X-RAY INVESTIGATIONS OF CARBOHYDRATES[1]

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Received October 12, 1939

CONTENTS

I. INTRODUCTION

In considering the results of x-ray investigations of crystals one should distinguish clearly between two cases: (*1*) If the investigated substance is simple and if large well-built crystals of high symmetry are obtainable, the analysis can be carried out using the most modern x-ray methods, interpreted with the aid of structure interference theory. In such a case the diagrams lead, without additional help, to the exact positions of all atoms in the crystal lattice. In the early days of x-ray investigation of crystal structures, W. H. and W. L. Bragg (4) determined the structures of diamond, rock salt, and calcite in this way. More recently, comparatively complicated structures have also been completely worked out. Usually the results of such a thorough investigation are presented in the form of a map showing the electron density throughout the elementary cell. Robertson (43), to whom we owe many of these complete structure determinations, has recently given a survey on this development.

(*2*) Up to the present time, however, only a comparatively small number of crystal structures have been successfully worked out in this way, using solely data from the x-ray measurements. Frequently the low symmetry of the crystals prevents such a straightforward analysis. In other cases

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[1] Presented at the Symposium on X-ray Studies of Substances of High Molecular Weight, held at the Ninety-eighth Meeting of the American Chemical Society in Boston, Massachusetts, September, 1939, under the auspices of the Divisions of Physical and Inorganic Chemistry, Colloid Chemistry, Organic Chemistry, Paint and Varnish Chemistry, and Rubber Chemistry of the American Chemical Society. Because of the unavoidable absence of Dr. Mark, the paper was read by Dr. Charles W. Stillwell.

single crystals of sufficient quality cannot be prepared, or there are so many atoms in the elementary cell that the mathematical difficulty of a direct analysis becomes insurmountable. It is then necessary to carry out the investigation with the aid of other physical or chemical properties of the substance being studied.

First of all, the chemical formula itself, especially in the case of organic materials, may offer certain reliable starting points for the development of a structural picture. Sometimes the optical behavior of the substance—its double refraction and rotatory power—may give additional clues for the investigation. In special cases the hardness and the tensile strength of the investigated material have given valuable additional information.

In such indirect determinations of structure it has proved to be profitable not to confine the investigation to a single substance but to extend it to a whole group of compounds which are structurally closely related. This procedure has been very successfully used by A. Mueller and co-workers (35)[2] in studying long-chain organic compounds and by W. L. Bragg (5)[3] and his collaborators in their extensive studies of the structure of silicates.

In the case of high polymeric substances—especially cellulose—one must also use this second method. It is necessary to try to obtain as much reliable x-ray diffraction information as possible, not only from cellulose in its different native states but also from its derivatives, degradation products, and even from glucose and cellobiose, the fundamental units of cellulose. In addition, it has proved to be important to get as much x-ray evidence as possible on the structures of the lower carbohydrates,—those belonging to the group of tetroses, pentoses, and hexoses. These studies of sugars of low molecular weight have given a sound fundamental basis for the inferences drawn in the field of high polymeric carbohydrates.

The interpretation of the x-ray diagrams has been successfully accomplished only by taking into account all the chemical evidence concerning the structure of organic substances, especially the laws of stereochemistry and the absolute dimensions of the atoms in Ångström units.

This paper gives a short survey of our present knowledge of the structure of all carbohydrates up to native and mercerized cellulose, while the following paper by Dr. Sisson shows how this knowledge can be evaluated in the analysis of orientation and swelling of cellulose samples and how the structure of this material is connected with its technical and biological properties.

[2] For a comprehensive survey see reference 54, pages 135–95.

[3] For a comprehensive survey see reference 54, pages 106–29.

II. INVESTIGATIONS IN THE ERYTHRITOL GROUP

The simplest substance which may be regarded as belonging to the large group of sugars and which has been investigated by x-rays is *inactive* erythritol, $CH_2OH \cdot CHOH \cdot CHOH \cdot CH_2OH$. The investigation showed that the molecule has the form of an open chain with four carbon atoms and that like substituents attached to the middle carbon atoms are *trans* with respect to each other (7, 48).

