NOTES

On The Hydrogen Bonds in the Helical Structure Proposed for Cellulose I

INTRODUCTION

The crystal structure of cellulose I is known to comprise two cellobiose residues per unit cell. From the now well-established crystal structure of cellobiose,[1,2] it has been possible to assign a helical form to the cellulose molecule with a pitch of 72 Å (along the *b*-axis) and seven cellobiose residues per turn.[3] Accordingly, two such chains pass through the corner and center of a unit cell in opposite directions, with a relative shift of about 2.6 Å. The possibilities of hydrogen bonds between the oxygen atoms in the proposed structure of cellulose I are discussed in this note.

INTERATOMIC DISTANCES O...O

Before examining the possibility of any pair of oxygen atoms making an H bond, it is necessary to know their exact positions in space. The cylindrical coordinates r, ψ, and Y are most convenient for the purpose. Table I gives these coordinates for the ten oxygen atoms in the first cellobiose residue, and those for the corresponding atoms in the succeeding residues are obtained by merely adding $-2\pi/7$ to ψ and 10.300 to Y. The coordinates for the same oxygen atoms in the reversed chain are computed as follows:

$$r' = r \tag{1}$$

$$\psi' = 2\pi - \psi \tag{2}$$

$$Y' = 72.100 + 2.575 - Y \tag{3}$$

Then, by means of a computer program, the distances equal to or less than 3.000 Å be-

TABLE I
Cylindrical Coordinates of Oxygen Atoms in a Cellobiose Residue

No.	Atom	r, Å	ψ, radians	Y, Å
1	O_1'	1.583	2.0196	0
2	O_2'	3.683	1.5051	1.552
3	O_5'	0.214	2.8504	1.738
4	O_6'	2.698	4.9384	2.415
5	O_3'	3.279	1.5158	4.250
6	O_1=O=O_4'	1.583	0.3785	4.937
7	O_5	2.136	1.1606	6.663
8	O_2	2.814	5.8093	6.674
9	O_6	4.267	1.6802	7.187
10	O_3	2.680	6.0775	9.489
[a]	O_4	1.583	1.1217	10.300

[a] This may be considered as the last atom in the first cellobiose residue or the first atom in the next residue.

tween any two oxygen atoms, one in the normal chain and the other in any of the four adjacent reversed chains, are evaluated.

HYDROGEN BONDS

Since the shape of the cellobiose molecule has been strictly retained in the derivation of the helical structure for cellulose I, the intramolecular H bond between O_5 and O_3' remains unaffected in every cellobiose residue in cellulose as well. Intramolecular hydrogen bond distance is 2.767 Å according to Chu Shirley and co-worker,[2] as against 2.80 Å observed earlier.[1] Besides, 19 intermolecular bonds are likely to occur, as indicated in Table II. Since the position of the hydrogen atom forming the bond cannot be precisely determined by means of x-rays[4] and a hydrogen bond is only believed to exist between two oxygen atoms, if they are separated by a distance of the order of 2.8 Å, for the purposes of the present investigation all O...O distances between 2.700 Å and 2.900 Å are considered most likely to form hydrogen bonds. The mean distance between hydrogen-bonded oxygen atoms for the values quoted in Table II works out to be nearly 2.82 Å. The classifications I, II, III, and IV refer to the quadrant in which the reversed chain carrying the hydrogen-bonded oxygen atom is located with reference to the normal chain and the usual crystallographic a- and c-axes.

TABLE II
Possible Intermolecular H Bonds in Cellulose I

	Identification[a]		Bond distances between normal and reversed chains			
No.	N–R	$O_N..O_R$	I	II	III	IV
1	5–8	O_3'–O_2	—	—	—	2.856
2	6–7	O_1–O_6	—	2.828	—	—
3	9–11	O_6–O_3'	2.900	—	—	—
4	10–10	O_3–O_1	—	—	2.873	—
5	16–18	O_1–O_2	—	—	2.734	—
6	18–21	O_2–O_3'	—	2.818	—	—
7	19–20	O_6–O_1	—	—	—	2.824
8	20–21	O_3–O_3'	—	2.803	—	—
9	22–22	O_2'–O_6'	—	—	2.772	—
10	33–34	O_5'–O_2'	2.812	—	—	—
11	34–35	O_6'–O_4	2.773	—	—	—
12	35–36	O_3'–O_3	—	2.852	—	—
13	36–37	O_1–O_6	—	—	—	2.898
14	44–44	O_6'–O_2'	—	—	—	2.845
15	46–46	O_1–O_3	2.782	—	—	—
16	49–50	O_6–O_1	—	2.897	—	—
17	59–59	O_6–O_5	—	2.781	—	—
18	60–60	O_3–O_1	—	—	—	2.718
19	67–67	O_5–O_6	—	2.780	—	—
Means			2.816	2.822	2.793	2.821

[a] The identification numbers refer to the oxygen atoms after arranging them in the ascending order of Y-coordinates in both the Normal (N) and the Reversed (R) chains.

DISCUSSION

From a perusal of the Table II, it is seen that of the 19 bonds mentioned above, 12 are in the second and the fourth quadrants and only 7 are in the first and the third quadrants.

This clearly indicates a predominance of hydrogen bonds in (101) planes and considerably fewer in (10$\bar{1}$) planes. This result is in good agreement with the observations in the literature[5] that the (101) planes are very strongly hydrogen bonded. Frey-Wyssling[6] also drew a similar inference from the mean distance of the O...O atoms for a structure with central reversed and corner chains with a relative shift of 0.25 *b*-axis, as in the present study, but without a helical shape for the cellulose molecule.

In view of the fewer bonds in the (10$\bar{1}$) planes, it is conceivable therefore that the weakest of the bonds in the (10$\bar{1}$) direction may be the first to break on swelling, for example, in the presence of caustic soda, resulting in a separation of the (101) planes as though they were "sheets."[7] Simultaneously, due to the diminution of bonds between (101) planes, there could be "a rearrangement of cellulose chains," as envisaged by Warwicker and Wright,[7] "in the sheets."

Finally, it is worth mentioning here that although Chü[8] has assigned the conformation I with two intramolecular H bonds to the structure of cellulose I and the conformation II with only one intramolecular H bond to cellulose II, the assumption, implicit in this work, of conformation II for cellulose I is not an obstacle to the clarification of cellulose structure.

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