Molecular and crystal structure of cellulose triacetate I: a parallel chain structure

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The crystal structure of cellulose triacetate I (CTA I), obtained by heterogeneous acetylation of ramie cellulose I, has been determined by a combined X-ray diffraction and stereochemical model analysis. The structure packs in a two chain, orthogonal unit cell with dimensions a = 23.63 Å, b = 6.27 Å, c (fibre repeat) = 10.43 Å, but with $P2_1$ symmetry. The two chains pack with parallel polarity and the two-fold screw axes coincide with the chain axes. In these respects, the structure of CTA I is similar to that of cellulose I. The conformations of the chain and of the glucose residue are similar to the conformation of the crystalline cellotriose undecaacetate, in that the ϕ, ψ angles, the O(6) rotational positions, acetate positions and bond and conformation angles are comparable in both structures. The reliability of the structure determination of CTA I is indicated by the crystallographic R = 0.242.

INTRODUCTION

Investigations into the crystal structure of cellulose triacetate (CTA) date back almost fifty years when interplanar d-spacings were first published[1]. This material is now recognized to crystallize in at least two polymorphic forms designated as CTA I and CTA II depending on the method of preparation. The CTA I polymorph is obtained by the heterogeneous acetylation of native cellulose while the CTA II polymorph arises if the acetylated material is precipitated from solution or swollen with solvent. Heterogeneous acetylation of cellulose II after suitable pretreatment also yields CTA II as does the treatment of CTA I with superheated steam[2]. Sprague *et al.* briefly review the earlier work on CTA and propose unit cells for both polymorphs without giving structural details[3]. The first crystal structure analysis on cellulose triacetate was performed by Dulmage who attempted to solve the structure of CTA II in a two dimensional projection normal to the fibre axis[4]. The proposed structure was based on a four chain orthorhombic unit cell in which pairs of chains were related by a two-fold screw axis located between them. Space group considerations required that neighbouring pairs be opposite, or antiparallel, in chain packing polarity. More recent work by Roche *et al.*, based on a complete three dimensional X-ray refinement[5], has revealed that the Dulmage model was essentially correct. Because a similar structure analysis has not been performed on CTA I and because the various reported interconversions between cellulose and CTA polymorphs have not been adequately explained, it became of interest to us to determine the detailed crystal structure of CTA I.

EXPERIMENTAL

Samples of CTA I were prepared by the method of Buras *et al.*[6] with slight modifications. Native ramie cellulose was pretreated in a solution of 90% acetic acid for periods of 10–30 min followed by rinsing in glacial acetic acid. The acetylation medium consisted of 250 ml of a 50/50 (v/v) mixture of freshly distilled acetic anhydride and benzene and three drops of 70% perchloric acid. The heterogeneous treatment was carried out at room temperature for 16–48 h prior to termination by immersion of the sample in ethanol. The product was rinsed several times in ethanol to remove traces of acid and benzene, and was heat-annealed at 230°–260°C in air for periods of 10–30 min. Heat treatment of the samples induced a marked improvement in the quality of the X-ray diffractograms. The above procedure was also repeated successfully with Valonia cellulose but well oriented X-ray patterns were not obtained due to the difficulty involved in drawing fibres from the acetylated vesicles.

X-ray diffractograms were recorded on flat film, multiple sheet packs of Ilford Type G Industrial X-Ray film both in an evacuated pinhole camera and a Searle X-ray Camera with toroidal focus. In both instances nickel filtered CuKα radiation was used and exposed films were developed with Kodak Liquid X-Ray Developer. A typical diffractogram is shown in *Figure 1*.

A total of 22 reflections on 4 layer lines were observed of which 20 were sufficiently well resolved for use in a least squares refinement of the unit cell parameters. The X-ray diagrams were scanned along the layer lines with a Joyce–Loebl recording microdensitometer and the layer line tracings were resolved into individual integrated intensity envelopes with a least squares curve resolution computer program. Resolved in this manner were 31 intensity envelopes containing the contributions of 72 *hkl* planes. The minimum observed d-spacing thus obtained was 2.17 Å, for the outermost reflection on the third layer line. Not observed on the tracings were predicted reflections from 24 *hkl* planes. These unobserved reflections were assigned an arbitrary integrated intensity equal to one half the minimum resolvable intensity in the corresponding region of diffraction angle. The integrated intensities were then corrected for Lorentz[7] and polarization factors, reflection arcing, distance of diffrac-

