Structure of Cellulose II

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Synopsis

A reduced unit cell derived from the presently accepted unit cell and a new parallel chain arrangement is proposed for cellulose II (regenerated cellulose). In the present structure, all the cellulose chains are identical and there is only one chain passing through each unit cell. The intensity data for all reflections with d spacings greater than 1.747 Å have been calculated and were found to be in good agreement with the corresponding observed x-ray intensities. The calculated agreement factor is $R = 0.50$. Two intrachain hydrogen bonds parallel to the fiber axis and one interchain hydrogen bond perpendicular to the fiber axis stabilize the structure. The hydrogen bonding network is in fair agreement with infrared dichroic data, and the chain arrangement conforms to stereochemical criteria. No short contacts are observed. The parallel chain is also compatible with the structure of cellotetraose and the accepted hypothesis of cellulose biosynthesis, as well as the latest parallel structure for Valonia.

INTRODUCTION

Besides the naturally occurring polymorph, namely, cellulose I, another cellulose modification, known as mercerized, or regenerated cellulose or cellulose II, can be obtained by treating cellulose I with a strong solution of alkali or by saponification of cellulose derivatives. The generally accepted unit cell for cellulose II is the one given by Andress[1] having the following monoclinic unit cell parameters: $a = 8.14$ Å, $b = 10.3$ Å (fiber repeat), $c = 0.14$ Å, $\beta = 62°$. This unit cell has two cellulose chains threading the ac-plane, one at the corner and the other at the center of the unit cell. A twofold screw axis was assumed to exist parallel to the fiber axis, and the chains were considered to be straight just as in the case of the Meyer and Misch[2] structure for cellulose I. However, the chain conformation widely accepted at present is the bent chain conformation proposed by Hermans.[3]

Crystallographically, the structure proposed by Andress can be called an antiparallel structure, which is one in which the chain in the corner runs in the opposite direction to the one at the center of the unit cell. The antiparallel configuration of the two chains had to be assumed in order to satisfy the crystallographic elements of the monoclinic unit cell which was so large as to contain two chains.

The antiparallel structure has often been criticized. From the similarity of x-ray diffraction patterns of cellulose II and cellotetraose, one can consider cellotetraose as the model compound for cellulose II. Crystallographic studies on cellotetraose[4,5] suggest a triclinic unit cell for cellotetraose with one molecule per unit cell. This result, if extrapolated to cellulose II, requires a parallel chain arrangement in the unit cell. Preston[6] and Roelofsen[7] have advocated the parallel chain arrangement for natural cellulose I because of certain considerations regarding the biosynthesis of cellulose chains. In a more recent publi-

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cation, Sarko and Muggli[8] on the basis of packing and x-ray analysis have also pointed out that the crystal structure of native Valonia is based on parallel packing of chains. Another polysaccharide, chitan, was investigated by Dweltz et al.[9] and Blackwell et al.[10] independently. The crystal structure analysis by both these teams confirmed the existence of a parallel chain arrangement for this polysaccharide. These studies further strengthen the concept of a parallel chain arrangement in naturally occurring polysaccharides.

Based on this parallel chain hypothesis proposed for natural polysaccharides, the authors have extended this concept to cellulose II as well, and several structures have been examined for this polymorph derived from cellulose I. A structure that is satisfactory in most respects has been found. This new structure, which is somewhat similar to that suggested earlier,[4] is described in this paper.

Even though Sarko and Muggli[8] have suggested that the most probable structure for cellulose II based on their unit cell was an antiparallel one, they go on to qualify that this structure is not yet substantiated by experiments in which sufficiently resolved x-ray diffraction data are available. Their antiparallel model has been proposed on the basis of maximum hydrogen bond formation alone for the large unit cell in which there are two chains per unit cell.

In the present paper, we have reexamined the basic unit cell and found that it is not necessary to retain the larger unit cell. A reduced unit cell, in which there is only one chain, is sufficient to index all the observed reflections. With this reduced unit cell, the possibility of having two antiparallel chains is ruled out, and hence only parallel structures are tenable. In the present generally accepted larger cell of Andress, antiparallel structures have generally been preferred by workers because these models lead to better hydrogen bond formation. However, the present paper suggests that this larger cell is not necessary, and therefore the parallel structures present in native polysaccharides should be preferred.

