This article was downloaded by:
On: *24 January 2011*
Access details: *Access Details: Free Access*
Publisher *Taylor & Francis*
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK

Journal of Macromolecular Science, Part A
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597274

The Structure of Cellulose by Conformational Analysis. Part 4. Crystalline Cellulose II

A. Pizzi[a]; N. J. Eaton[a]
[a] National Timber Research Institute Council for Scientific and Industrial Research, Pretoria, Republic of South Africa

To cite this Article Pizzi, A. and Eaton, N. J.(1987) 'The Structure of Cellulose by Conformational Analysis. Part 4. Crystalline Cellulose II', Journal of Macromolecular Science, Part A, 24: 8, 901 — 918
To link to this Article: DOI: 10.1080/00222338708076925
URL: http://dx.doi.org/10.1080/00222338708076925

PLEASE SCROLL DOWN FOR ARTICLE

Full terms and conditions of use: http://www.informaworld.com/terms-and-conditions-of-access.pdf

This article may be used for research, teaching and private study purposes. Any substantial or systematic reproduction, re-distribution, re-selling, loan or sub-licensing, systematic supply or distribution in any form to anyone is expressly forbidden.

The publisher does not give any warranty express or implied or make any representation that the contents will be complete or accurate or up to date. The accuracy of any instructions, formulae and drug doses should be independently verified with primary sources. The publisher shall not be liable for any loss, actions, claims, proceedings, demand or costs or damages whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

J. MACROMOL. SCI.–CHEM., A24(8), pp. 901-918 (1987)

THE STRUCTURE OF CELLULOSE BY CONFORMATIONAL ANALYSIS. PART 4. CRYSTALLINE CELLULOSE II

A. PIZZI and N. J. EATON

National Timber Research Institute
Council for Scientific and Industrial Research
Pretoria 0001, Republic of South Africa

Downloaded At: 18:23 24 January 2011

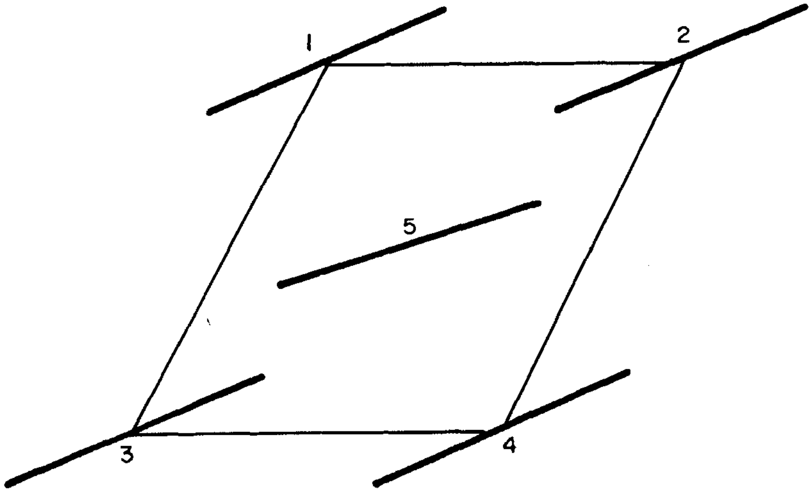
ABSTRACT

The Kolpack, Weih, and Blackwell antiparallel central chain model was found to be the most energetically stable for the crystalline structure of cellulose II. Computational results indicated that the two most probable Sarko models are considerably less stable and less probable. The conformations of the monomers terminating the crystalline zone have been described. The predominance of van der Waals and H-bond interactions in the crystalline zone have been confirmed, and the H-bond values, locations, and distribution in the crystalline zone have been accurately mapped. The cellulose II crystallite has been confirmed to be considerably more stable than the cellulose I crystallite. Positions of atomic groups from the *ab initio* conformational analysis are consistent with the x-ray data for the Kolpack, Weih, and Blackwell model.

INTRODUCTION

Recently, *ab initio* conformational analysis calculations have been used to study the crystalline and amorphous structure of cellulose I [1-3]. This approach is different from the classical one of x-ray diffractometry. Information on a crystalline or amorphous structure can be gleaned by applying it. The same approach was applied in this study to the structure of cellulose II (Scheme 1).

Copyright © 1987 by Marcel Dekker, Inc.



SCHEME 1. Cellulose II.

Downloaded At: 18:23 24 January 2011

While considerable indirect evidence of the structure of cellulose II is available, direct evidence is available only from a few advanced x-ray diffraction studies [4-6]. Considering the wide field of important commercial products, such as paper, in which cellulose II is present, it is indeed amazing that so much less "direct-evidence" studies than for cellulose I are available that are specifically aimed at clarifying the crystalline structure of cellulose II. The study presented in this article is then a contribution to the present knowledge of the crystalline structure of cellulose II by using an experimental approach different from the classical x-ray diffraction one.