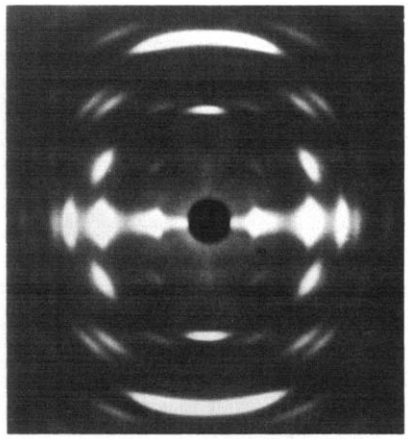

Figure 1 X-ray diffraction diagram of CTA I. Fibre axis is vertical

ted ray to film, and tracing direction other than radial, and were converted to relative observed structure factors (F_{obs}). A total of 96 reflections, contributing to 48 structure factors, could be included in this manner in the X-ray structure refinement.

The density of the CTA I sample was 1.29 g/cm^3, determined by flotation in a mixture of CCl_4 and xylene. It was observed that the apparent density of the material increased with time of immersion in the solvent mixture, apparently due to absorption of liquid. Therefore, the value of 1.29 g/cm^3 represents an upper limit to the density of CTA I since a period of time was required to perform the flotation experiment.

RESULTS

Determination of unit cell parameters

The fibre repeat distance (c) was determined by averaging the measurements from several resolved reflections on the first three layer lines and the result was held invariant in the least squares refinement of the other two unit cell dimensions. The refinement with 20 observed reflections resulted in an orthogonal cell of dimensions a = 23.63 Å, b = 6.27 Å, and c = 10.43 Å. All reflections were equally weighted at 1.0 in the refinement, with the exception of 200 and 201 which were assigned a weight equal to 0.5. The calculated density of 1.24 g/cm^3 for this unit cell, assuming it contains two chains of CTA, is in reasonable agreement with the observed density. Other unit cells such as one, two and four chain orthogonal and monoclinic cells were considered, but were rejected based on density calculations and/or failure to account for all observed reflections. The monoclinic unit cell proposed by Sprague *et al.*[3] was examined in great detail but was also rejected because it did not correctly predict two medium intensity reflections on the equator (d = 8 Å and d = 6.1 Å). In addition, the density calculated for the Sprague cell, 1.39 g/cm^3, was appreciably higher than that observed for our sample. It should be noted that Sprague and other authors might have incorrectly assigned an hkl = 003 Miller index to the very strong reflection on the third layer of the CTA I pattern. Tilting the sample to the Bragg angle for the true third order meridional revealed that the latter was not present and that the strong observed reflection was actually an off-meridional one at d = 3.33 Å. Fibre repeat distances calculated from the apparent 003 reflection are therefore incorrect.

The location of the two chains in the unit cell was determined from Patterson projections and the calculation of two dimensional R values with equatorial intensities. Both indicated chain locations at x,y = 0,0 and $a/2$,0 as the most probable arrangement. It was still possible that the axis of the second chain could be moved slightly in the y-direction from the position at $a/2$,0.

The X-ray diffractograms revealed no obvious systematic absences and a space group determination could not be made directly although it was assumed to be $P2_1$. The observed second and fourth order meridionals supported this assumption. The common orthorhombic space group $P2_12_12_1$ was ruled out due to the presence of an odd order $h00$ reflection.

Structure refinement

The structure analysis procedure consisted in principle, of the following four steps: (1) a conformational analysis in which single chain models consistent with the fibre repeat were refined to a minimum conformational energy in accordance with stereochemical criteria; (2) a chain packing refinement which simultaneously minimized both the packing and conformational energy of the unit cell against the same stereochemical criteria; (3) an X-ray refinement minimizing R, the crystallographic reliability index defined by:

$$R = \frac{\Sigma \| F_o | - | F_c \|}{\Sigma | F_o |}$$

where F_o and F_c are the observed and calculated structure factors, respectively; and (4) a combined X-ray and stereochemical refinement which determined the most probable structure in both regards. The details of these procedures have been previously published[8–10]

