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The Structure of Cellulose by Conformational Analysis. 3. Crystalline and Amorphous Structure of Cellulose I

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The Structure of Cellulose by Conformational Analysis. 3. Crystalline and Amorphous Structure of Cellulose I

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ABSTRACT

The Meyer/Misch and related models were found to be the most energetically stable for the crystalline structure of cellulose I. The cellobioside structure is the monomer of cellulose I because structures having cellobiose as monomer have proven to be energetically much less stable. The conformation of the monomers terminating the crystalline zone and initiating the amorphous zone have been accurately described. The cause and mechanism of termination of the crystalline zone have been identified and described. A few new considerations regarding the conformation and appearance of the amorphous zones in cellulose I, in which the chains are in helicoidal conformations, are discussed. 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.

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INTRODUCTION

Conformational analysis studies of the structure of cellobiose, methyl-β-cellobioside and of a single-strand cellulose polymer chain have been carried out in the previous two parts of this study [1, 2]. A few conformations of minimum total energy were identified in the various cases. The helix conformations describing the amorphous regions of cellulose I (cellobioside model) and cellulose II (cellobiose model) were quantitatively described [1, 2].

This article deals with the total energy balance and the conformation of the cellulose chain in the cellulose I crystalline network by taking into account inter- and intrachain van der Waals, H-bond, electrostatic, and torsional interactions. The energy minima obtained were afterwards also checked for improvements which could be obtained by deformation of the glucopyranose ring in the crystalline packing according to systems already reported [13]. The exact position of the H bonds of the minimum total energy network have also been pinpointed. All the interactions between all atoms, included side-chains, have been taken into account according to the mathematical expressions described in the two previous articles [1, 2]. Comparison of the most accepted models for the structure of cellulose I crystallite have been made on a total minimum energy basis and the most likely structure determined. Comparison between structures based on cellobiose and methyl-β-cellobioside conformations as monomers have been carried out, and the energetically correct monomer conformation and structure determined.

EXPERIMENTAL

Single cellotetraose and methyl-β-cellotetraoside chains (4-glucose rings), were strained from the helicoidal conformations of minimum total energy optimized in the previous articles [1, 2] to the "twofold" helix conformations which required, from their respective (Φ,Ψ) energy maps [1, 2], the minimum amount of energy for the rotation of both the intra- and intermonomers β-glucosidic linkages.

Thus,

1. The methyl-β-cellotetraoside (Φ,Ψ) conformation (-49°,-130°) (-58°,-171°)(-49°,-130°) of minimum total energy = -1.39 kcal/mol was strained into the energetically most favorable of the "twofold" helix (Φ,Ψ) conformations (-50°,-130°)(-25°,-155°) (-50°,-130°) of minimum total energy = +4.19 kcal/mol. Energy necessary for transformation = 5.58 kcal/mol (per chain of 4 glucose rings).
2. The methyl-β-cellotetraoside (Φ,Ψ) conformation (0°,-161°) (-16°,-138°)(-0°,-161°) of minimum total energy = -1 kcal/mol

was strained into the energetically most favorable of the "twofold" helix (Φ,Ψ) conformations (-15°,-165°)(-39°,-141°)(-15°, -165°) of minimum total energy = +7 kcal/mol. Energy necessary for transformation = 8 kcal/mol (per chain of 4 glucose rings).

3. The cellotetraose (Φ,Ψ) conformation (32°, 138°)(59°,173°)(32°, 138°) of minimum total energy = -2.226 kcal/mol was strained into the energetically most favorable of the "twofold" helix (Φ,Ψ) conformations (40°,140°)(21°,159°)(40°,140°) of minimum total energy = +10.401 kcal/mol. Energy necessary for transformation = 12.627 kcal/mol (per chain of 4 glucose rings).

Each of these "twofold" helix conformations was then used to check the energy balance of the Meyer and Mark [3], Meyer and Misch [4], and related models [5, 6] based on x-ray diffraction evidence. What was looked for was whether the energy decrease obtained by placing the most favorable "twofold" helix cellulose polymers in the crystalline network of the model (and by minimizing by side-chains bond rotations the van der Waals, H-bond, and electrostatic interactions between the parallel cellulose chains) is greater than the energy increase due to the straining of the chain from the helicoidal conformation of minimum total energy.

The "twofold" helix sequence of four glucose rings was replicated to the apexes of the crystalline cell of Meyer and Misch (a = 8.35 Å; b = 7.9 Å; β = 84°) with the chains axes parallel to each other. First, the interaction of two cellotetraose-oside-like chains parallel to each other in the x,y plane were minimized by rotation of the bonds of the side chains. Then the two lower chains in the same plane but shifted along the z-axis by 7.9 Å and according to β = 84° were added and the interactions in all the x,z planes along the y-axis were minimized. The central chain was then inserted in the network and its interactions with the other four chains of the crystalline cell were minimized by both shifting the central chain along its axis and rotating the side chains around their bonds.

In the case of the Meyer and Misch and related models [4-6], the central chain is antiparallel to the direction of the other four chains. To obtain the atom coordinates of this central chain (thus its relative position), the following technique was used. The equation of the plane containing the atoms C4, O(4-1') and C1' of the central β-glucosidic linkage of the four glucose rings structure was obtained as well as the midpoint (= x_1) of the straight line connecting C4 and C1'. Following this, the vector through point x_1, at right angles to this plane was determined. Two points, x_2 and x_3, were arbitrarily selected on this vector and the same computer program used for rotating bonds was used to rotate the whole four glucose rings chain around the x_1, x_2 segment by 180°.

