6683 (12)	H*M*(21)	399	20	1086
C(5)	−352 (22)	732 (3)	6173 (11)	H*M*(22)	648	41	1118
C(6)	−1348 (24)	858 (4)	5018 (12)	H*M*(23)	648	−1	1093
C*A*(2)	5910 (27)	298 (5)	9436 (12)	H*M*(31)	809	135	897
C*M*(2)	5724 (33)	219 (5)	10702 (15)	H*M*(32)	768	130	1032
C*A*(3)	4594 (25)	1208 (4)	9232 (15)	H*M*(33)	673	166	965
C*M*(3)	6931 (30)	1392 (5)	9552 (18)	H*M*(41)	−112	188	703
C*A*(4)	1958 (39)	1619 (5)	6464 (17)	H*M*(42)	−14	209	594
C*M*(4)	462 (63)	1961 (5)	6665 (19)	H*M*(43)	122	214	721
C*A*(6)	−509 (25)	831 (4)	3118 (13)	H*M*(61)	303	77	279
C*M*(6)	1459 (33)	785 (5)	2360 (16)	H*M*(62)	151	100	180
O(1′)	−342 (15)	−1498 (2)	6207 (7)	H*M*(63)	123	57	185
O(2′)	−1316 (14)	−1011 (2)	4403 (7)	H(1′)	224 (24)	−119 (3)	576 (12)
O(3′)	−2098 (14)	−292 (2)	5385 (7)	H(2′)	−248 (27)	−87 (4)	614 (13)
O(5′)	1231 (15)	−1050 (2)	7334 (7)	H(3′)	122 (22)	−51 (3)	513 (10)
O(6′)	1885 (16)	−595 (3)	9268 (7)	H(4′)	−63 (21)	−39 (3)	729 (10)
O*A*(2′)	−5197 (20)	−961 (4)	4421 (9)	H(5′)	401 (23)	−70 (4)	691 (11)
O*A*(3′)	−786 (18)	−165 (3)	3637 (8)	H(61′)	459 (24)	−89 (3)	878 (11)
O*A*(6′)	4510 (22)	−634 (4)	10718 (10)	H(62′)	487 (25)	−48 (4)	864 (12)
C(1′)	747 (22)	−1172 (3)	6203 (11)	H*M*(21′)	−172	−123	256
C(2′)	−1016 (22)	−900 (3)	5590 (11)	H*M*(22′)	−417	−103	213
C(3′)	−34 (21)	−521 (3)	5640 (10)	H*M*(23′)	−424	−144	264
C(4′)	911 (21)	−421 (3)	6878 (10)	H*M*(31′)	−567	0	472
C(5′)	2660 (21)	−722 (3)	7350 (11)	H*M*(32′)	−557	−8	337
C(6′)	3642 (24)	−662 (4)	8534 (12)	H*M*(33′)	−451	29	388
C*A*(2′)	−3602 (26)	−1043 (4)	3955 (12)	H*M*(61′)	−92	−45	1054
C*M*(2′)	−3412 (38)	−1199 (5)	2740 (15)	H*M*(62′)	90	−28	1154
C*A*(3′)	−2265 (23)	−150 (4)	4309 (11)	H*M*(63′)	16	−70	1160
C*M*(3′)	−4705 (25)	23 (4)	4054 (13)	H(1″)	10 (25)	−268 (4)	638 (12)
C*A*(6′)	2536 (27)	−602 (5)	10426 (13)	H(2″)	266 (22)	−231 (3)	808 (11)
C*M*(6′)	532 (35)	−509 (7)	11052 (15)	H(3″)	−165 (22)	−205 (3)	711 (10)
O(1″)	3383 (19)	−2832 (2)	6982 (9)	H(4″)	251 (23)	−168 (4)	678 (11)
O(2″)	−514 (17)	−2585 (3)	8256 (8)	H(5″)	27 (26)	−212 (4)	515 (12)
O(3″)	−104 (15)	−1820 (2)	8464 (8)	H(61″)	191 (22)	−158 (3)	458 (10)
O(5″)	3030 (21)	−2329 (3)	5927 (10)	H(62″)	417 (26)	−170 (4)	519 (13)
O(6″)	3635	−2012	3749	H*M*(11″)	652	−326	740
O*A*(1″)	1692 (27)	−3228 (3)	5833 (14)	H*M*(12″)	628	−344	612
O*A*(2″)	1976 (26)	−2665 (4)	9742 (11)	H*M*(13″)	483	−361	714
O*A*(3″)	−3823 (25)	−1722 (6)	8283 (15)	H*M*(21″)	−328	−292	930
O*A*(6″)	279	−1842	2811	H*M*(22″)	−220	−278	1056
C(1″)	1788 (28)	−2558 (4)	6683 (13)	H*M*(23″)	−130	−315	1003
C(2″)	1199 (24)	−2360 (3)	7675 (12)	H*M*(31″)	−17	−148	1020
C(3″)	−132 (23)	−2017 (3)	7396 (11)	H*M*(32″)	−285	−159	1045
C(4″)	1151 (24)	−1795 (3)	6541 (12)	H*M*(33″)	−237	−122	977
C(5″)	1563 (31)	−2026 (4)	5522 (13)	H*M*(61″)	429	−234	198
C(6″)	2951 (39)	−1816 (5)	4734 (14)	H*M*(62″)	282	−206	112
C*A*(1″)	3306 (30)	−3140 (4)	6441 (14)	H*M*(63″)	150	−241	161
C*M*(1″)	5394 (31)	−3386 (5)	6778 (19)				