It was found that the determination of the structure of CTA I could not be approached in the above manner without some modification. The reasons necessitating modification were essentially two-fold. The additional number of structural parameters introduced by the acetate groups had the effect of complicating the potential energy surface calculated in the packing refinement to the point where the global pack-

Table 1 Calculated and observed d spacings

hkl	d (obs.) (Å)	d (calc.) (Å)
200	11.4	11.8
300[a]	8	7.88
110	6.10	6.06
210	5.50	5.54
410	4.35	4.30
600	3.93	3.94
610	3.35	3.33
420	2.73	2.77
201	7.70	7.82
211	4.95	4.89
601	3.63	3.68
421	2.71	2.68
002	5.22	5.22
202	4.78	4.77
112	3.95	3.95
312	3.65	3.57
602	3.13	3.14
203	3.33	3.34
113	3.02	3.02
213	2.89	2.94
603	2.62	2.61
004	2.57	2.61

[a] Diffuse reflection, precise measurement difficult

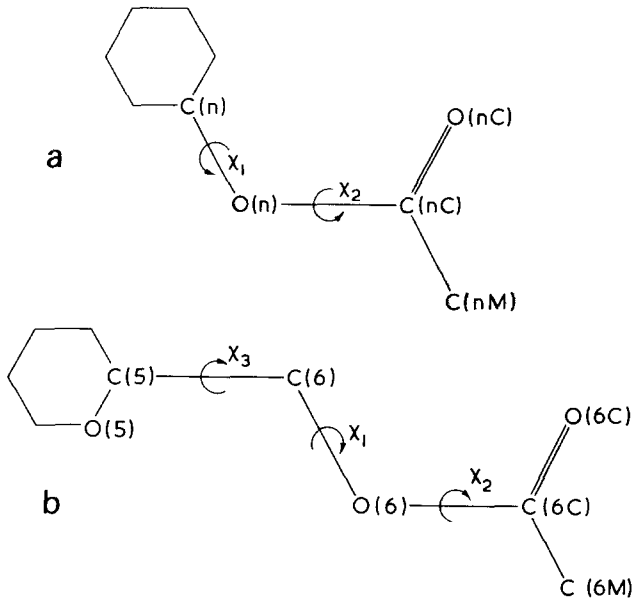

Figure 2 Nomenclature of acetate rotations. (a): C(2) and C(3) acetates; (b): C(6) acetate. Conformation angle for C(nC), χ_1 is 0° when C(n-1)–C(n)–O(n)–C(nC) is *cis*. (Note: n = 2,3,6). Conformation angle for O(nC) and C(nM), χ_2 is 0° for O(nC) and 180° for C(nM) when C(n)–O(n)–C(nC)–O(nC) is *cis*. Conformation angle for O(6), χ_3, is 0° when O(5)–C(5)–C(6)–O(6) is *cis*. Pure *gg* = –60°, *gt* = 60°, *tg* = 180°

ing energy minimum actually consisted of a large number of local minima. Secondly, the lack of hydrogen bonds in poly(saccharide acetates) decreases the depth of the global minimum thus making it difficult to recognize. For example, in the structure analysis of cellulose II, the final structure was almost identical with the model predicted by hydrogen bonding considerations alone[9]. Since a detailed stereochemical packing analysis was not feasible here, the refinement procedure was modified by directly submitting conformationally acceptable models to the X-ray refinement, i.e. step (3) followed step (1). Models with acceptable *R* factors were then checked for short non-bonded contacts and were adjusted to relieve these interactions if necessary. All acceptable models were then refined according to step (4).

Most probable chain conformation.