In this manner the position of the antiparallel central chain was obtained. The same total energy minimization process was also

TABLE 1. Minimum Total Energy and Energy Contributions of Cellulose Chain Combinations in Cellulose I Crystal

Model	Minimum total energy (kcal/mol)	Approximate energy decrease gained by crystallite formation (kcal/mol)	Minimum total energy contributions		
			van der Waal (kcal/mol)	H bond (kcal/mol)	Electrostatic (kcal/mol)
Two parallel chains (x,y projection plane):					
Meyer/Mark:					
Cellobioside monomer: 4 rings	-20.246	-28.6	+21.77	-41.00	-1.01
3 rings	-17.06	-20.9	+16.33	-32.63	-0.76
Meyer/Misch:					
Cellobioside monomer: 4 rings	-20.246	-28.6	+21.77	-41.00	-1.01
Cellobiose monomer	-10.42	-31.2	+29.55	-41.80	+1.83
Two parallel chains (y,z projection plane):					
Meyer/Mark:					
Cellobioside monomer: 4 rings	-	-4	-4	-	-
3 rings		-3	-3		
Meyer/Misch:					
Cellobioside monomer: 4 rings	-	-4	-4	-	-
Cellobiose monomer	-	-4	-4	-	-

Five chains in crystalline network:

Meyer/Mark:						
Cellobioside monomer:	4 rings[a]	-26.42	-	+47.89[b]	-82.00	+7.69
	3 rings	-43.35	-	+34.36	-80.76[c]	+3.05
Meyer/Misch:						
Cellobioside monomer:	4 rings	-46.722	-67.7	-6.73	-48.50	+8.50
Cellobiose monomer		-27.07	-79.0	-	-	-

[a]Combination of minimum total energy: other negative combinations are possible, but none with lower minimum total energy due to van der Waals interactions between the four peripheral chains and the central chain.

[b]Due to van der Waals interactions between central chain and the peripheral ones of +54.62 kcal/mol (due to groups which cannot be rotated).

[c]Due to the presence of -15.50 kcal/mol H bonding sum of small interactions between central chain and peripheral ones.

carried out by shifting the chain along its axis and by rotating the side-chains groups around their bonds. The minimum total energies obtained, and their van der Waals, H-bond, and electrostatic contributions, are shown in Table 1 for the Meyer/Mark, the Meyer/Misch, and related models.

Energy minimization by distortion of the glucopyranose ring [13] was also checked, but the minimum of energy obtained in the case of the five chains crystal was found to be considerably higher than that obtained without distortion of the ring and by H-bond stabilization, indicating that the crystal appears to prefer stabilization by H-bond network rather than to distort the pryanose rings. This is in agreement with x-ray analysis results.

In Table 2 the H-bond positions and values, at the conformation of minimum total energy for the most favorable model, the Meyer/Misch-type of the cellotetraoside chain (-50°,-130°)(-25°,-155°)(-50°,-130°), as well as those of the respective unfavorable cellobiose model, are shown. The H-bond pattern of the former conformation, which is not only the most favorable but also the only one likely to exist in crystalline form (see Discussion), is shown in Fig. 1 for two parallel chains in the x,y planes. In Fig. 2 the total network is shown.

Table 3 reports the variation of minimum energy obtained by varying the position of the central chain along its axis for both the Meyer/Misch and related conformations before minimization of the total energy by side-chain bonds rotations. Figure 3 shows the conformations of total minimum energy which are likely to occur at the upper and lower ends of the crystalline zones. Figure 4 shows one of the two most likely conformations, in schematic form, of the amorphous region (see Discussion).

It must be noted that in order to interpret the values of the rotational angles of the side-chains bonds, the following convention was used. The position of 0° for the rotational angles of the side chains was assumed to be the position relative to their glucose ring in which the atoms of the side chain present themselves after total energy minimization of monomer and single cellulose chain (from Parts 1 and 2 of this series).

Where rotation of the side chain was not carried out during energy minimization, the 0° position is the one in which the atoms of the side chain present themselves, relative to their glucose ring, in the x-ray crystallographic data already reported [7, 8]. The rotation is always considered to be positive when, viewing along the bond toward its related glucose ring, the rotation is performed clockwise. The values of the rotation of the side-chains bonds corresponding to the position of minimum total energy of the crystal structure, which needed to be readjusted from those shown in Table 3, are shown in Fig. 2.