EARLIER STUDIES ON CELLULOSE II

Jones[11] established the method of building models for cellulose based on stereochemical criteria and infrared data. His models were characterized by four parameters: an angle ϕ, representing the mutual orientation of two glucose residues related by a screw axis along the chain; an angle θ, representing the orientation of the plane of the ring in the unit cell; an angle ϵ, which represents the inclination of the line joining two consecutive bridge oxygen atoms O_1 and O_1' with the fiber axis; and a shift r, showing the relative displacement of the central chain with respect to the corner chain. These parameters were varied according to stereochemical criteria and infrared data. For different conformations, the structure factors were calculated for parallel as well as antiparallel chain arrangements using the accepted Andress unit cell.

Of the 16 parallel chain models studied by Jones, only two were compatible with stereochemical criteria. The general conclusion was that for cellulose II no parallel chain structure was found which was stereochemically feasible and in agreement with both spectroscopic as well as x-ray intensity data. For antiparallel chain arrangements, two structures with chains of alternating polarity were found to be more promising than the parallel chain arrangements discussed above. Both these structures, described by Jones as V and VI, had $\phi = 34°$ and r shifts equal to $0.29b$. For structure V, it was found that $\Delta\theta = (\theta_{corn} - \theta_{cent})$ should be 20°. For structure VI, $\theta_{corn}/\theta_{cent} = 50°/23°$.

The calculation of the intensities by Jones[12] indicated that although the overall agreement between observed and calculated x-ray intensities was better than that obtained for cellulose I, it was still far from satisfactory, as such structures did not account for the very weak low order (h 1 l) reflections observed on the first layer line of the fiber diagram. This disparity was not reduced by types of disordering acceptable on stereochemical grounds. The major part of the disagreement was tentatively attributed to regarding the observed coherent scattering as emanating from fully ordered unit cells of the accepted dimensions and symmetry and to neglecting contributions from oriented amorphous regions.

In their recent study, Sarko and Muggli[8] have also carried out packing analyses for cellulose II whose crystal structure is unknown and cannot be directly determined from diffraction data alone because of the limited number of observed reflections. They have suggested that an antiparallel model is superior from hydrogen bond formation criteria and as yet cannot be substantiated by experiment. They also mention that, in the case of cellulose, parallel and antiparallel packing polarities are nearly indentical. Moreover, present available diffraction data may not yield information even on a gross feature of the structure, such as chain polarity.

Therefore, in order to arrive at a more satisfactory structure it was necessary for us to reconsider the unit cell parameters as well as the packing chain arrangements. This has been done in the present study, and a very satisfactory structure has been obtained which is in fairly good agreement with the presently available x-ray intensity data, infrared dichroic data, as well as stereochemical criteria. It may, however, be mentioned that infrared dichroic measurements are not very accurate in the case of fibrous materials and in this case merely suggest a paucity of hydroxyl stretching frequency directions in or about halfway between the equatorial plane and the fiber axis.

UNIT CELL OF CELLULOSE II

The monoclinic unit cell for Fortisan (cellulose II) as given by Wellard[13] has the following parameters: a = 7.92 Å, b = 10.34 Å (fiber repeat), c = 9.08 Å, β = 62.7°. The unit cell employed in the present work is a reduced cell derived from this unit cell. The relationship between these two unit cells is schematically shown in Figure 1. The new reduced cell is shown by the dashed lines.

The a parameter of the new cell is half the short diagonal [101] of the old cell, and the new c parameter is half the long diagonal [$\bar{1}$01] of the old cell. The fiber repeat, namely, the b parameter, remains unchanged. Thus, the present proposed cell is also monoclinic and has the following parameters: a = 4.46 Å, b = 10.34 Å (fiber repeat), c = 7.25 Å, β = 98.6°.

The accurate focusing technique of Legrand[14] and the continuous cylindrically symmetric intensity data of Norman[15] established the absence of odd-order $0k0$ meridional reflections. It was therefore assumed that there is a twofold screw axis parallel to the fiber axis in the case of cellulose II. Since no other systematic absences have been reported, the space group $P2_1$ has been assigned.