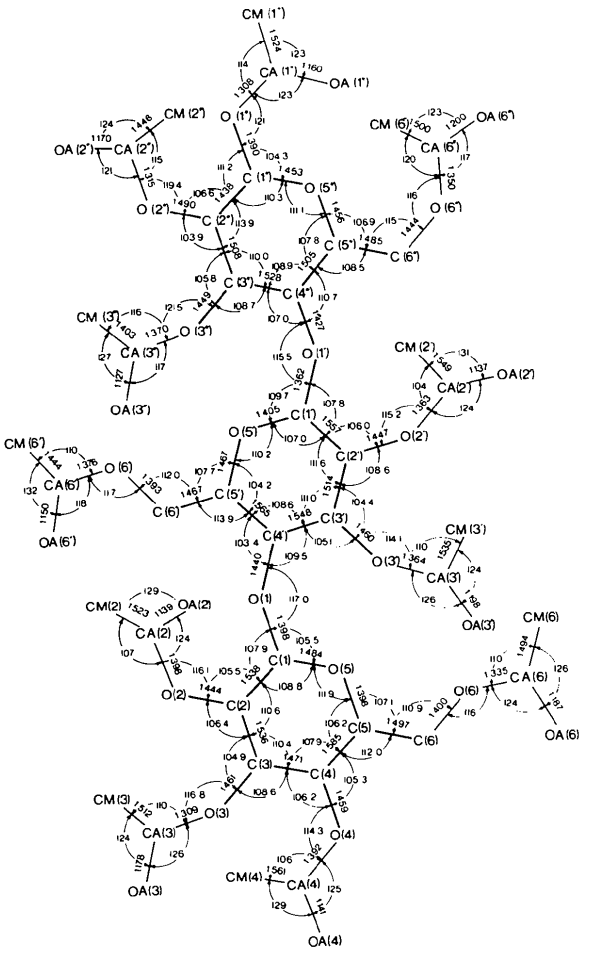

Fig. 2. Bond distances (Å) and angles (°) for β-cellotriose undecaacetate.

The C–C ring bond lengths average 1·495, 1·546 and 1·533 Å for the reducing, middle and non-reducing residues respectively. In the three residues the exocyclic C(5)–C(6) bond is found to be consistently shorter than the average C–C ring bond. This point has already been reported by Ham & Williams (1970) and by Takeda, Yasuoka & Kasai (1977). When the anomeric and bridge C–O bonds are excluded, the exocyclic C–O bond lengths average 1·458 Å, which is slightly greater than the mean value of 1·426 Å listed by Arnott & Scott (1972). The bond lengths of the glycosidic bridges are: C(1)–O(1) = 1·398 (14), O(1)–C(4′) = 1·440 (14), C(1′)–O(1′) = 1·362 (14) and O(1′)–C(4″) = 1·427 (15) Å.

The bond angles at the bridge O atoms are of particular interest. The values of 117·0 and 115·5°, for C(1)–O(1)–C(4′) and C(1′)–O(1′)–C(4″) respectively, are consistent with those found for oligosaccharides with a (1→4) linkage (Chu & Jeffrey, 1968; Fries, Rao & Sundaralingam, 1971; Quigley, Sarko & Marchessault, 1970; Gress & Jeffrey, 1977; Hirotsu & Shimada, 1974; Leung, Chanzy, Pérez & Marchessault, 1976).