It is important to note that only in a five chains crystal is the energy -20.246 (Table 1) between two chain parallel in the x,y projection plane. If a crystal formed of more chains is considered, the decrease of energy gain will always be equal to that obtained when the two chains

TABLE 2. (1) H-Bonds Positions and Values; Meyer/Misch/Mark Conformations/ x,y-Plane Projection Parallel Chains; Cellobioside and Cellobiose as Monomers (Fig. 1 cellobioside); All at the Position of Minimum Total Energy of the Structures. (2) Values of Bond Rotations (rotational angles) of Side Chains

Cellobioside monomer		Cellobiose monomer			
Atoms involved in H bond (Fig. 1)	H-bond value (kcal/mol)	Atoms involved in H bond (no figure given)	H-bond value (kcal/mol)	List of bonds rotated and values of rotational angle	
O6---H115	-0.626	H7---O37	-0.0003	Cellobioside structure	
H7---O37	-0.025	H7---O40	-0.672		
H7---O101	-0.315	H11---O40	-2.932	C5,O6	-27°
H7---O107	-2.884	H28---O20	-3.425	C9,O10	-9°
H7---O114	-0.677	H7---O107	-3.029	C16,O19	+80°
H11---O107	-0.409	H7---O114	-0.356	C26,O27	+102°
H11---O114	-0.982	O10---H108	-0.144	C36,C39	+168°
O20---H28	-2.400	O10---H115	-0.324	C39,O40	-83°
H21---O27	-0.010	H11---O107	-0.615	C47,O48	-130°
H32---O59	-0.558	H11---O114	-0.387	C51,O52	-1°
O40---H49	-4.530	H32---O59	-2.665	C58,C61	-178°
O40---H115	-0.127	O40---H108	-0.429	C68,O69	+102°
O40---H119	-0.261	O40---H115	-2.824	C103,C106	+90°

(continued)

TABLE 2 (continued)

Cellobioside monomer		Cellobiose monomer			
Atoms involved in H bond (Fig. 1)	H-bond value (kcal/mol)	Atoms involved in H bond (no figure given)	H-bond value (kcal/mol)	List of bonds rotated and values of rotational angle	
H41---O48	-0.013	H41---O114	-1.160	C113,O114	+85°
H41---O118	-2.530	H41---O118	-0.098	C145,C148	+146°
H41---O146	-0.131	H53---O84	-3.203	C148,O149	+154°
O48---H85	-0.033	O48---H150	-0.011	C155,O156	+152°
O48---H119	-0.184	H49---O146	-0.220		
H49---O118	-0.239	H49---O149	-0.171	Cellobiose structure	
H49---O149	-0.102	O52---H150	-0.274		
O52---H85	-0.089	H53---O149	-0.114	C5,O6	+188°
O52---H150	-0.295	O84---H157	-1.991	C9,O10	+6°
H53---O84	-3.576	H85---O149	-2.292	C16,O19	+111°
O62---H70	-2.399	H98---O127	-3.155	C26,O27	+123°
H63---O69	-0.010	H115---O107	-0.581	C36,C39	-19°
O84---H157	-0.557	H108---O114	-1.174	C39,O40	-173°
H85---O149	-2.940	H108---O124	-0.111	C47,O48	+68°
H85---O156	-0.403	H119---O146	-2.665	C51,O52	+4°

O93---H128	-0.033	H104---O171	-3.155	C58,C61	+140°
H94---O127	-0.873	H157---O149	-0.202	C68,O69	+123°
O97---H128	-0.089	H70---O62	-3.424	C103,C106	+170°
H98---O127	-3.577			C113,O114	+16°
O107---H115	-2.443			C145,C148	-135°
H119---O146	-0.558			C148,O149	+175°
O135---H172	-0.033			C155,O156	+88°
H136---O171	-0.873				
O139---H172	-0.089				
H140---O171	-3.577				
O149---H157	-0.809				
H150---O156	-0.001				
Residual	-0.740				
Total	-41.00	Total	-41.8033		