This reduced cell has been found to be quite adequate, as all the observed reflections can be indexed suitably. There is no need to have a larger cell. Crystallographically, the smallest acceptable unit cell is the correct one, and therefore the present cell should be preferred to the older and large unit cell which had to have two chains. Table IV shows all the observed d spacings which have been

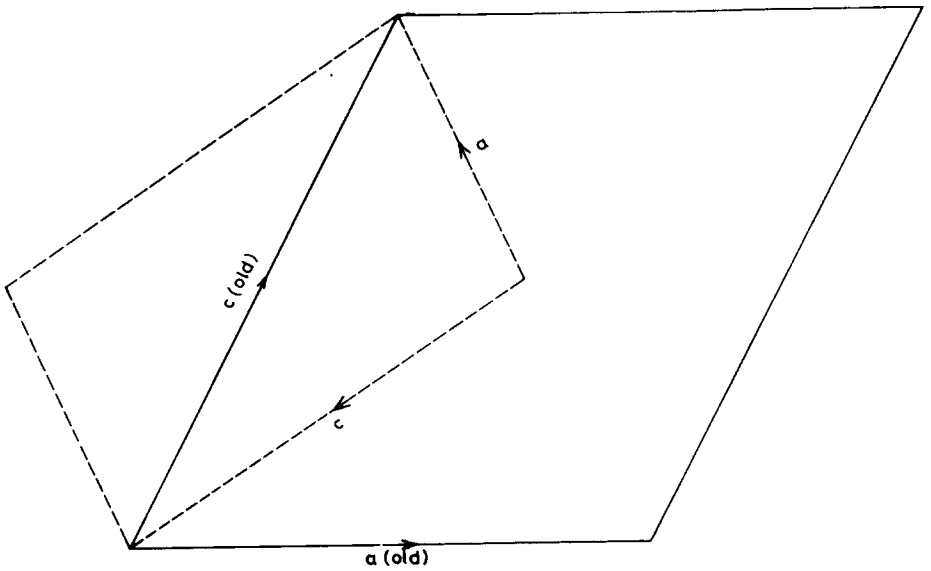

Fig. 1. Relationship between the presently accepted unit cell and the proposed reduced unit cell. The new reduced cell is shown by broken lines.

suitably indexed on the basis of the present reduced cell. No observed reflection is unaccounted for. In some cases the reflection is rather broad or diffuse and can be accounted for by overlapping of intensity from two or more reflections with d spacings very close to one another, as is the case with many polymers having rather low order.

From the way in which the unit cell has been derived, it is obvious that it contains only two anhydroglucose residues. Since cellulose is a polymer with a crystallographic chain repeat of 10.34 Å, and since the $\beta(1 \rightarrow 4)$ repeat distance of a single residue from stereochemical criteria is 5.17 Å, there must be two residues in a repeat of 10.34 Å. Therefore, both these residues must belong to the same chain. According to the space group requirement, these two must be related to each other by a screw operation.

From the above considerations it is evident that only one chain can pass through the new cell without steric hindrance. Consequently, all the chains must run in the same direction making the structure of cellulose II parallel crystallographically.

MOLECULAR STRUCTURE OF CELLULOSE

Cellulose is a polymer of D-glucopyranose in which pyranose rings are connected by $\beta(1 \rightarrow 4)$ glucosidic linkages. From minimum energy criteria the pyranose ring can assume two conformations, namely, the chair form and the boat form. Of these two, the Sachse chair form is the most probable conformation in the solid state. This conclusion is supported by crystal structure analyses of D-glucose[16] and of β-cellobiose.[17] The coordinates of the glucose molecule used in the present work were those published by Jones.[11] Based on the cordinates proposed by Jones,[11] scale models were built in crystallographic array in such a way that good lateral hydrogen bonding between neighboring chains was achieved. For different chain arrangements in the unit cell, structure

factors were calculated using a Fortran II program on an IBM 1620 computer with the standard expression for the structure factor for the space group $P2_1$.