This article deals with the total energy balance and the conformation of the cellulose chain in the cellulose II crystalline network by taking into account inter- and intrachain van der Waals, H-bond, electrostatic, and torsional interactions.

EXPERIMENTAL

Single methyl-β-cellotetraoside chains (4-glucose rings) were strained from the helicoidal conformation of minimum total energy ($\Phi°$, $\Psi°$) (-49°, -130°) (-58°, -171°) (-49°, -130°) optimized in the previous articles [1, 2] to the "two-fold" helix conformations which are required from the (Φ°, Ψ°) energy maps [1, 2] to obtain the minimum amount of energy for the rotation of both the intra- and intermonomers β-glucosidic linkages. The "two-fold" helix conformation was then used to check the energy balance of the Kolpak, Weih, and Blackwell [4] and of the two most probable Sarko [5, 6] antiparallel-central-chain models based on x-ray diffraction evidence. The structures were optimized according to the same procedure and the same van der Waals, H-bond, electrostatic, and torsional functions used in the preceeding article [3] to optimize the structure of crystalline cellulose I.

Two different cases for each model were optimized, namely: 1) a crystal composed of 20 glucose residues with each of the five chains comprising 4 glucoses each, and 2) a crystal composed of 11 glucose residues with each corner chain composed of 2 glucose residues and the central antiparallel chain composed of three glucose residues. The 20 chains crystals configuration defines the real structure better as it takes into account interactions not considered by previous studies of cellulose II [4-6], while the 11-chains configuration is directly comparable to what is obtained by previous x-ray studies [4-6].

Also the contributions to the van der Waals energy of nonrotatable groups have been calculated, which cannot be eliminated during minimization of the total energy of the structure when shifting the position of the central chain along the longitudinal axis (the crystallographic axis) of the crystal, before energy optimization. This has been found to be a good indication of the central chain shift which corresponds to the optimized minimum of energy.

The following parameters were used:

Kolpack, Weih, Blackwell model [4]: Monoclinic unit cell a = 8.02 Å, b = 8.95 Å, c = 10.36 Å, γ = 116.6° A; corner chain rotation = 22.0°, central chain rotation = 62.7°, central chain shift = 0.227 c.

First Sarko model [5]: Monoclinic unit cell a = 7.96 Å, b = 9.09 Å, c = 10.31 Å, γ = 117.3°, corner chain rotation = 31°, central chain rotation = 64°, central chain shift = -2.97 Å.

Second Sarko model [6]: Monoclinic unit cell a = 7.92 Å, b = 9.08 Å, c = 10.34 Å, γ = 117.3°, corner chain rotation = 25°, central chain rotation = 55°, central chain shift = -3.43 Å.

We have used, simply for mathematical conveniency, the opposite sign of that used by Sarko [5, 6] for the direction of the central chain shift (thus -3.43 Å in Sarko is +3.43 Å in this article).

Downloaded At: 18:23 24 January 2011

RESULTS AND DISCUSSION

The calculations and energy minimizations were carried out for the Kolpak, Weih, Blackwell [4] model and for the two most probable Sarko [5, 6] models. The results in Table 1 indicate that, for the Kolpak, Weih, and Blackwell model, the minimum energy of the structure is found at a 2.2-2.3 Å shift of the central antiparallel chain in respect of the corner chains. This can be seen from the minimum (and lack of) nonrotatable repulsive van der Waals interactions at the 2.2 and 2.3 Å shifts. This is in good accord with the relevant x-ray data and their refinement [4]. The use of nonrotatable repulsive van der Waals interactions is based on the conformational analysis requirement that the conformation of minimum total energy of a structure in the stability of which the van der Waals interactions are preponderant will be the one at which such interactions can be minimized. Nonrotatable van der Walls repulsive contributions are the ones which cannot be eliminated by any conformational adjustment of the molecular skeleton without creating even higher van der Waals nonrotatable, noneliminable, repulsive contributions. In theory, they must then be absent for a structure to be stable, hence the minimum at 2.2-2.3 Å central chain shift in Table 1. In cases in which they cannot be eliminated, the principal and first requirement is that the structure of minimum total energy will exist in the conformation at which such repulsive noneliminable contributions are at their minimum. Second, in such cases the conformation of minimum total energy is likely to be the structure in which the maximum possible optimized H-bond contribution is greater than the van der Waals repulsive nonrotatable interactions.

As the cellulose I crystallite of similar dimensions has a total minimum energy of -46 kcal/mol [3] and the cellulose II crystallites are well known to be in a considerably more stable energy situation [4-6], this means that for a maximum allowable interchain H-bond contribution of approximately -60 kcal/mol and an electrostatic contribution of approximately -9 kcal/mol, any nonrotatable van der Waals contribution must be at least much lower than +24 kcal/mol. In Table 2, this means that the Sarko conformation appears to be stable and only marginally more stable than cellulose I for a shift of the central antiparallel chain in a very different range than what is proposed in all the best Sarko models [5, 6]. In Table 1 the same argument limits the shift of the central chain to 1.8 to 2.5 Å; coupled with the first requirement above and with the x-ray data of Kolpack, Weih, and Blackwell [4], the minimum is in the approximate range 2.2-2.3 Å.