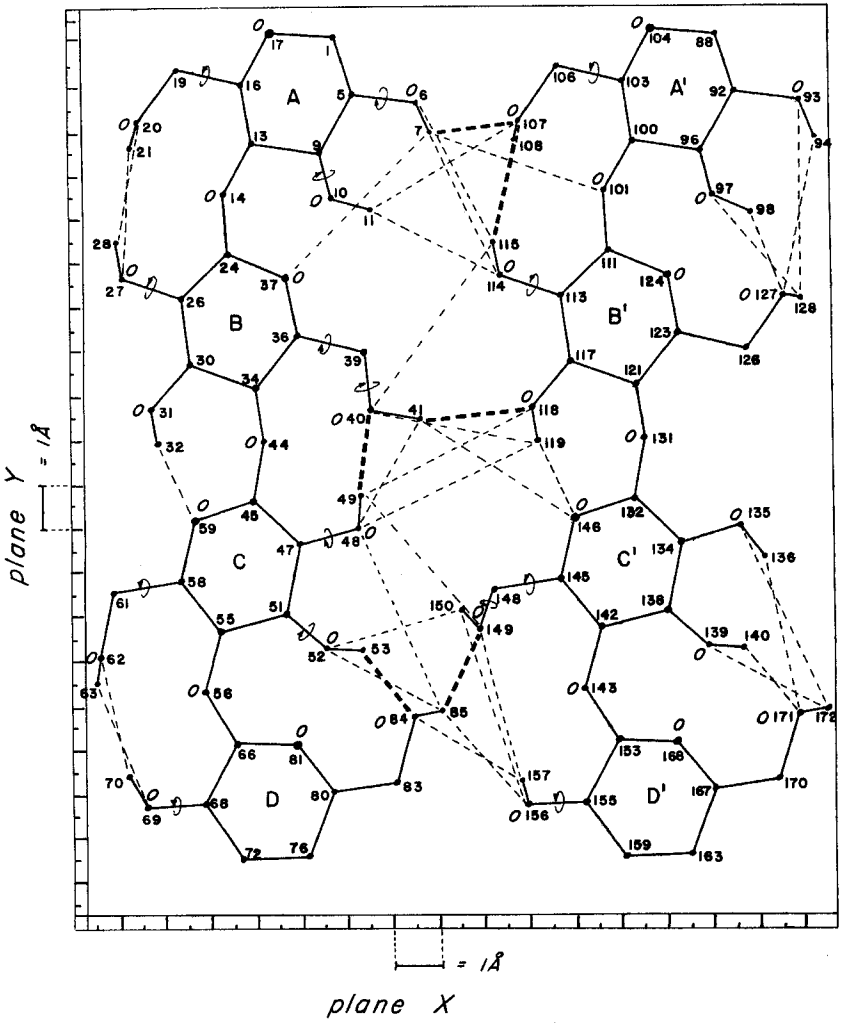


FIG. 1. Parallel chains in crystal when chains are limited to four glucose rings; position of all H bonds and rotational angles are indicated. H-bonds of terminal parts not representative of H-bond pattern in the body of long chain, but only of finite cellotetraoside chains system.

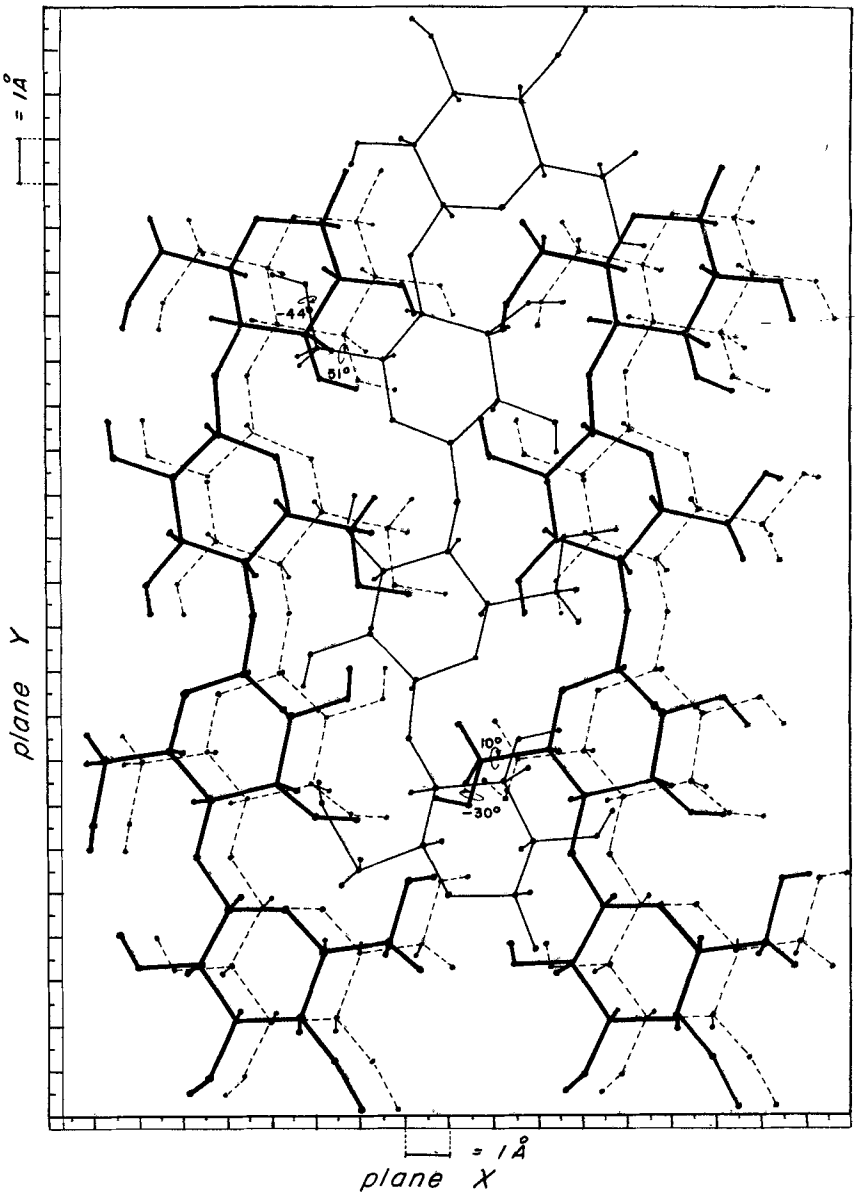


FIG. 2. Five-chains crystal of finite cellotetraoside chains system.

TABLE 3. Total Energy Variation before Minimization Obtained by Shifting Central Chain of Crystal along its Axis

Without energy minimization		1st stage of energy minimization	
Y-axis shift (Å)	Total energy (kcal/mol)	Y-axis shift (Å)	Total energy (kcal/mol)
-2.9	+128.61	-	-
-1.5	+306.69	-	-
0.0	+266.25	-	-
+1.5	+366.98	-	-
+2.3	+50.91	-	-
+2.4	+44.18	-	-
+2.5	+42.27	+2.5	+2.751
+2.6	+45.73	+2.6	+0.785
+2.7	+53.880	+2.7	+1.42
+2.8	+64.723	-	-
+2.9	+78.96	+2.9	+6.871
+3.2	+128.37	-	-

have the angles whose values are 51 and -44° in Fig. 2 for chains positioned parallel to each other. Thus, the decrease of energy gain passes from the -20.246 kcal/mol value to -16.417 kcal/mol, and this is the value which must be used for energy calculations on crystals containing a number of parallel chains larger than 5.

