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The Conformation of the Anhydrocellobiose Units in Cellulose I and II

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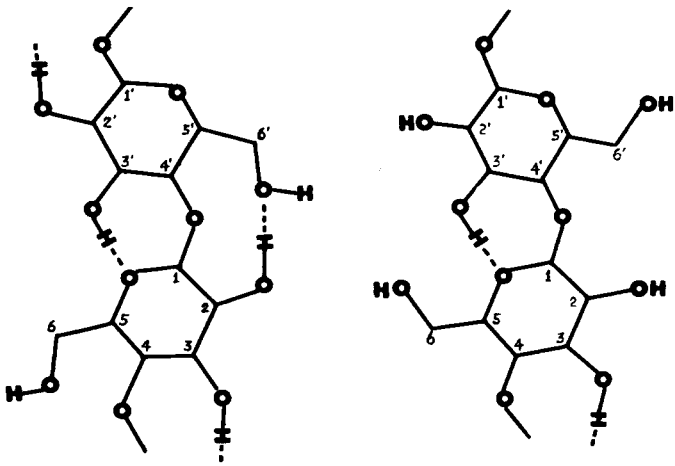
Synopsis

It is postulated from energetic considerations that the anhydrocellobiose unit in cellulose I has a conformation differing from that in cellulose II. Conformation I has two intramolecular hydrogen bonds, while conformation II has only one. This difference arises from a different orientation of the C(6)-hydroxyl group in the two conformations. Their interconversion is shown to be dependent upon the polarity of the medium. The assignment of conformation I to cellulose I and conformation II to cellulose II and the equilibrium between them appear to be consistent with a number of experimental observations reported in the literature.

INTRODUCTION

From x-ray diffraction and polarized infrared spectroscopic studies, two possible conformations of the anhydrocellobiose unit in cellulose have been proposed. These are given below, where the two conformations are distinguished as I and II:



I II

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At the moment, opinion is divided as to whether the units in both cellulose I and cellulose II are in one of these conformations or whether each one occurs in a different conformation (Table I).

TABLE I
Assignment of Conformations by Various Authors

Conformation I	Conformation II	Authors
Cellulose II		Mann and Marrinan[1]
	cellulose I and cellulose II	Marchessault and Liang[2,3]
Cellulose I		Jones[4]
	cellobiose	Jacobson et al.,[5] Brown[6]
Cellotetraose		Poppleton and Mathieson[7]
Cellulose I	cellulose II	this work

It is proposed in this paper that the anhydrocellobiose units in cellulose I have conformation I, while those in cellulose II have conformation II. This conclusion is based on a number of considerations which will be described separately.

RESULTS

Energy Content of Crystal Lattice

In bringing together a number of cellulose chains, free from strain and hydrogen bonds, to form a crystal, a certain amount of energy is used in overcoming various forces and a net reduction in the energy of the system is achieved, which may be termed the crystal lattice energy, E_L. Firstly, there is a reduction in potential energy as work is done by the attractive van der Waal's forces against the repulsive London forces, E_P. Secondly, there is a release of energy E_H owing to the formation of hydrogen bonds. Finally, there is an increase in energy E_S when any bond is forced into a strained configuration. Consequently,

$$-E_L = -E_P - E_H + E_S. \quad (1)$$

This equation should apply to both cellulose I and cellulose II. Any differences in conformation between the two species should be reflected as a difference in one or more of these energy terms:

$$-(E_L^I - E_L^{II}) = -(E_P^I - E_P^{II}) - (E_H^I - E_H^{II}) + (E_S^I - E_S^{II}). \quad (2)$$

From the heats of swelling in alkaline solution and the heats of wetting in water, Okamura[8] and Ranby[9] have concluded that the difference in lattice energies ($E_L^I - E_L^{II}$) is slight, ca. 0.3 kcal/mole of anhydroglucose unit (AGU). Cellulose I is, as one might expect, the less stable form. Similar conclusions have been reached by the author using somewhat different

assumptions and the data on heats of solution and wetting of Fainberg and Mikhailov.[10]