The energy calculations for the two Sarko [5, 6] models indicated that the minimum energy of both structures is in the 1.7 to 2.4 Å shift of the anti-

Downloaded At: 18:23 24 January 2011

parallel central chain. Table 2 indicates that the calculated minimum energy as a function of central chain shift for the most favorable of the two Sarko models (31°; 64°; -2.57 Å) is at a 1.9-2.1 Å shift. This is shown by the minimum of nonrotatable repulsive van der Waals interaction at 2.0 Å shift. These calculated data are not in accord with the chain shifts obtained by Sarko by refining x-ray data [5, 6], which are of 2.97 and 3.43 Å for the two models. The minimum values of the nonrotatable repulsive van der Waals interactions are also much higher than for the Kolpack, Weih, and Blackwell model, suggesting the Sarko models to be energetically less favorable.

The chain shift discrepancy appears to be due to: 1) the inadequate packing energy term [5] in the function used by Sarko in refining his x-ray data to define the conformations of minimum energy. This term tends to strongly slant the interactions in favor of electrostatic ones and also to exaggerate the differences obtained (in Table 2 the electrostatic minimum obtained with our function is in the 3.0-3.5 Å shift range, consistent with what is obtainable with Sarko's function). Thus, it describes only one type of nonbonded interaction, the weakest one, and by a mathematical expression which does not represent it correctly. The other terms, by minimizing indirectly the energy of the system through geometrical parameters only, imply a rigid-spheres approach which has been shown to be inadequate to describe the reality of complex molecular structures. 2) The model's deficiency that only two chains of two glucoses each were used by Sarko in his refinement. Thus, when the two chains are progressively shifted in relation to each other along the crystallographic *c*-axis by 3 Å or more, the total energy will continue to decrease because fewer and lower interchains interactions are present. This is obviously not the case if the much longer chains of cellulose would have been used. Two chains also do not clarify the jigsaw puzzle situation present in a crystal.

For these reasons, doubts may be expressed as to the validity of all the multitude of crystalline cellulose II and cellulose I models calculated by Sarko [5, 6] by this method.

The values of interchain interactions in the structure obtained from the Kolpak, Weih, and Blackwell model for 5 chains of 4 glucoses each (4-4 structure) are shown in Table 4; those for 5 chains, the corner chains being composed of two glucoses and the central one of three glucoses (2-3 structure), are shown in Table 5. While the 2-3 structure (Table 5) which is the most common pictorial representation of the crystal [4-6] shows attractive total interactions for both the whole crystal and between each chain pair, this is not the case for the 4-4 structure (Table 4). For the latter, the total crystal energy shows the whole crystal to be stable and its formation favorable

Downloaded At: 18:23 24 January 2011

Downloaded At: 18:23 24 January 2011

TABLE 1. Total Energy Variation and van der Waals, H-Bond, and Electrostatic Components[a]

C-axis direction shift increment	Total	van der Waals	H-bond	Electrostatic	Nonrotatable van der Waals[b]
-3.5	1 099.95	1 126.16	-38.51	12.31	–
-3.0	1 962.41	1 988.40	-37.72	11.73	–
-2.5	5 148.48	5 170.85	-35.00	12.62	–
-2.0	4 930.06	4 950.47	-33.03	12.62	–
-1.5	4 226.24	4 245.80	-31.89	12.33	–
-1.0	2 864.60	2 885.21	-33.94	13.32	–
-0.5	2 287.40	2 313.49	-38.61	12.52	256.99
0.0	1 778.90	1 802.15	-37.28	14.03	267.44
0.5	1 785.65	1 808.61	-37.62	14.66	56.36
1.0	1 817.14	1 834.36	-32.45	15.23	75.63

Downloaded At: 18:23 24 January 2011

1.5	1 007.10	1 019.77	-29.22	16.55	26.84
1.8	482.18	497.17	-30.30	15.31	11.28
1.9	587.47	602.41	-30.14	15.20	8.94
2.0	738.22	752.50	-29.73	15.45	6.98
2.1	952.39	966.96	-29.71	15.14	5.36
2.2	1 259.91	1 275.17	-30.50	15.24	0.00
2.3	1 701.45	1 717.51	-30.65	14.60	0.00
2.5	3 261.78	3 277.69	-30.80	14.89	11.97
3.0	15 699.01	[c]	-31.63	13.41	[c]
3.5	20 255.02	[c]	-33.03	12.91	[c]

[a] Before side-chains minimization. Obtained by shifting central antiparallel chain along its axis for Kolpak, Weih, and Blackwell model; chain angles, Blackwell convention: corner chains = 22.0°; central antiparallel chain = 62.7°.