In Fig. 2 the four rotational angles are changed from Fig. 1 from +146°→+197°, from +154°→+110°, from +146°→+156°, and from +154°→+124° (variation Δ° = +51°, -44°, +10°, -30° of Fig. 2).

DISCUSSION

Conformation of Crystalline and Amorphous Zones

The results shown in Table 1 indicate that the Meyer/Misch [4] and related models [5, 6] appear to be the ones correctly describing the appearance of the crystalline network of cellulose I. The crystalline network formed by the five cellulose chains according to Meyer/Misch

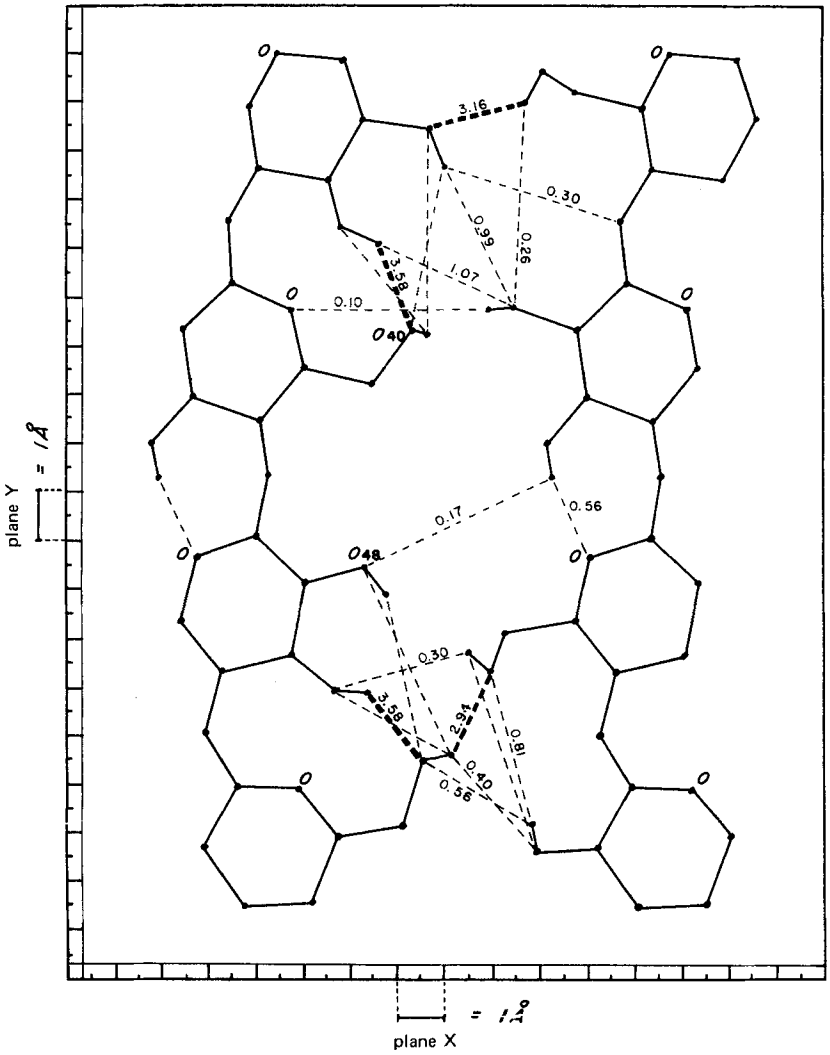


FIG. 3. Top four glucose rings representing most probable conformation and H-bonds pattern of upper terminal section of crystalline zone before start of amorphous zone. (Bottom four glucose rings of lower terminal section of crystalline zone before start of amorphous zone.)

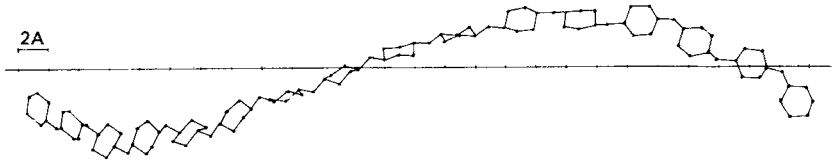


FIG. 4. Representation of one of the two most probable helix configurations of the amorphous zone of cellulose I chain (based on -49°,-130° monomer).

and others [4-6] fits very well with energetic and x-ray data. The minimum of total energy was found for a shift of the central antiparallel chain along its axis of 2.6 Å, which compares well with the 2.9 Å value deduced by Meyer and Misch from their x-ray diffraction data [4] (see Tables 1 and 3 and Fig. 2). After a few minor side-chains bond rotations, necessary to minimize the total energy (see Fig. 2 and the Experimental section), the five chains network had energy much lower than the sum of the energy increases caused by straining into "twofold" helix conformation the five chains in the crystal model. This clearly indicates that the formation of the crystal is, energetically, considerably more favorable for the cellulose chain than to remain in its amorphous helicoidal conformation.