In the infrared spectra of cellulose, after the samples have been exchanged with D_2O to eliminate the OH absorption band of the amorphous material, the main OH stretching peaks of cellulose I are at lower frequencies than those of cellulose II.[11,12] Qualitatively, one might therefore expect that the hydrogen bonds in cellulose I are stronger than those in cellulose II, and in fact Saidaliev and co-workers[13] report the hydrogen bonding energy of cellulose I to be in the order of 1.0 kcal/mole of hydroxyl (3.0 kcal/mole of AGU) greater than that of cellulose II. No correction was made for the differences in crystallinity of the cellulose I and cellulose II samples.

Substituting the above approximate values of lattice and hydrogen bonding energies into eq. (2), we obtain

$$0.3 = -(E_P^I - E_P^{II}) - 3.0 + (E_S^I - E_S^{II}).$$

Since it seems unlikely that the intermolecular spacing in cellulose I and II is sufficiently different to result in $(E_P^I - E_P^{II})$ being a significant quantity, then, as a first approximation, we may assume

$$E_S^I - E_S^{II} \sim 3.3 \text{ kcal/mole of AGU.}$$

The above calculations indicate that the higher hydrogen bonding energy in cellulose I is largely counterbalanced by a greater strain energy, resulting in similar values of lattice energies for both celluloses.

Returning now to the two possible conformations, I and II, their main difference is in the orientation of the C(6)-hydroxyl group which has a *tg* conformation (denotes[14] the C(6)-O(6) bond is *trans* to the C(5)–O(5) bond and *gauche* to the C(4)-C(5) bond) in I, and a *gt* conformation in II. In glucose, the calculated difference in energy between these two conformations is about 1.5 kcal/mole,[15] the energy of the *tg* conformation being higher. (Another possible conformation, with the C(6)-hydroxyl group in *gg* conformation, has an energy content intermediate to the *gt* and *tg* conformations.[15]) In cellulose, this difference in energy between the *gt* and *tg* conformations could be expected to be higher than in glucose because of additional steric interference between the C(6)-hydroxyl in *tg* conformation and the C(2)-hydroxyl of the adjacent anhydroglucose unit. Thus, it seems reasonable to assume from energetic considerations that cellulose I has conformation I and cellulose II has conformation II.

Cellulose III

When either cellulose I or cellulose II is treated with liquid ammonia, cellulose III is formed. Although samples of cellulose III prepared from both cellulose I and cellulose II appear to have identical unit cell dimensions,[16] some differences in the relative intensities of their x-ray diffraction patterns[16] and in infrared absorption spectra[17] have been noted. More-

over, when cellulose III is heated in water, it reverts to the cellulose from which it was formed.[18] This implies that cellulose III has a built-in "memory" of its origin, the nature of this probably being a certain hydrogen bond which persists through this interconversion. Since the transformation of cellulose I to cellulose III involves a significant change in relative positions of the cellulose chains, this important hydrogen bond seems most likely to be an intra- rather than an interchain bond. The present assignment of the different conformations to cellulose I and II does provide a difference in intrachain hydrogen bonding which could persist in liquid ammonia and serve as a "memory unit."

However, in a strong swelling agent such as concentrated aqueous alkali, both the inter- and intrachain hydrogen bonds may be broken. The swelling action of the reagent increases the interchain spacing so that the C(6)-hydroxyl groups could rotate and assume the most stable conformation (*gt*). This would explain why cellulose II only is recovered irrespective of whether the initial sample was cellulose I or cellulose II.

These well-established experimental facts lend support to the assignment of conformation I to cellulose I and conformation II to cellulose II.