[b] Nonrotatable van der Waals values also included in total van der Waals in third column.

[c] Very high.

Downloaded At: 18:23 24 January 2011

TABLE 2. Total Energy Variation and van der Waals, H-Bond, and Electrostatic Components[a]

Central chain shift	Total energy	van der Waals	H-bond	Electrostatic	Nonrotatable van der Waals
-3.5	472.62	491.76	-31.33	12.19	102.32
-3.0	487.37	508.82	-33.11	11.67	58.09
-2.5	545.02	567.94	-35.06	12.13	35.08
-2.0	764.62	791.26	-37.71	11.07	41.78
-1.5	2415.50	2448.58	-40.22	10.14	56.66
-1.0	6021.89	6050.19	-39.25	10.95	62.05
-0.5	3631.63	3659.30	-36.64	11.97	71.49
0.0	1722.51	1743.74	-35.49	14.25	92.75
0.5	1384.32	1405.05	-35.05	14.32	94.95
1.0	892.60	914.38	-35.73	13.96	100.56
1.5	281.64	307.86	-38.87	12.65	37.50
1.7	164.29	192.95	-41.43	12.77	25.77

Downloaded At: 18:23 24 January 2011

1.8	125.84	155.63	-42.56	12.78	22.80
1.9	96.79	128.92	-44.30	12.17	18.75
2.0	77.43	111.16	-45.94	12.21	17.84
2.1	64.88	100.08	-47.46	12.26	20.17
2.2	57.33	94.78	-48.92	11.48	21.54
2.3	54.96	94.42	-50.04	10.58	22.41
2.4	57.89	98.05	-50.89	10.73	32.52
2.5	63.60	105.17	-51.92	10.35	40.64
2.6	72.36	115.18	-53.05	10.23	49.81
2.7	84.46	127.60	-53.20	10.06	59.83
3.0	132.78	174.87	-52.12	10.04	93.56
3.5	220.24	256.92	-46.78	10.10	128.20

[a] Before side-chains energy minimization obtained by shifting central antiparallel chain along its axis for Stipanovic and Sarko model (chain angles, Blackwell convention: corner chains = 31°; central antiparallel chain = 64°).

Downloaded At: 18:23 24 January 2011

TABLE 3. H-Bond Position and Values[a]

Fig. 1, chains 1 and 2		Fig. 2, chains 3 and 4		Fig. 3, chains 2, 3, and 5	
Atoms involved in H-bond (Figs. 1, 2, 3)	H-bond value, kcal/mol	Atoms involved in H-bond (Figs. 1, 2, 3)	H-bond value, kcal/mol	Atoms involved in H-bond (Figs. 1, 2, 3)	H-bond value, kcal/mol
O6–H401	-0.39	O180–H289	-0.14	O101–H401	-0.37
H7–O101	-0.24	O184–H282	-0.12	O107–H401	-1.39
O10–H108	-0.12	O184–H289	-0.34	H108–O400	-4.19
O10–H401	-2.07	H185–O275	-0.42	H108–O432	-0.12
H11–O101	-0.42	H185–O281	-0.71	O114–H401	-1.64
H11–O107	-0.71	H185–O288	-0.27	H115–O396	-3.17
H11–O114	-0.27	O194–H202	-2.40	H115–O388	-2.15
H11–O396	-0.11	H206–O233	-0.56	O146–H389	-0.20
H11–O400	-0.28	O214–H223	-3.86	O146–H359	-0.28
O20–H28	-2.40	O214–H293	-0.25	O146–H355	-0.12
H32–O59	-0.56	O214–H324	-0.73	O149–H355	-0.24
O40–H49	-4.53	H215–O292	-2.17	O149–H359	-1.05
O40–H150	-0.37	O222–H324	-2.62	H150–O385	-0.91
O40–H119	-0.35	H227–O323	-2.33	H150–O396	-0.31
O48–H150	-2.43	O236–H244	-2.40	H157–O354	-2.63