Also of considerable importance is the finding that the model which energetically justifies the existence of the cellulose I crystallites has considerably higher probability when the cellobioside structure, rather than cellobiose, is the monomer. This confirms what has already been indicated by IR data [9], namely that methyl-β-cellobioside is present as monomer in cellulose I. To grasp this point, it is easy to see from the values in Table 1 that in the case of cellobiose as monomer in the Meyer and Misch model, the formation of the five chains crystal lowers the minimum of energy from a value of $-2.226 \times 5 = -11.13$ kcal/mol for five chains in helicoidal, unstrained form, to a value of -27.07 kcal/mol for a crystal composed of five "bent-chains"; the energy advantage is thus 15.94 kcal/mol in favor of the crystal. In the case of cellobioside as monomer, the formation of the crystal lowers the minimum of energy from a value of $-1.39 \times 5 = -6.95$ kcal/mol to a value of -46.72 kcal/mol for the five chains crystal; the energy advantage is thus 39.77 kcal/mol, more than double that for cellobiose. The formation of the crystal is then considerably more favorable when the cellobioside is the monomer.

It is also of interest to note that the second conformation of the cellotetraoside (cellobioside monomer (0°,-161°)), which is also a favorite conformation for the amorphous region of cellulose I, can also form a crystallite, but not quite as easily as the chain based on the (-49°,-130°) cellobioside monomer. As above, the formation of the five chains crystal lowers the energy level from a minimum of

$-1 \times 5 = -5$ kcal/mol to a minimum value of -37 kcal/mol. The possibility of forming a crystal is present, but is energetically less favorable. Thus, for chains with cellobioside (-49°,-130°) as monomer, the energy balance favor of crystal formation is 1.99 kcal/mol per glucose ring (in a five chains crystal), while for chains with cellobioside (0°,-161°) as monomer it is 1.5 kcal/mol.

For cellobiose the same value is only 0.8 kcal/mol. This means that the (-49°,-130°) conformation is likely to fall in the crystalline pattern of cellulose I much more easily than the (0°,-161°) conformation. It also explains the increase in the percentage crystallinity of cellulose I obtained when wood is heated. While it is likely that most of the monomers in the (-49°,-130°) conformation are already in the "twofold" helix crystal form, heating will cause partial redistribution in the type of conformations present in the amorphous region. Thus, a fraction of the amorphous (0°,-161°) monomers is likely to rearrange directly to crystalline form or to a (-49°,-130°) conformation which then will fall with more ease into the crystalline form. This observation has serious conceptual consequences. It means that the probability of finding a (-49°,-130°) conformation in the amorphous regions is lower. This means that a high percentage of the amorphous regions are composed of cellobioside monomers of (0°,-161°) conformation connected by β-glucosidic linkages of $(\Phi^\circ,\Psi^\circ) = (-16^\circ,-138^\circ)$ [2]. The helix formed by one of the two conformations is shown in Fig. 4.

It is also of interest to note that when deformation of the glucopyranose rings [13] is allowed, the minimum energy obtained was considerably less favorable than that obtained by simple energy minimization through inter- and intramolecular H bonds without ring deformation. We observed, as expected, that while the van der Waals energy sometimes became (not in all cases) slightly lower, the decrease or even loss of the H-bond contribution, even after optimization of the rotational angles of the side chains, was so marked as to render the total energy balance not as favorable. The reasons for this are that:

1. On deforming the ring, the decrease in the van der Waal hard spheres overlaps improves the van der Waals energy balance for atoms which may be slightly too near each other.
2. However, as many atoms in the undeformed system have distances fairly near to the minima obtainable by the use of Buckingham or Lennard-Jones functions, distortion of the glucopyranose ring also causes a slight worsening of the van der Waals energy balance. The combination of these two effects will give a total van der Waals energy balance sometimes slightly higher and sometimes slightly lower than that obtained without ring deformation.
3. However, as the H-bond interactions are very directional, and this is reflected in the mathematical function used to describe it [1], small directional variations can cause a considerable decrease in the H-bond contribution to the total energy balance. This indi-

cates that, in general, a crystallite formed by chains with undeformed, or very little deformed, glucopyranose rings and stabilized by a strong interchain H-bond networks are energetically more favorable for a model in which the rings are deformed and the H-bond network is weaker. This conclusion is also more in line with the finding of other author's x-ray analysis.

We were somewhat surprised that the Meyer/Mark model [3] was not the one of highest probability. It is necessary to elaborate on this model. The Meyer/Mark model appears to be allowed and favorable when the total energy interactions of five parallel chains no longer than three glucose rings each are considered. As the chains lengthen, the model becomes unfavorable. Thus, for chains of four or more glucose rings, a noticeable increase in the value of the total minimum energy develops.

This is due to "bumping" between groups of the central chain with groups of one or two of the other chains, which increases the value of the van der Waals interactions beyond reasonable limits. The interactions of the groups of atoms involved are not affected by bonds rotations (i.e., hydrogen atoms directly linked to the glucose ring) and the energy cannot, as a consequence, be lowered in this manner. We tried to eliminate this effect, first by moving the central chain along its axis in 0.1 Å intervals from +6 Å to -6 Å, but this did not solve the problem. Second, we tried to shift the central parallel chain slightly off-center in several directions and again, in all the new positions, shifting the chain along its axis. All this, however, was to no avail. Third, we tried to improve the situation by allowing deformation of the glucopyranose rings involved, but this did little to improve the situation.