The presence of a strong second order meridional reflection in the CTA I diffractogram suggested the existence of a two-fold screw axis in the fibre direction, as is the case in cellulose. An initial chain model was constructed in accordance with this evidence and was assigned the bond lengths, bond angles and conformation angles of the middle residue of the cellotriose undecaacetate structure determined by Pérez and Brisse[12]. These parameters were used in preference to the standard values of Arnott and Scott which had been obtained from underivatized glucose residues[13]. Models with the O(6) atom in four rotational positions, at *gg*, *gt*, *tg*, and *gg* + 180°, were considered in the conformational analysis. The first three O(6) positions are the well known staggered positions while in the fourth, the O(6) is staggered with respact to the C(5) and O(5) atoms but is eclipsed by the H(5) atom. It was found that the sequence of steps performed in the analysis was critical in locating well defined energy minima. Best results were obtained when the bond angle at the glycosidic oxygen (bridge angle) was adjusted first, by rotation about the virtual bond (i.e. the vector joining successive glycosidic oxygens in the chain[8]), followed by the introduction of the acetate group rotations and the O(6) rotation later in the refinement. (*Figure 2* illustrates 'acetate rotation' and defines the nomenclature used in reference to these groups.) In some cases it was observed that the O(6) rotation had to be fixed near the desired staggered position during the initial stages of the refinement while the O(2) and O(3) acetate rotations were varied in order to locate conformational minima. In these cases unfavourable non-bonded contacts forced the O(6) rotation away from the staggered position to one of higher energy faster than the acetate rotations could relieve the short contacts. Final refinement was conducted with all of the above parameters as variables and the O(6) rotation constricted to within narrow limits if necessary. In addition, the rotation of the plane defined by O(nC), C(nC) and C(nM) about the O(n)–C(nC) bond (*Figure 2*) was introduced at this point.

Final results of the conformational analysis indicated that the O(6) *tg* model could be ruled out due to very short contacts between the O(6) and O(2) acetate groups which could only be relieved by extensive rotation of O(6) away from the low energy positions. The remaining models, with O(6) at *gg*, *gt* and *gg* + 180°, were all shown to be about equally probable. It should be noted that the ring conformation angles as well as all bond lengths and bond angles were not refined in this analysis since it was previously observed that these parameters will change during the course of the final X-ray refinement[9].

X-ray analysis.

To prevent refinement to local X-ray minima it was first necessary to adjust those parameters which most greatly affected the *R* factor. Such parameters were the chain rotations and the relative chain translation. Likely values for them were determined by a systematic search through a complete range of rotations and translations. The search was conducted using models of refined conformation which were left invariant in the process. Although all models were not tested, those examined did suggest approximate starting positions for the X-ray refinement. Since the space group

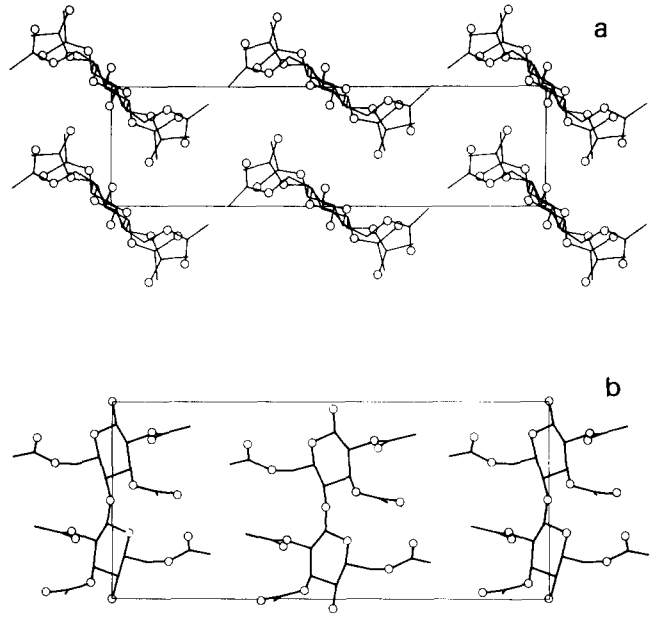

Figure 3 Projections of the CTA I structure on (a) *a–b* plane of the unit cell; (b) *a- c* plane of the unit cell. The hydrogen atoms are not shown

Table 2 Most probable models of CTA 1

Model[a]	Bridge angle (degrees)	Chain rotations[b] (degrees)		Relative chain translation[b] (Å)	R^c	Short non-bonded contacts
		Chain 1	Chain 2			
Parallel:						
O(6)*gt* (50°)	115.7	178.3	165.8	−0.03	0.303	3
O(6)*gg* (−47°)	118.2	176.0	166.8	−0.41	0.258	None
O(6)*gg* + 180° (116°)	119.2	151.1	162.0	0.95	0.377	1
Antiparallel:						
O(6)*gt* (60°)	115.2	170.5	97.9	0.83	0.298	3
O(6)*gg* (−51°)	120.8	153.0	89.1	−0.67	0.298	None
O(6)*gg* + 180° (127°)	121.5	145.9	103.1	0.39	0.383	None

[a] O(6) is at 0° when the bond sequence O(5)–C(5)–C(6)–O(6) is *cis*. Rotation of C(6)–O(6) is positive clockwise looking from C(5) to C(6), and pure *gt* = 60°, *tg* = 180°, *gg* = −60°.