Downloaded At: 18:23 24 January 2011

H53–O84	-2.51	H268–O301	-0.87	H181–O410	-2.19
H53–O354	-0.43	H268–O432	-0.25	H181–O404	-1.32
O62–H70	-2.40	H272–O301	-3.58	H185–O379	-0.40
O67–H259	-1.07	O292–H324	-0.63	O211–H380	-0.22
O84–H157	-0.24	H293–O320	-0.56	O214–H369	-0.14
H85–O143	-1.81	H293–O362	-0.25	O214–H380	-0.12
H85–O153	-0.41	H293–O385	-0.30	H215–O362	-0.35
H85–O354	-0.53	H310–O345	-0.87	O222–H369	-2.21
H94–O127	-0.87	H314–O345	-3.58	H223–O375	-1.18
H98–O127	-3.58	O323–H369	-3.61	H223–O379	-0.08
H108–O114	-0.43	H324–O368	-0.64	H227–O362	-0.14
O118–H150	-0.73	H324–O362	-0.64	H227–O368	-2.11
H119–O146	-0.56	O345–H355	-0.23	H259–O365	-1.91
H136–O171	-0.87			H359–O385	-0.53
H140–O171	-3.58			O368–H376	-2.34
				H380–O407	-0.56
				O396–H433	-0.17
				H397–O388	-2.34
				H411–O417	-0.41
				Total	-108.75

---

[a] H-bonds higher than −0.1 kcal/mol. Crystal composed of 5 chains of 4 glucoses each: structure refined from Kolpak, Weih, and Blackwell model (corner chain = 22.0°; central antiparallel chain = 62.7°).

TABLE 4. Interchain Energies of Cellulose II Crystallite[a,b]

Chains	van der Waals	H-bond	Electrostatic	Total
1-2	-6.45	-9.47	1.41	-14.51
1-3	-1.42	-0.04	0.05	-1.40
1-4	-0.80	0	0.12	-0.67
1-5	-10.96	-4.48	0.69	-14.75
2-3	-0.05	0	0.06	0.00
2-4	-1.33	0	0.12	-1.22
2-5	0.35	-17.97	1.44	-16.18
3-4	-3.78	-10.93	0.80	-13.91
3-5	25.94	-13.16	2.94	+15.72
4-5	-20.35	-5.14	1.16	-24.33
Total	-18.85	-61.19	8.79	-71.25

[a] In kcal/mol.

[b] 5 Chains, 4 glucoses each. Kolpak, Weih, and Blackwell model.

Downloaded At: 18:23 24 January 2011

(-71.25 kcal/mol) but the energy value between chains 3 and 5 shows a repulsive interaction (+15.72 kcal/mol). While this does not destabilize the crystal, as the total energy balance is favorable, it is an unexpected finding (the effect cannot be eliminated by any of the manipulations tried). This may be an indication of 1) the Kolpak, Weih, and Blackwell model being partially incorrect although all the other evidence indicates that this is not the case, and 2) the side groups of the D3 glucose residues (the repulsive interaction is D3-D5, Fig. 3) being in the conformation of an end-of-crystal glucose residue and not as in the body of the crystal (correction of this point minimizes but does not completely eliminate the problem).

Figures 1, 2, and 3 show the structure of chains 1 and 2 (Fig. 1) and 3 and 4 (Fig. 2) and 2, 3, and 5 (Fig. 3) at the conformation of minimum total energy of the whole crystal with the interchains H-bond network for the refined Kolpak, Weih, and Blackwell model. In this regard, comparison of Figs. 1 and 2 shows that the O40–H49 and O214–H223 H-bonds are slightly different, both

TABLE 5. Interchain Energies of Cellulose II Crystallite[a,b]

Chains	van der Waals	H-Bond	Electrostatic	Total
1-2	-3.86	-3.29	0.77	-6.39
1-3	-0.49	0	0.02	-0.47
1-4	-0.33	0	0.02	-0.30
1-5	-10.09	-0.71	0.26	-10.53
2-3	-0.02	0	0.01	-0.01
2-4	-0.50	0	0.01	0.49
2-5	2.70	-8.50	1.05	-4.75
3-4	-3.00	-8.49	0.65	-10.87
3-5	-1.01	-7.87	1.42	-7.46
4-5	-11.20	-2.23	1.03	-12.40
Total	-27.79	-31.09	5.23	-53.65

[a] In kcal/mol.

[b] 5 Chains. Corner chains 2 glucoses each; central chain 3 glucoses; Kolpak, Weih, and Blackwell model.

Downloaded At: 18:23 24 January 2011

within the x-ray data previsions, and have slightly different values (Table 3). This difference and the differences of the atoms positions for the glucose rings A1-A4 and D1-D4 indicate that the cases shown in Figs. 1 and 2 represent only the conformation of surface chains top and bottom of the crystal of cellulose II; and the A1, A2, A3, A4, A5 and D1, D2, D3, D4 the conformation of the glucose rings at the upper and lower end of the crystal or before start of the amorphous zone [3]. The conformations of the B1, B2, B3, B4, B5, C1, C2, C3, C4, C5, and possibly of D5 glucose rings are consistent with the conformations of the glucose residues along the whole length of the top and bottom surfaces and of the inner part of a cellulose II crystallite of any length and are consistent with the x-ray data of Kolpak, Weih, and Blackwell [4].