Earlier infrared spectra show two very strong bands at 3447 and 3488 cm^{-1} with parallel dichroism. These bands have been assigned to intramolecular hydrogen bonds. One of these two bands is due to the hydroxyl stretching of the $O_3(H)—O_5$ hydrogen bond. To accommodate this intrachain hydrogen bond, the value of ϕ must lie between 25° and 40°. The value of ϕ used in the present study was 40°. The orientation of the chain in the unit cell was varied by changing the parameter θ, i.e., the angle between the plane containing three successive bridge oxygen atoms and the plane perpendicular to the c axis (new reduced cell).

The orientations of the glucose residues with respect to each other were kept fixed, with $\phi = 40°$ and $\epsilon = 20.9°$. The two rings on the same chain were related to each other by the twofold screw axis. The orientation of the chain as a whole within the unit cell, namely, θ, was varied systematically until good general agreement between the calculated and observed structure factors was obtained. The positions of a few individual atoms were also changed. All these changes were within the limits dictated by infrared data and stereochemical criteria. The variation in θ was entirely carried out by trial and error. The structure factors calculated with $\theta = 63°$ gave a fairly good agreement between observed and calculated structure factors.

The other band appearing in the infrared spectrum of cellulose II with parallel dichroism can be assigned to the stretching mode of the hydrogen bond between the O-2 and O-6 atoms in the adjacent pyranose rings in the same chain. This is the second intrachain hydrogen bond. The primary hydroxyl oxygen atom O-6 can assume various positions. Of the many positions investigated by Jones,[11] only one, described by him as L_0, was found to be suitable in order to establish this hydrogen bond. To make this bond distance even better, a small distortion was introduced in the ideal L_0 position suggested by Jones.

For the parallel chain structure proposed for cellulose II, the final values of the various chain parameters are as follows: $\phi = 40°$, $\epsilon = 20.9°$, and $\theta = 63°$. The oxygen atom O-6 is in the L_0 position described by Jones (with a slight distortion to make the bond distance better). Since there is only one chain per unit cell, the parameter r does not enter the calculations ($r = 0$).

Figure 2 shows the projection along the a axis of the final structure. Atoms in this figure are shown by dark circles, and covalent bonds are shown by continuous lines. Hydrogen bonds are shown by broken lines. Figure 3 shows the projection along the fiber axis. In this projection only one molecule on each of four adjacent chains has been drawn in order to avoid overlapping of atoms. The six-membered rings are chair shaped and are connected to each other along the chain axis by bridge oxygen atoms in the $\beta(1 \rightarrow 4)$ linkage. From Figures 2 and 3 it is evident that there are three hydrogen bonds for every anhydroglucose residue. Of these three bonds, two are intramolecular bonds, $O_3(H)—O_5'$ and $O_2(H)—O_6'$. Both these bonds make small angles with the fiber axis and can be described as parallel bonds. The third hydrogen bond, $O_3—(H)O_6''$, is an intermolecular (or interchain) bond. This makes a very large angle with the fiber axis and can be considered to be a perpendicular bond.

A bond scan computer program written by Ahmed[18] was utilized to calculate the bond distances and bond angles in the structure. All the hydrogen bonds are listed in Table I. These results are compatible with infrared dichroic re-