The internal C–C–C ring angles are close to tetrahedral (range 107·9–113·9°, mean 110·3°). The six endocyclic C–C–O bond angles (range 104·3–110·3°, mean 107·8°) have an average value noticeably smaller than the value of 110·0° listed by Arnott & Scott (1972). The three endocyclic C–O–C bond angles vary very little and average 111·1°. The exocyclic C–C–O angles show a wide range of variation, from 103·4 to 111·2°, and average 106·8°.

Molecular conformation

As a thorough comparison between the crystalline conformations of β-cellobiose octaacetate and β-cellotriose undecaacetate, as well as the resulting implications with respect to the crystalline structure of cellulose triacetate, will be presented elsewhere (Pérez & Brisse, 1977*b*; Marchessault, Brisse & Pérez, 1977), only the main features of the molecular geometry and conformation of β-cellotriose undecaacetate are reported here.

The molecular conformation involves $^4C_1$ pyranose rings. The relative orientation of contiguous pyranosides is customarily described by the torsion angles around the glycosidic bonds C(1)–O(1), O(1)–C(4′) and C(1′)–O(1′), O(1′)–C(4″), and are denoted as the conformational angles φ, ψ.* The conformation of the primary acetate substituent at C(6) is described by the torsion angles: χ [O(5)–C(5)–C(6)–O(6)] and θ [C(5)–C(6)–O(6)–C*A*(6)], referred to as [$\chi(5)$, $\theta(6)$], [$\chi(5')$, $\theta(6')$] and [$\chi(5'')$, $\theta(6'')$] in the unprimed, primed and double-primed residues respectively. The torsion angles of interest are listed in Table 5.

The torsion angles relating the two residues within the non-reducing moiety (φ = 24°, ψ = −20°) correspond to the maximum elongation of this part of the molecule. This relative orientation of the non-reducing residues is markedly different from that found when the reducing end is involved (φ = 46°, ψ = 12°). The corresponding angles in β-cellobiose octaacetate are 44 and 16°. This difference has been discussed in terms of the *exo*-anomeric effect (Marchessault, Brisse & Pérez, 1977).

The primary acetate groups on the non-reducing residues exist in a similar conformation: $\chi(5)$ = −52°, $\theta(6)$ = 160° and $\chi(5')$ = −65°, $\theta(6')$ = 168°. According to the terminology proposed by Sundaralingam (1968) this conformation corresponds to

* φ = H(1)–C(1)–O(1)–C(4′); ψ = C(1)–O(1)–C(4′)–H(4′). The hydrogen positions used were not those found in the crystal structure. Instead these positions were computed on the basis of a perfect tetrahedral coordination according to the convention of Sundararajan & Rao (1969).

Table 5. *Torsion angles* (°)

Torsion angles about the glycosidic bonds

	Unprimed–primed residues	Primed–double-primed residues
C(1)–O(1)–C(4′)–C(3′)	102	134
C(1)–O(1)–C(4′)–C(5′)	−143	−108
C(4′)–O(1)–C(1)–O(5)	−98	−75
C(4′)–O(1)–C(1)–C(2)	146	169

Endocyclic torsion angles

	Unprimed residue	Primed residue	Double-primed residue
C(1)–O(5)–C(5)–C(4)	68	73	65
C(5)–O(5)–C(1)–C(2)	−62	−70	−62
O(5)–C(1)–C(2)–C(3)	53	57	54
C(1)–C(2)–C(3)–C(4)	−54	−49	−51
C(2)–C(3)–C(4)–C(5)	59	52	53
C(3)–C(4)–C(5)–O(5)	−65	−61	−61