Interconversion of Cellulose I and II

When cellulose is in solution, for example in cupriethylenediamine, the C(6)-hydroxyl group has freedom of rotation and an equilibrium mixture of possible conformations should result. The relative amounts of conformations I and II will depend on the equilibrium constant K of the conformation I $\rightleftharpoons$ conformation II conversion, which is related to their energy difference ($\Delta E_{\mathrm{I}\rightleftharpoons\mathrm{II}}$) by the equation

$$\Delta E_{\mathrm{I}\rightleftharpoons\mathrm{II}} = -RT \ln K. \tag{3}$$

In order to calculate this energy difference, both the intrachain hydrogen bonding energies and the hydrogen bonding energies of the remaining hydroxyl groups with the solvent, as well as the strain energy, must be taken into consideration. That is,

$$\Delta E_{\mathrm{I}\rightleftharpoons\mathrm{II}} = -(E_{\mathrm{H}}{}^{II} - E_{\mathrm{H}}{}^{I}) + (E_S{}^{II} - E_S{}^{I}). \tag{4}$$

Since both conformations have one hydroxyl group, OH(3), per anhydroglucose unit, bonded intramolecularly, and one hydroxyl group, OH(6), available for intermolecular bonding, the net difference in hydrogen bonding energy will be mainly dependent upon how the remaining hydroxyl group, OH(2), is bonded. In conformation I, it forms an intramolecular bond, and in conformation II, it is available for intermolecular bonding with the solvent. Therefore,

$$\Delta E_{\mathrm{I}\rightleftharpoons\mathrm{II}} = -(E_{\text{H-inter}} - E_{\text{H-intra}}) + (E_S{}^{II} - E_S{}^{I}). \tag{5}$$

The hydrogen bonding energy in native cotton is reported to be 5.5 kcal/mole of hydroxyl.[13] If we assume that this intramolecular hydrogen bond,

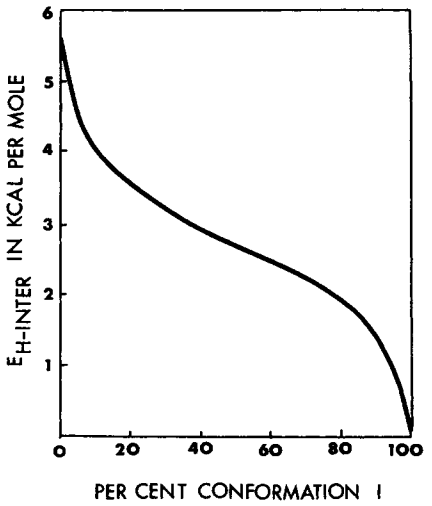

Fig. 1. Calculated equilibrium concentration of conformation I in solvents of different hydrogen bonding energies.

0(2)-H...0(6), has an energy of 6.0 kcal/mole,* and introduce the value of strain energy (3.3 kcal/mole of AUG) derived earlier, then

$$\Delta E_{I \rightleftharpoons II} = -E_{H\text{-inter}} + 2.7. \quad (6)$$

Now the strength of the intermolecular hydrogen bond will depend upon the polarity of the solvent. In a highly polar medium, $E_{H\text{-inter}}$ may approach or even exceed 6.0 kcal/mole of hydroxyl, resulting in $\Delta E_{I \rightleftharpoons II}$ being[1] highly negative and the equilibrium being therefore largely in favor of conformation II. If cellulose were soluble in a nonpolar medium in which intermolecular hydrogen bonds with the solvent would not be formed, $E_{H-inter}$ would be small and $\Delta E_{I \rightleftharpoons II}$ would be largely positive. Conformation I would then be the most stable and therefore the preferred species.

From eqs. (3) and (6), we have

$$E_{H\text{-inter}} = RT \ln K - 2.7 \text{ kcal.} \quad (7)$$

By assuming various values of $E_{H\text{-inter}}$ from 0 to 6 kcal/mole, it is possible to calculate, from the equilibrium constant K, the relative percentages of conformations I and II which would exist in solutions having various values of $E_{H\text{-inter}}$. These calculated values are plotted in Figure 1. Thus, the relative concentrations of the two conformations in solution will depend upon the polarity of the medium. Cellulose is normally regenerated in an aqueous medium in which $E_{H\text{-inter}}$ is high, of the order of 4–5 kcal/mole, and the regenerated cellulose is expected and observed to be largely cellulose II. However, there should be a minor amount of cellulose I in equilib-

* This is per mole of O(2)-H...O(6) bond, but is also equivalent to per mole of AGU, since each anhydroglucose unit has only one of such hydrogen bond.

rium. Indeed, Macchi and co-workers[19,22] have recently identified cellulose I in a cellulose which was precipitated from a very dilute solution in cupriethylenediamine by slow dialysis. They estimate the amount to be less than 10% of the total.