[b] Chain 1 is at $x = 0$, $y = 0$ and chain 2 is at $x = a/2$, $y = 0$. Chain 1 is at 0° position when $O(4)_1$ is at 0, $-y$, 0; chain 2 is at 0° position when $O(4)_3$ is at $a/2$, $-y$, z. Positive rotation is clockwise looking down the *c* axis. Translation is chain 2 relative to chain 1 along *c*. ($O(4)_1$ and $O(4)_3$ are in the first residues of chains 1 and 2, respectively).

[c] Calculated with isotropic temperature factor $B = 5.0$

was assumed to be $P2_1$ with the screw axis in the fibre direction, it was necessary to consider both parallel (*P*) and antiparallel (*AP*) chain packing polarities in the search. The preliminary results showed that *R* factor minima for both the parallel and antiparallel models existed only for chain rotations which resulted in the chains forming sheets roughly in the (210) direction of the unit cell. Within the sheets, individual chains were translated less than ± 1 Å relative to one another along the chain axis.

Once starting positions were determined in this fashion, the three acceptable chain conformations with different O(6) rotations were subjected to the X-ray refinement in both packing polarities. Typically, 10 parameters were allowed to vary: (1) two chain rotations and relative chain translation within narrow limits (±5°, ±0.5 Å, respectively); (2) acetate rotations including χ_1 and χ_2 (*Figure 2*); (3) O(6) rotation (χ_3) near *gg*, *gt*, or *gg* + 180°. After successful refinement of these 10 parameters, the ring conformation angles and the rotation of the glucose residue about the virtual bond linking successive glycosidic oxygens were added as variables, bringing the total number of variable structural parameters to 16. The final refinement was generally conducted with added stereochemical constraints to prevent the appearance of short non-bonded contacts (see equation (2) in ref 9). In these refinements, all observed and unobserved reflections were used and all were weighted equally. The results of the X-ray refinement of the best six models are shown in *Table 2* and suggest strongly that the structure of CTA I is based on a parallel chain packing polarity. The best parallel model, with $R = 0.258$, has an O(6) rotational position within 13° of *gg* and contains no unacceptably short contacts. The two chains of the unit cell are unequally rotated about the *c* axis which is consistent with the presence of equatorial reflections that demand a two chain unit cell. The chains are also staggered very little in the *c* direction in contrast to the structure of celluloses I and II.

All other models, in particular the two antiparallel structures with the next lowest *R* factors (both at $R = 0.298$), could be rejected in comparison with the best parallel model by the Hamilton significance test[14]. The parallel model was indicated by this test at a better than 95% significance level.

In addition to the models shown in *Table 2*, a number of models with unequal O(6) rotations were examined. These models were constructed with all possible combinations of *gt*, *gg*, and *gg* + 180° O(6) rotations in different chains, in accordance with the two-fold screw axis along the chain. The presence of the two-fold axis ruled out mixtures of rotations on alternating residues of the same chain. The *R* values for all of these models were typically in the range of 0.34–0.45 and were therefore not considered further.

An attempt was also made to construct Dulmage type structures for CTA I in which the two-fold screw axis was located between the two chains of the unit cell. Initial *R* factors were calculated for trial structures with various locations of the symmetry related pair of chains within the unit cell. Results clearly indicated that these structures were not probable and a more detailed refinement was not performed.

In the subsequent refinement of the parallel O(6) *gg* model all bond angles and conformation angles were included as variables, in addition to the parameters described previously. A total of 37 structural parameters were refined. The results showed that the bond and conformation angles generally remained within one standard deviation of the values determined by Pérez and Brisse for cellotriose undecaacetate[12]. A few exceptions were noted, particularly in the exocyclic and acetate angles which were found to vary by as much as three standard deviations. This is to be expected since the CTA I and cellotriose undecaacetate structures do not pack in an identical environment.