Exocyclic torsion angles

	Unprimed residue	Primed residue	Double-primed residue
C(1)–O(5)–C(5)–C(6)	−173	−165	−178
C(5)–O(5)–C(1)–O(1)	180	173	179
O(1)–C(1)–C(2)–C(3)	166	175	169
O(5)–C(1)–C(2)–O(2)	167	174	167
O(2)–C(2)–C(3)–C(4)	−168	−166	−166
C(1)–C(2)–C(3)–O(3)	−171	−162	−167
O(3)–C(3)–C(4)–C(5)	173	164	169
C(2)–C(3)–C(4)–O	O=O(4) 171	O=O(1) 164	O=O(1′) 173
O–C(4)–C(5)–O(5)	O=O(4) −179	O=O(1) −177	O=O(1′) −178
C(3)–C(4)–C(5)–C(6)	178	−178	−176
O(1)–C(1)–C(2)–O(2)	−79	−67	−77
O(2)–C(2)–C(3)–O(3)	75	81	77
O(2)–C(3)–C(4)–O	O=O(4) −75	O=O(1) −83	O=O(1′) −72
O–C(4)–C(5)–C(6)	O=O(4) 65	O=O(1) 65	O=O(1′) 66
O(5)–C(5)–C(6)–O(6)	−52	−64	60
C(4)–C(5)–C(6)–O(6)	64	52	176
C(5)–C(6)–O(6)–CA(6)	160	168	88

the *gauche–gauche* form (abbreviated *gg*). However, a different conformation is displayed by the primary acetate group on the reducing residue: $\theta(6'') = 60°$, $\chi(5'') = 88°$; this corresponds to the *gauche–trans* form (abbreviated *gt*).

Here again, the situation is comparable to that in β-cellobiose octaacetate where the primary acetate groups were found to be stereochemically different. In the solid state the behaviour of the reducing end of the two oligomers so far studied is strikingly comparable. This feature seems to distinguish significantly the reducing end from the non-reducing moieties.

If the two non-reducing residues were considered as a dimeric segment of cellulose triacetate, the repeat unit would be 10·56 Å. Although the exact nature of the chain symmetry of the polymer has not yet been established, the observed fibre repeat is 10·54 (2) Å (Roche & Chanzy, 1977). It is therefore very probable that the solid-state conformation of cellulose triacetate II will involve glycosidic torsion angles with values very

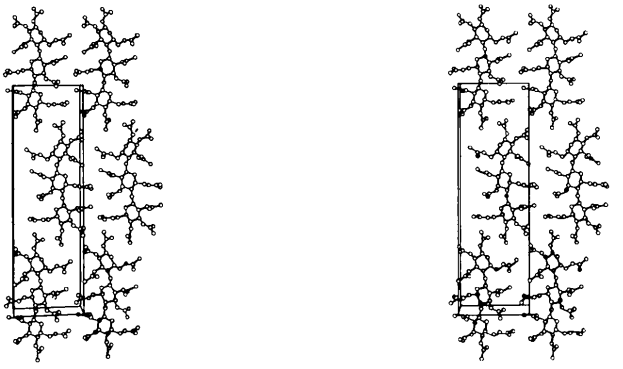

Fig. 3. Packing of the molecules of β-cellotriose undecaacetate.

close to those found for the relative orientation of the non-reducing residues in β-cellotriose undecaacetate.

Molecular packing

The packing of the molecules in the unit cell is shown by the stereoscopic pair of Fig. 3. There is a near coincidence of the developing chain axis with the largest unit-cell dimension. In this space group, the molecules can only organize themselves in a 'parallel' manner. There are no particularly short intermolecular contacts and the molecules are held together by van der Waals forces only.

Conclusions

A recent study of the effect of acetate substituents on the conformations of di- and polysaccharides (Marchessault & Sundararajan, 1975) showed that conformational analysis of polysaccharide chains is most reliable when chain coordinates are derived from the single-crystal structure of directly related dimers. The present finding of a distinctive stereochemical behaviour at the reducing end of β-cellobiose and β-cellotriose acetates precludes the extrapolation of any conformational information derived from the structure determination of a disaccharide to the related polysaccharide. Even though the respective arrangement of the unprimed and primed residues in β-cellotriose undecaacetate seems to suggest a conformation close to that of the polymer, it remains to be shown whether or not the structural knowledge of oligomers, such as a trimer, is sufficient to yield in a straightforward manner the structure of a polysaccharide. The structure of β-cellotetrose acetate would be the logical model to confirm the specificity of the reducing residue and the constancy of the relative orientation of successive anhydroglucose triacetate groups.

We are grateful to Professor R. H. Marchessault of this Department and to Dr H. D. Chanzy, CERMAV, Grenoble, France, for their continuous interest in this work. We are very thankful to the National Research Council of Canada for its financial assistance (CNR-A-5968).

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