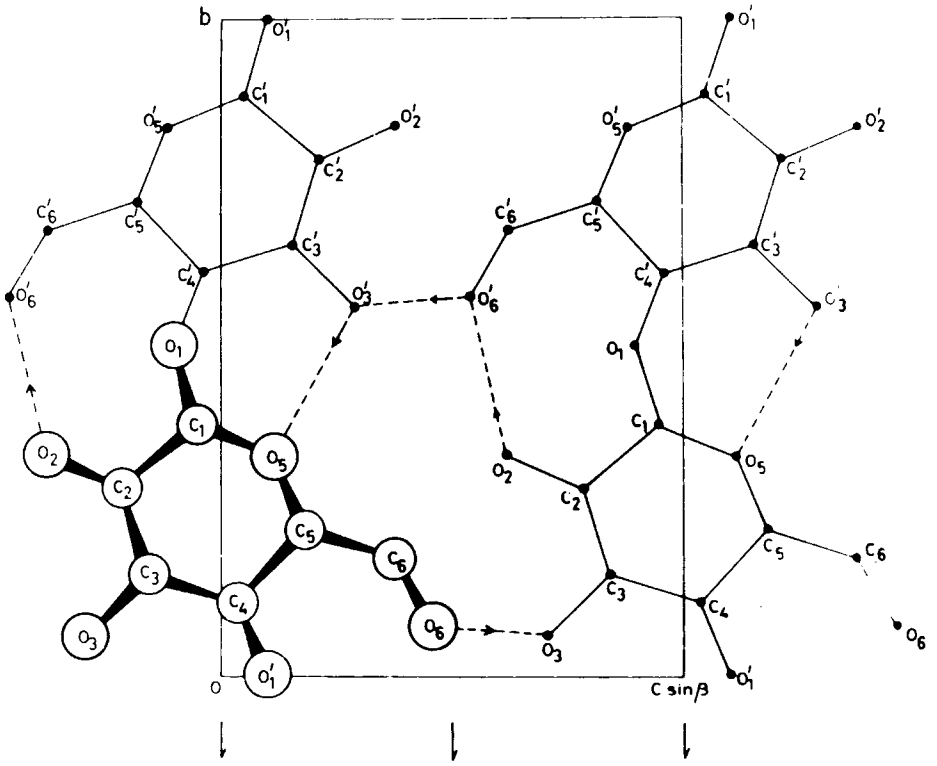

Fig. 2. The *a* projection of the structure of cellulose II.

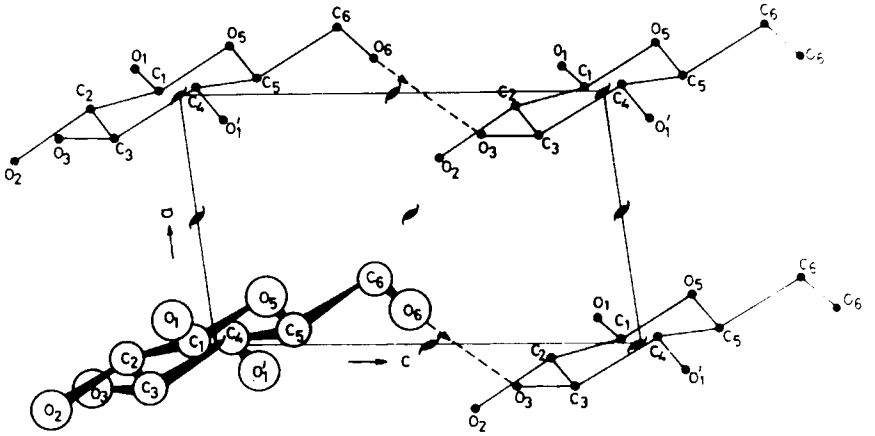

Fig. 3. The *b* projection of the structure of cellulose II. To avoid overlapping of atoms, only one anhydroglucose residue at each corner of the unit cell is shown.

quirements. Table II gives a list of the various bond lengths. No short contacts have been observed. Table III gives the fractional coordinates of all carbon and oxygen atoms of the anhydroglucose residue near the origin of the unit cell.

The Miller indices *hkl* and the corresponding *d* spacings of all the observed and calculated reflections are tabulated in Table IV. The calculated intensities

TABLE I
Hydrogen Bond Distances for Cellulose II

Bond	Distance Å
$O_3(H)—O'_5$	2.699
$O_2(H)—O'_6$	2.662
$O_6(H)—O''_3$	2.609

TABLE II
Intramolecular Covalent Bond Distances for the Final Structure of Cellulose II

Bond	Distance, Å
$C_1—C_2$	1.536
$C_1—O_1$	1.431
$C_1—O_5$	1.430
$C_2—C_3$	1.542
$C_2—O_2$	1.424
$C_3—C_4$	1.540
$C_3—O_3$	1.423
$C_4—C_5$	1.540
$C_5—C_6$	1.541
$C_5—O_5$	1.426
$C_6—O_6$	1.426
$C'_4—O_1$	1.430

TABLE III
Fractional Coordinates of the Anhydroglucose Molecule Situated at the Origin of the Reduced Unit Cell