The final model thus obtained was then subjected to a refinement in which the O(6) rotations on all four residues of the unit cell were allowed to vary independently near the *gg* position. However, all four rotations remained within a few degrees of the position previously determined thereby indicating that the two-fold screw axis coincides with the helix axis and that the two chains of the structure possess essentially identical conformations. Anisotropic temperature factors (see equation (3) in ref 9) were then refined for the best model which dropped the *R* factor to 0.242. (The resulting temperature factors were: $B_x = 0.013$, $B_y = 6.22$, $B_z = 12.9$ which indicates that the largest degree of disorder is in the fibre direction as expected. The drop in the *R* factor from 0.258 to 0.242 upon addition of the anisotropic temperature factors was not significant as judged by the Hamilton test.) A comparison of the observed and calculated structure factors for this structure is presented in *Table 3* and its atomic coordinates are given in *Table 4*.

DISCUSSION

The results of this study on CTA I are in agreement with the

Table 3 Comparison of observed and calculated structure factors

hkl	F_{calc}	F_{obs}	*hkl*	F_{calc}	F_{obs}
200	31.35	37.74	(911, 721, 621)	12.15	15.54
300	5.07	8.53	202	7.12	5.33
(010, 400, 110)	18.91	24.48	302[a]	2.99	2.11
210	78.54	77.15	(012, 122, 402, 212)	18.82	22.08
310[a]	4.01	2.30	(312, 502)	4.21	20.20
500[a]	1.88	2.42	412[a]	2.24	4.35
410	46.93	49.63	(602, 512)	7.52	14.93
510[a]	4.32	2.54	(702[a], 612[a])	6.37	4.42
600	8.91	15.89	(122, 022, 222)	11.71	12.55
(700, 610)	25.30	23.78	(712, 802, 322)	12.53	11.93
(120[a], 020[a])	7.50	4.20	422[a]	12.70	5.80
(710, 800, 220, 320)	15.51	13.80	(812, 902, 522, 622)	13.86	13.94
420	22.91	30.10	(103, 203)	34.82	34.83
(810, 900, 520)	19.61	7.81	303[a]	8.53	2.88
(910, 620)	14.48	15.61	(013, 113, 403, 213)	29.36	20.36
201	7.13	4.93	(313, 503)	10.68	12.80
301[a]	1.66	2.00	413[a]	4.89	3.45
011[a]	6.08	2.00	(603, 513)	20.77	26.59
(111, 401, 211)	37.41	36.36	(703, 613)	11.59	13.02
311[a]	6.19	3.50	(023[a], 123[a])	5.18	5.50
501[a]	4.66	3.50	(713, 803, 223, 323, 423)	16.96	16.95
411	8.94	6.70			
(601, 511)	15.52	16.88	Meridional reflections:		Visual intensity
(701, 611)	12.33	5.16	001	0.00	—
(021[a], 121[a], 221[a])	10.52	4.40	002	15.81	strong
(711, 801, 321, 421)	16.00	21.68	003	0.00	—
(811[a], 901[a], 521[a])	11.99	5.72	004	11.08	weak

[a] Unobserved reflections

Table 4 Cartesian atomic coordinates of one residue of each of the two chains of the unit cell