Thus, the Meyer/Mark model is energetically favorable and stable for chains of up to three glucose rings length. For chains longer than three glucose rings, this model is energetically not possible. A solution to the problem may be that the five parallel chains are not in "twofold" helix conformation, but that the monomers are slightly rotated of a few degrees around the monomers connecting central β-glucosidic linkage. But this, of course, does not really correspond to the model derived by x-ray diffraction data. Furthermore, even in the case of chains of three glucose rings length, the total energy minimum in the Meyer/Mark model is found when the central chain is totally parallel to the other four chains (not shifted at all along the length of its axis). We do not want to say that the Meyer/Mark model is totally impossible (after all, the energy balance for three glucose rings chains is better than in the Meyer/Misch model), but that, notwithstanding all the modifications made, we have not been able to find a configuration in which this model is energetically stable.

Conformation of Crystallite End Groups and Mechanism of Crystalline to Amorphous Zone Transformation

A few important details in Fig. 1 must be pointed out and discussed. The relative positions and values of the hydrogen bonds and the other interactions shown between the B,C rings and the B',C' rings are the ones present in the body of the cellulose I crystal along its length, with the exception of the terminal glucose units of the crystal. The exact representation of the body of the crystal will have the O84, H85 atoms in similar position as the O40, H41 of the previous group to also form a 4.59 kcal/mol intrachain H bond. The O84, H85 are in the positions indicated in Fig. 1 only because four glucose-long chains were taken into consideration and the complete energy minimization for this chain length was carried out. The appearance of the two parallel chains in the body of the crystal is then as shown in Fig. 5.

Another important point explained by conformational analysis is the mechanism, hence the monomer structure, terminating the cellulose I crystallite and starting the amorphous region, and vice versa. The first question that should be asked is: Why does a crystalline region terminate and an amorphous region start? The answer can be found in the interaction between the C39, O40, H41 group of ring B with the O48, H49 group of ring C (Figs. 1, 2, and 3). The O40, H49 H-bond is very strong and imparts rigidity and continuity to the structure, maintaining it in its crystalline form (Fig. 1). However, the minimum of total energy of the ABA'B' rings system, if taken by itself, is not that presented in Fig. 1, but that presented in Fig. 3. In Fig. 3 the O4, H49 H-bond does not exist. However, the sum of the H-bonds values between the A, B, A', and B' rings is -10.45 kcal/mol for the combinations in Fig. 3, while it is only -8.2 kcal/mol for the combinations in Fig. 1. Thus, the combination in Fig. 3, when taken as isolated from

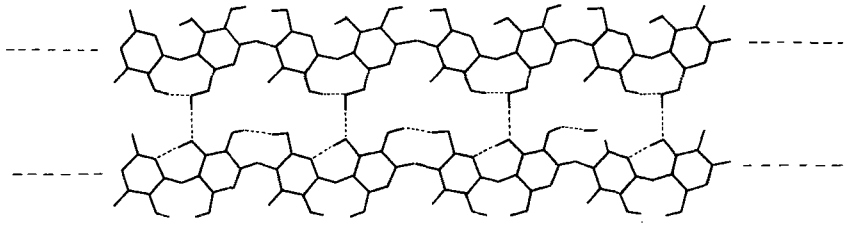


FIG. 5. Schematic representation of the position of the stronger H bonds between two parallel chains of indefinite length in the body of the crystal.

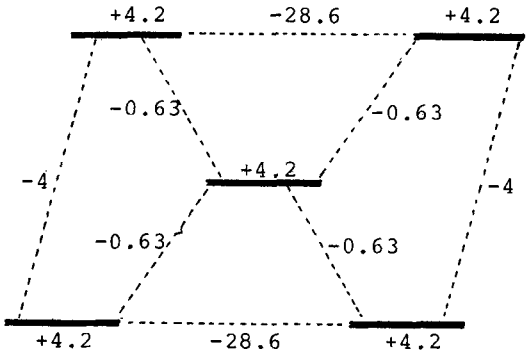
the rest of the molecule, is the more favorable one (by 0.55 kcal/mol per each glucose ring). The combination in Fig. 1 is, however, the most favored overall along the length of the polymer.

This means that rotation around the C36, C39 bond may be quite easy and the conformation in Fig. 1 can, with some ease, transform itself in the situation in Fig. 3, which is more energetically favorable for the isolate ABA'B' rings system. After this has happened, rotation is possible around the C47, O48 bond to the position shown in Fig. 3 with the loss of 0.24 + 0.18 = 0.42 kcal/mol (see figures), and the localized gain to the CDC'C' rings system is 0.87 kcal/mol by H-bonds pattern rearrangements.

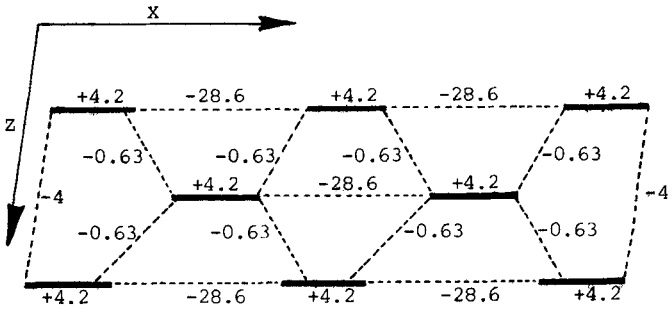
Thus, the conditions for termination of the crystalline region are the rotations of the bonds C36, C39 and C47, O48 (or of one of them) from the positions of Fig. 1 to the positions of Fig. 3. This will not happen often, of course, as the overall energy balance of the chains in the crystal region is more favorable for the H-bonds combinations shown in Fig. 5 and in Fig. 1 (for the BCB'C' rings system), but statistically, it will happen when the "localized" better energy balance conditions shown in Fig. 3 occur. The monomers involved lose the rigidity due to the O40, H49 H-bond which pegs them in the crystalline form, and the possibility of an amorphous region starting are considerably enhanced. Thus the ABA'B' and the CDC'D' rings system shown in Fig. 3 are most probably the conformations presented by the upper and lower terminal rings of the crystalline region before the start of the helicoidal amorphous regions. The actual amorphous region starts with the O6, H7 group in the position shown in both Figs. 1 and 3.