Atom	Monoclinic fractional coordinates		
	x	y	z
C-1	−0.0134	0.3810	−0.0489
C-2	−0.0518	0.2830	−0.2077
C-3	−0.1715	0.1540	−0.1407
C-4	0.0319	0.1100	0.0353
C-5	0.0634	0.2210	0.1766
C-6	0.2692	0.1770	0.3518
O-1	0.1012	0.5000	−0.1109
O-2	−0.2603	0.3320	−0.3563
O-3	−0.1691	0.0580	−0.2793
O-5	0.1940	0.3310	0.1006
O-6	0.1404	0.0744	0.4450

$|F_c|^2$ are those obtained from the contribution by carbon and oxygen atoms alone. Hydrogen atoms have not been considered, as their contribution to the intensity data is likely to be very small.

A temperature factor, with $B = 9$ Å^2, has been applied in order to suitably reduce the intensities of the high-angle reflections. This is thus an artificial factor which attempts to take care of the temperature affect as well as the high amount of disorder in a fiber which is responsible for the rapid fading away of intensities at higher Bragg angles in the diffraction pattern.

The observed intensity data $|F_0|^2$ are those given by Mann et al.[19] for cellulose II. The data were collected using CuK_α radiation ($\lambda = 1.5418$ Å) and have now

TABLE IV
Calculated and Observed Intensities for Cellulose II

Miller indices	Calculated $\sin^2\theta/\lambda^2$	Intensity: Calculated $\lvert F_c\rvert^2$	Intensity: Observed $\lvert F_0\rvert^2$ [a]	Observed $\sin^2\theta/\lambda^2$	Observed d spacings, Å
001	0.0047	676.0	500.0	0.0048	7.240
100	0.0128	4134.5	4500.0	0.0129	4.410
$10\bar{1}$	0.0153	4900.0	4500.0	0.0153	3.710
002	0.0189	0.6			
101	0.0197	216.1	17.5	0.0197	3.560
$10\bar{2}$	0.0274	39.7	35.0	0.0280	2.990
102	0.0360	179.6	102.5	0.0365	2.620
003	0.0425	0.1			
$10\bar{3}$	0.0488	0.0			
200	0.0512	42.2	750.0	0.0516	2.248
$20\bar{1}$	0.0516	702.2			
201	0.0603	0.6			
$20\bar{2}$	0.0615	42.2	125.0	0.0592	2.057
103	0.0619	146.4			
004	0.0757	84.6	62.5	0.0753	1.823
202	0.0788	10.2			
$10\bar{4}$	0.0798	4.0			
$20\bar{3}$	0.0808	28.1			
010	0.0235	0.0			
011	0.0070	104.0	17.5	0.0064	6.270
110	0.0151	38.4	55.0	0.0150	4.09
$11\bar{1}$	0.0177	739.8	35.0	0.0183	3.70
012	0.0212	34.8			
111	0.0220	216.1	20.0	0.0230	3.30
$11\bar{2}$	0.0297	84.6	87.5	0.0310	2.843
112	0.0384	306.2	312.5	0.0390	2.531
013	0.0449	458.2	400.0	0.0460	2.333
$11\bar{3}$	0.0512	127.7			
210	0.0535	62.4	205.0	0.0532	2.170
$21\bar{1}$	0.0540	196.0			
211	0.0626	13.7			
$21\bar{2}$	0.0638	96.0	212.5	0.0637	1.981
113	0.0642	179.6			
014	0.0780	2.9	56.2	0.0775	1.797
212	0.0811	196.0			
$11\bar{4}$	0.0822	0.8			
$21\bar{3}$	0.0831	3.2			
020	0.0093	204.5	100.0	0.0094	5.160
021	0.0140	130.0	587.5	0.0132	4.36
120	0.0221	79.2	185.0	0.0220	3.38
$12\bar{1}$	0.0238	219.0	55.0	0.0252	3.15
022	0.0282	110.0			
121	0.0290	156.2	105.0	0.0292	2.93
$12\bar{2}$	0.0367	11.6	162.5	0.0380	2.567
122	0.0454	249.6	140.0	0.0460	2.332
023	0.0519	14.4	87.5	0.0535	2.163
$12\bar{3}$	0.0582	30.2	100.0	0.0591	2.058
220	0.0606	7.3			
$22\bar{1}$	0.0609	50.4	375.0	0.0681	1.917
221	0.0697	24.0			
$22\bar{2}$	0.0708	67.2			
123	0.0712	114.5			