The conformation of the external side groups of the corner chains have been found to be identical to that of cellulose I. Figure 4 shows a different conformation of the O410/H411 group. It is different because these figures represent the 2-3 structure and the B3 and B5 glucose rings are in this the

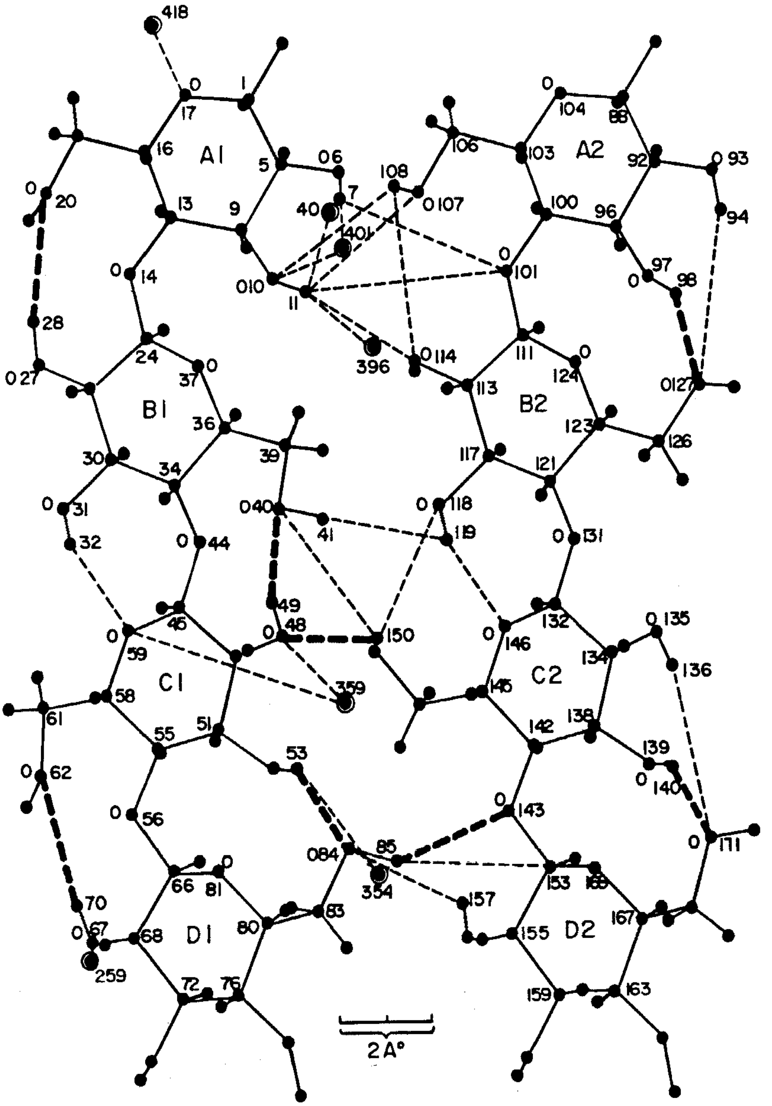


FIG. 1. Top surface chains (Chains 1 and 2) in a five-chains cellulose II crystallite when chains are limited to four glucose residues each. Positions of H-bonds are indicated by broken lines, the heavier lines representing H-bonds stronger than -1 kcal/mol. H-bonds and group configurations of B1, B2, C1, and C2 residues are representative of H-bond pattern in the body of long chains. A1, A2, D1, and D2 residues configurations are indicative of upper and lower ends of cellulose II crystallite. Refinement of Kolpak, Weih, Blackwell model [4].