Crystals of More Than Five Chains

It is interesting to discuss the cases of crystalline zones of more than five chains from the point of view of their energy balance. In a five-chain crystal the values of the interactions are as follows:

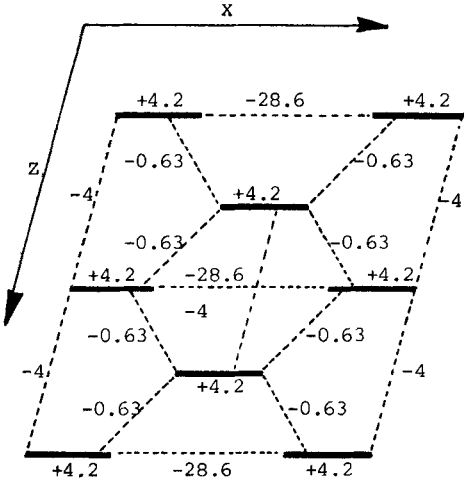


which gives an energy minimum of -46.72 kcal/mol (Table 1) (the +4.2 values are the minimum of energy of the polymers strained into "twofold helix"), thus of -2.336 kcal/mol for each glucose ring. It is easy to see from this that the crystal can grow more easily in one direction than the other. Thus, for a crystal of eight chains, such as I and II:



I

Total minimum = -126.44 kcal/mol
Minimum per each glucose ring = -3.95 kcal/mol



II

Total minimum = -77.24 kcal/mol
Minimum per each glucose ring = -2.41 kcal/mol

This indicates (i) that it is energetically favorable for the crystal to grow in size in any of the two possible directions (x or z) and, (ii) that it is more favorable for the crystal to grow along direction x than along direction Z. This means that the crystalline zones of elementary and subelementary microfibrils are most likely to have a distinctly rectangular section with the longer side of the section along the x-axis. This does not exclude growth of the crystal along the z-axis. It only means that there will be greater growth along the x-axis than the z-axis, and that the xz-section of the crystallite has no (or very little) likelihood to be square-like.

Relative Combination of Amorphous and Crystalline Regions

A last point of interest from this conformational analysis study is the appearance of the combination of amorphous and crystalline regions in cellulose I. The percentage crystallinity of wood cellulose varies between 50% and 60% [10]. At 50% crystallinity this means that if the cellulose crystallites are 200 Å [11], the amorphous region which will contain an equal amount of glucose residues will have a shorter length due to its helix configuration.

Thus, for a 200-Å long crystallite, each chain in the crystal will contain 39 glucose residues. An amorphous chain of 39 glucose residues, if formed of cellobioside monomer of (-49°,-130°) conformation (the helix of which presents a 360° rotation or step every 7.5 monomers = 15 glucose rings), will have a length along the helix axis of approximately 153 Å. In Fig. 4 this helix is shown for a total 360° rotation (15 glucose rings). This means that the amorphous region will present slightly more than $2\frac{1}{2} \times 360°$ steps between two consecutive crystallites. For 60% crystallinity the average number of glucose residues in the amorphous zone will be approximately 31 and the length of the amorphous zone will be approximately 122 Å. These values for lengths will be different if the helix with cellobioside monomer (0°,-161°) conformation is present.

CONCLUSIONS

From the results of this conformational analysis study, in which all the possible interactions between all possible atoms were taken into consideration, it appears that cellulose I is composed of amorphous zones in which the cellulose chains have a helicoidal configuration and crystalline zones. The crystalline zones are better described by the Meyer/Misch and related models in which a central antiparallel chain shift of 2.6 Å along its axis is present in the cryatallographic cell than by models in which the central chain is parallel to the others. The Meyer/Mark model, however, cannot be completely discarded.

When all the interactions are taken into consideration, these latter models are energetically valid for chains of up to three glucose residues each, but are energetically impossible for longer chains due to "bumping" of atoms where no decrease by bond rotation of the unwanted interaction is possible.

The cellobioside structure, rather than cellobiose, is the monomer present throughout cellulose I. No H bonds are present between overimposed chains along the z-axis. The helixes in the amorphous zones can be each formed of a single type of conformation or a mixture of different helixes with each formed by monomers in a single conformation, or of helixes formed by a mixture of monomers in different conformations. The β-glucosidic linkages are at least similar every second one along the chain; two consecutive β-glucosidic linkages are never in the same Φ,Ψ configuration. What was found by this conformational analysis is consistent with IR and x-ray diffraction data on the nature of cellulose.

While in the Meyer/Misch-type model no H bonding of any significance is present between the central chain and the others in the Meyer/Mark model, when this model is allowed, H bonding of the order of 15 kcal/mol (for four glucose chains) is present between the central chains and the others (Frey-Wissling modification) [12].

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