Miller indices	Calculated $\sin^2\theta/\lambda^2$	Intensity: Calculated $\lvert F_c\rvert^2$	Intensity: Observed $\lvert F_o\rvert^2$ [a]	Observed $\sin^2\theta/\lambda^2$	Observed d spacings, Å
030	0.0210	0.0			
031	0.0251	130.0	482.5	0.0261	3.09
130	0.0338	141.6	33.7	0.334	2.739
$13\bar{1}$	0.0364	130.0	255.0	0.0368	2.608
032	0.0399	718.0	183.7	0.0408	2.477
131	0.0407	176.9			
$13\bar{2}$	0.0484	185.0	376.2	0.0520	2.196
132	0.0571	112.4	223.7	0.0575	2.087
033	0.0636	132.2	151.3	0.0655	1.954
$13\bar{3}$	0.0699	302.8			
230	0.0723	3.6	87.5	0.0718	1.866
$23\bar{1}$	0.0726	56.2			
231	0.0813	1.4			
232	0.0825	246.5	70.0	0.0852	1.713
133	0.0829	9.6			
040	0.0373	625.0	300.0	0.0376	2.581
041	0.0421	31.4	115.0	0.414	2.458
140	0.0502	86.5	292.5	0.0510	2.215
$14\bar{1}$	0.0527	136.9			
042	0.0563	104.0			
141	0.0571	163.8			
$14\bar{2}$	0.0648	141.6	236.5	0.0705	1.885
142	0.0734	39.7	122.5	0.0830	1.746
043	0.0800	65.8			

[a] In order to scale the calculated and observed intensities, the observed intensity values as given by Mann et al.[19] have been multiplied by a constant factor 0.25.

been suitably scaled to one fourth the original values in order to compare them with the calculated values. These are the true intensities as the Lorentz polarization and absorption corrections have already been applied by them.

In order to determine the crystallographic reliability of our presently proposed structure, the agreement factor, or residual,

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

was calculated and found to be 0.50. This is practically the same value as that obtained by Jones,[12] namely, $R = 0.499$ for his L_{10}/L_1 configuration and $R = 0.492$ for his U_1/L_7 configuration. Thus, equivalent agreement has been obtained using the earlier available x-ray intensity data. When more accurate observed x-ray intensity data become available, it will be interesting to see which of the structures proposed so far for cellulose II are in better agreement.

DISCUSSION

A comparison of the presently available observed and the new calculated intensities indicates that there is already fairly good agreement, except for some meridional and near-meridional reflections. This is probably due to orientation

effects which are usually present in fibrous polymers. Further refinement of the structure has not been attempted as the calculated data are based on the assumption that there is perfect ordering of the chains within the unit cells in all the three dimensions and that every unit cell is identical to the next. In practice, however, this assumption is not justified, and there is a certain amount of disorder present along all the three axes. In fact, no two unit cells can be considered to be really identical. This disorder along the chains can account for very considerable changes in intensity of certain reflections, depending upon the type of disorder present. The disorder present in any fibrous polymer can make adjacent unit cells nonidentical, and this can lead to large differences between the observed and calculated x-ray intensities. It can also account for small differences in the local arrangements of side chains, particularly the primary hydroxyl group $O_6(H)$. This in turn can lead to minor variations in hydrogen bond strengths, as well as orientations. These hydrogen bond variations can then explain the infrared observations of more stretching frequencies in the OH region than can be explained on the basis of the present proposed structure, which is a perfectly repeating one in three dimensions.

The agreement between the observed and calculated intensities for the present structure suggests that the structure proposed here is only a very good first approximation of that which is actually present in the polymer. Various types of disorder can now be introduced, and the changes brought about in the intensity data by this disordering can be studied in order to further improve the agreement between the observed and calculated x-ray intensity for the actual paracrystalline structure of the fibrous material. The disorders can also be arranged to explain any additional infrared dichroic bands that are observed.

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