Downloaded At: 18:23 24 January 2011

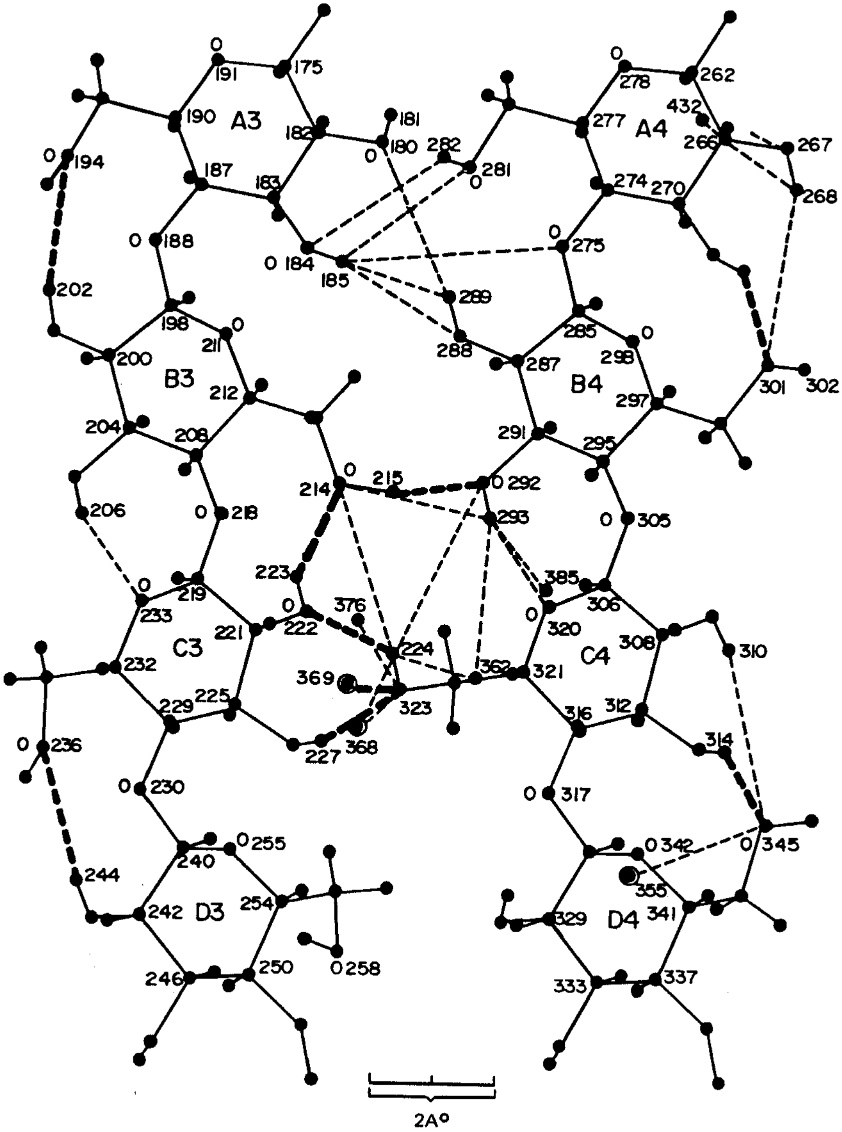
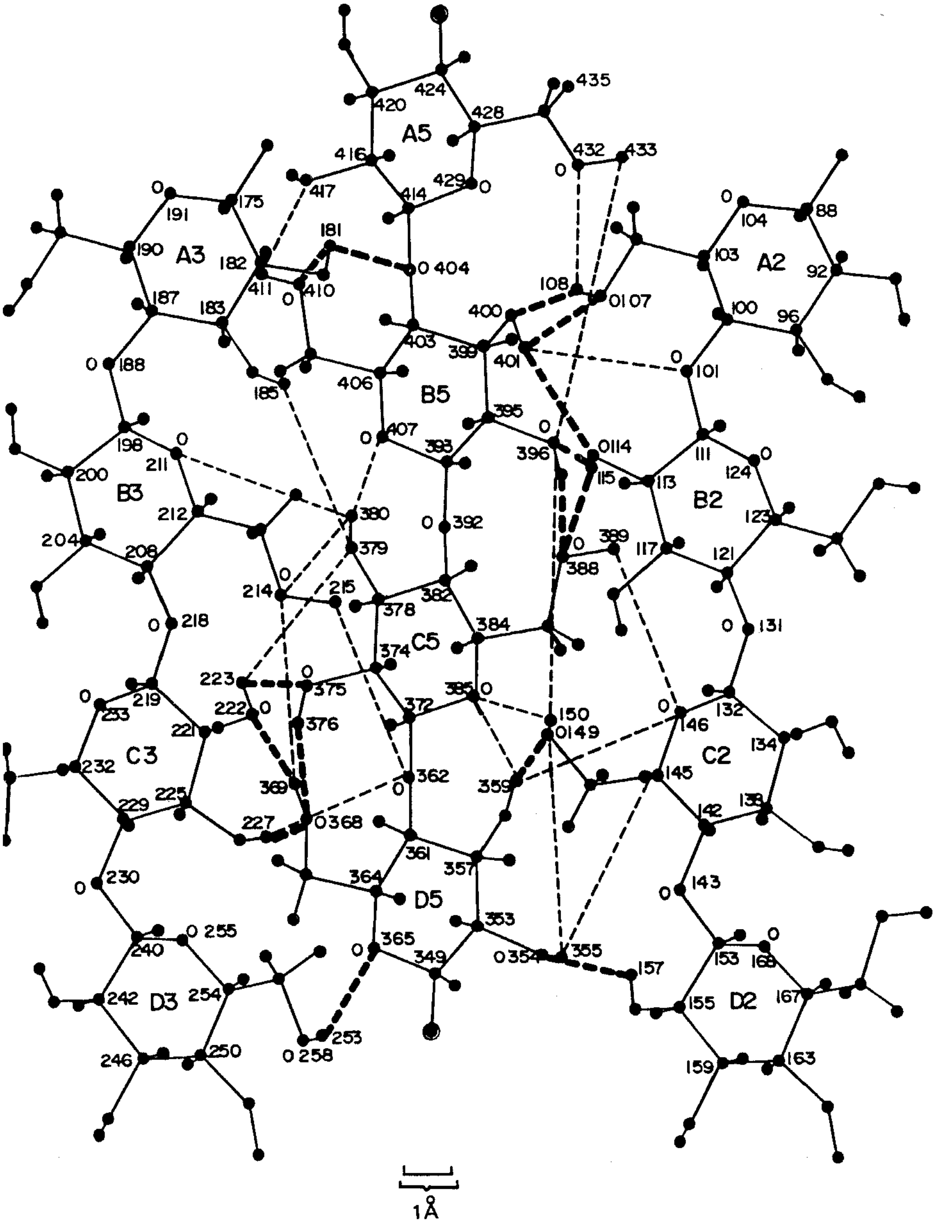