	Chain 1				Chain 2		
Atom	*x* (Å)	*y* (Å)	*z* (Å)	Atom	*x* (Å)	*y* (Å)	*z* (Å)
O(2)	−2.197	1.508	3.511	O(2)	9.403	1.138	3.102
O(2C)	−2.223	3.743	3.281	O(2C)	9.022	3.341	2.872
O(3)	−1.117	1.895	0.807	O(3)	10.408	1.693	0.398
O(3C)	−3.400	1.720	0.351	O(3C)	8.182	1.156	−0.058
O(4)	0.540	−0.763	0.000	O(4)	11.987	−0.745	−0.409
O(5)	0.950	−0.285	3.452	O(5)	12.796	−0.130	3.043
O(6)	3.049	−1.179	1.977	O(6)	15.011	−0.678	1.568
O(6C)	4.073	−2.733	3.123	O(6C)	16.268	−2.050	2.714
C(1)	−0.251	0.211	3.994	C(1)	11.531	0.168	3.585
C(2)	−0.850	1.272	3.042	C(2)	10.771	1.120	2.633
C(2C)	−2.738	2.758	3.500	C(2C)	8.670	2.286	3.091
C(2M)	−4.242	2.636	3.850	C(2M)	7.205	1.927	3.441
C(3)	−0.979	0.707	1.643	C(3)	10.733	0.542	1.234
C(3C)	−2.369	2.321	0.486	C(3C)	9.104	1.914	0.077
C(3M)	−2.497	3.831	0.255	C(3M)	8.737	3.385	−0.154
C(4)	0.332	0.036	1.163	C(4)	12.135	0.089	0.754
C(5)	0.667	−1.061	2.243	C(5)	12.640	−0.941	1.834
C(6)	1.844	−1.877	1.933	C(6)	13.932	−1.560	1.524
C(6C)	4.173	−1.738	2.554	C(6C)	16.209	−1.051	2.145
C(6M)	5.339	−0.923	2.319	C(6M)	17.230	−0.061	1.910
H(1)	−0.933	−0.582	4.088	H(1)	10.984	−0.724	3.679
H(2)	−0.283	2.155	3.048	H(2)	11.190	2.082	2.638
H(3)	−1.805	0.065	1.553	H(3)	10.020	−0.223	1.143
H(4)	1.278	0.438	0.944	H(4)	13.004	0.636	0.534
H(5)	−0.168	−1.678	2.399	H(5)	11.914	−1.683	1.990
H(6A)	1.727	−2.315	0.986	H(6A)	13.887	−2.011	0.577
H(6B)	1.894	−2.651	2.641	H(6B)	14.105	−2.315	2.232

previous findings that native cellulose I is a parallel chain structure[15,16]. The results also agree with the general observation that CTA I saponifies to cellulose I and that CTA II which is obtained by precipitation from solution saponifies to cellulose II. However, it has also been reported that CTA II which has been produced from CTA I by swelling in 70–75% formic acid, will saponify to cellulose I[17]. Acid concentration appears critical in this conversion because swelling with more concentrated acid always results in CTA II that saponifies to a mixture of celluloses I and II while acid of lower concentration does not effect conversion of CTA I to CTA II. In the light of what is known about the structures

of cellulose I and CTA II, the saponification of the 70–75% formic acid produced sample of CTA II implies a change in packing polarity from antiparallel (CTA II) to parallel (cellulose I). This is not consistent with all other results which indicate that a change in polarity does not take place during saponification.

Although the reasons for this anomalous transformation are not known, the fact that the acid concentration appears to be critical for it to occur suggests the following manner in which it could proceed. The swelling action of the acid in the critical concentration range may be incomplete in that it destroys the CTA I lattice but does not permit sufficient chain mobility to result in a complete change of packing polarity. Some of the antiparallel chain structure will form, however, and will crystallize in the CTA II lattice. The remainder, a swollen but still parallel structure, may be either much too strained by numerous small crystallites of CTA II interspersed in it to crystallize, or alternatively, it may partially crystallize with parallel polarity but in the CTA II lattice, onto the CTA II crystallites. The former alternative, i.e. a sizeable amorphous parallel fraction, appears on the surface as the more probable of the two, although the existence of another polymorphic crystal structure of CTA is not at all improbable. In either case, because the major portion of the resulting structure is parallel, it will saponify to cellulose I, with a minor component of cellulose II mixed in. If CTA I indeed co-crystallizes with CTA II in the latter lattice, a careful analysis of the diffraction intensities would show its presence.

The bond and conformation angles of the final structure of CTA I show that the conformational features of the chain are similar to those of the middle residue of the cellotriose undecaacetate[12]. The ϕ, ψ angles for the polymer are 22° and −48°, respectively, while for the trimer they are 24° and −20° (between the middle and non-reducing residues). In both, the O(6)'s are near the *gg* rotational position. The rotational positions of the acetates are likewise very similar and are those that we have observed in other poly(saccharide acetate) structures[11,18]. The similarities between the trimer and the polymer demonstrate, once again, the value of crystal structure analysis of oligomeric model compounds.

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