From single-crystal x-ray diffraction studies, the C(6)-hydroxyl group is indicated to be in the *gt* conformation (as in II) in cellobiose,[5,6] but to be in *tg* conformation (as in I) in cellotetraose.[7] No explanation for this difference has been published. However, according to the present theory, the reason for this must be the polarity of the media from which the crystals of cellobiose (from aqueous ethanol, more polar) and cellotetraose (from aqueous acetone, less polar) were grown.

Thus, the assignment of conformation I to cellulose I and conformation II to cellulose II and the equilibrium between the conformations are consistent with the predominance of cellulose II and of minor amounts of cellulose I in regenerated celluloses, and also with the conformations of cellobiose and cellotetraose isolated from aqueous ethanol and aqueous acetone, respectively.

Amorphous Cellulose

From eq. 6, $\Delta E_{\mathrm{I}\rightleftharpoons\mathrm{II}}$ becomes zero at $E_{\text{H-inter}}$ value of 2.7 kcal/mole of hydroxyl, i.e., conformations I and II would have an equal probability of existence. In amorphous cellulose, the interchain hydrogen bonding energy is likely to be somewhat greater than 2.7 kcal/mole (approximately equal to the hydrogen bonding energy in cellulose II minus the heat of crystallization, estimated to be in the order of 4 kcal/mole), and conformation II would therefore be expected to be the major component. The infrared absorption spectra of amorphous cellulose and cellulose II are similar,[21] confirming the likelihood that conformation II predominates in amorphous cellulose. This also implies that native cellulose, which is predominantly cellulose I, is unlikely to crystallize from aqueous solutions or from the amorphous state. Indeed, it has been shown that polymerization and crystallization of cellulose occur simultaneously during biosynthesis.[22,23]

Regenerated Cellulose

Since the relative proportions of conformations I and II are dependent upon the value of $E_{\text{H-inter}}$, the composition and thereby the properties of a regenerated cellulose would be influenced by the solvent system from which the cellulose is regenerated.

Viscose rayons regenerated from cellulose xanthate are low in crystallinity, presumably due to the presence of a "high" proportion of conformation I which hinders the growth of cellulose II crystals. Manjunath and Peacock[24] have reported the recrystallization of cellulose I in viscose rayons. This phenomenon may not be entirely due to the residual cellulose I in the intermediate soda cellulose as they suggested, but due rather to the presence of conformation I in equilibrium.

Cuprammonium rayon has a higher degree of crystallinity than viscose rayons, probably because cuprammonium hydroxide is a better solvent for cellulose. The cellulose regenerated from it would contain a higher proportion of conformation II, leading to more extensive crystallization of cellulose II.

Regenerated celluloses with still higher degrees of crystallinity, e.g., Fortisan, can be produced only by the saponification of cellulose acetate. The replacement of hydroxyl groups with acetoxyl groups prevents the formation of intramolecular hydrogen bonding as in conformation I, and the *tg* conformation becomes highly unfavorable. Therefore, the saponified product should contain a still higher proportion of conformation II.

Thus, the postulated equilibrium between conformation I and conformation II seems to explain the different degrees of crystallinity of regenerated celluloses obtainable by various processes. The postulate may provide a basis for further improvement of regenerated cellulose by controlling this equilibrium.

CONCLUSIONS

In conclusion, the conformation of the anhydrocellobiose units in cellulose I and II and the equilibrium between the conformations as proposed in this paper appear to be consistent with a number of experimental observations reported in the literature. It is to be expected that the present theory may lead to a better understanding of the molecular morphology and properties of celluloses.

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