FIG. 2. Bottom surface chains (Chains 3 and 4) in a five-chains cellulose II crystallite when chains are limited to four glucose residues each. Positions of H-bonds are indicated by broken lines, the heavier lines representing H-bonds stronger than −1 kcal/mol. H-bonds and group configurations of B3, B4, C3, and C4 residues are representative of H-bond pattern in the body of long chains. A3, A4, D3, and D4 residues configurations are indicative of upper and lower ends of cellulose II crystallite. Refinement of Kolpak, Weih, Blackwell model [4]. Note that O214/H223 configuration is slightly different from O40/H49 in Fig. 1.

Downloaded At: 18:23 24 January 2011

Downloaded At: 18:23 24 January 2011



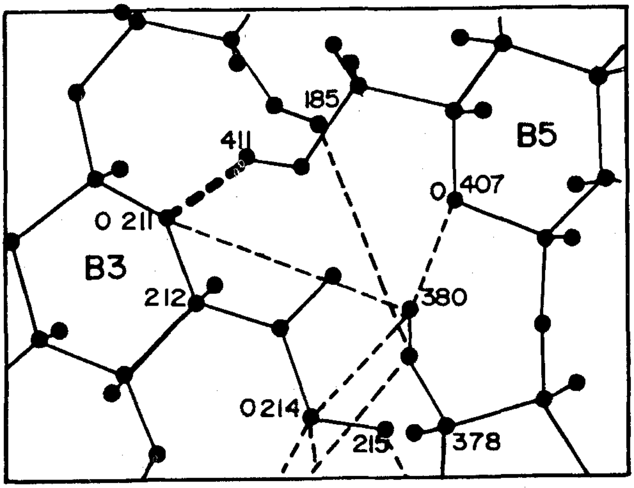


FIG. 4. Detail of B3 and B5 showing O410/H411 difference in configuration for five-chains cellulose II crystallite model with corner chain (B3) and center chain (B5) composed respectively of only 2 and 3 glucose residues

FIG. 3. Chains 2, 3, and 5 (central, antiparallel) in a five-chains cellulose II crystallite when chains are limited to four glucose residues each. Positions of H-bonds are indicated by broken lines, the heavier lines representing H-bonds stronger than −1.0 kcal/mol. H-bonds and group configurations of B2, B3, B5, C2, C3, C5, and D5 residues are representative of H-bond pattern in the body of long chains. A2, A3, A5, D2, and D3 residues configurations are indicative of upper and lower ends of cellulose II crystallite. Intrachain H-bonds for Chains 2 and 3 are not shown (cf. Figs. 1 and 2) but are shown for Chain 5. Refinement of Kolpak, Weih, Blackwell model [4].

Downloaded At: 18:23 24 January 2011

upper terminal residues of the crystal and the O410/H411 group maximizes the H-bond by turning inwards. Table 3 details the position and values of all the H-bonds stronger than -0.1 kcal/mol in the crystal.

In conclusion, the Kolpak, Weih, and Blackwell model appears to be the one currently describing the structure of the body of the cellulose II crystallite and the most probable of the best models available once all the possible interactions are computed by conformational analysis. The minimum total energy of -71.25 kcal/mol is consistent with the accepted evidence that crystalline cellulose II is a structure more stable than crystalline cellulose I (-46.72 kcal/mol) [3].

REFERENCES

[1] A. Pizzi and N. Eaton, *J. Macromol. Sci.–Chem.*, *A21*, 1443 (1984).
[2] A. Pizzi and N. Eaton, *Ibid.*, *A22*, 105 (1985).
[3] A. Pizzi and N. Eaton, *Ibid.*, *A22*, 139 (1985).
[4] F. J. Kolpak, M. Weih, and J. Blackwell, *Polymer*, *19*, 123 (1978).
[5] A. J. Stipanovic and A. Sarko, *Macromolecules*, *9*, 851 (1976).
[6] A. Sarko and R. Muggli, *Ibid.*, *7*, 486 (1974).

Received May 27, 1986
Revision received January 6, 1987

Downloaded At: 18:23 24 January 2011