The symmetry of the single molecule inside the crystal lattice is that of a center of symmetry (C_i). This is interesting, owing to the fact that we have an inactive compound before us which contains two asymmetric carbon atoms. These atoms have the same rotatory power but with inverse sense and hence compensate each other. An inner molecular compensation of the rotatory power can be effected by a plane of symmetry or by a center of symmetry. In the first case it would mean that the molecule itself shows the *cis*-configuration, while the latter indicates that the arrangement inside the molecule points to *trans*.

It was first pointed out by Reis that a center of symmetry is much more probable if one assumes that polar forces of any kind determine the spatial arrangement of the different parts of a large molecule, because a center of symmetry brings groups of equal charge further apart and brings groups of opposite charge nearer to each other. This is just what one would expect to obtain if equal charges repel each other and opposite charges attract.

As far as present evidence goes, large molecules with inner molecular compensation of rotatory power always have a symmetry center; a plane of symmetry has not yet been observed.

Much work has been done on pentaerythritol and its derivatives (15, 21, 26, 28, 36, 38, 52). The first investigations led to the conclusion that the symmetry of this molecule inside the crystal lattice was pyramidal. This would be in definite disagreement with the expectations of stereochemistry, from which one would predict a tetrahedral arrangement of the four equivalent substituents. A very careful examination of the situation, made by many authors, finally showed that the first x-ray investigation was correct but that the crystal class cited in the literature was wrong. A redetermination of the crystal class gave S_4. Together with the x-ray data this leads to a tetrahedral arrangement of the four groups.

To make this quite sure, a number of derivatives, such as pentaerythritol tetrachloride, pentaerythritol tetrabromide, pentaerythritol tetraiodide, pentaerythritol tetranitrate, pentaerythritol tetraacetate, and pentaerythritol tetraformate, have been investigated (6, 11, 24, 51). They crystallize in the tetragonal and rhombic systems. In all cases a complete symmetry analysis of the molecules could be carried out, which showed that all of these molecules show a symmetry in complete agreement with the expectations of stereochemistry. So far, this group of sugars fits exactly into the framework of classical stereochemistry, without providing any surprises.

Another derivative of pentaerythritol which crystallizes in the hexagonal system is dibenzalpentaerythritol. The symmetry analysis of this substance showed that the three valence directions of the carbon atom marked by a cross in figure 1 are in one plane (30). This means a rather strong deformation of the original valence directions, which may be attributed to the presence of the two rings on each side of the central carbon atom. We have before us a molecule of the spirane type, where valence distortions are not unfamiliar.

All these investigations lead to the conclusion that the atomic diameters characteristic of the carbon and oxygen atoms are strictly constant in carbohydrate structures, though there may be valence angle distortions producing considerable deviations from the normal tetrahedral configuration.

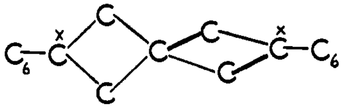


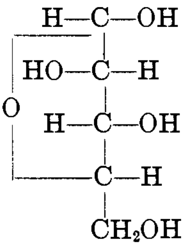
FIG. 1. Structure of dibenzalpentaerythritol

III. SUGARS WITH FIVE, SIX, AND MORE CARBON ATOMS

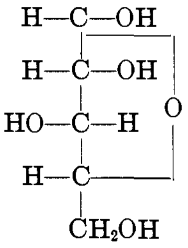
Molecules of this type may be regarded as especially interesting and important, owing to the fact that *β-d*-glucose, the elementary chemical unit of cellulose, belongs to this group. Two possible arrangements have to be kept in mind for these molecules,—the open-chain form and the closed-ring form. Both have been found during the investigation of well-crystallized low molecular substances, in which the most advanced x-ray technic has been utilized.

The two isomeric alcohols dulcitol and mannitol, having the formula $C_6H_{14}O_6$, have been carefully investigated. Dulcitol crystals are monoclinic; those of mannitol are rhombic. In both cases the elementary cell contains four asymmetric molecules. From intensity measurements it has been shown that each of these molecules has the form of a straight zigzag chain, the diameter of the carbon atom being 1.5 Å. This is in complete agreement with the conclusions reached from the investigation of long-chain paraffins and their derivatives. It shows that the presence of the hydroxyl groups does not seriously affect the shape of the carbon skeleton (29).

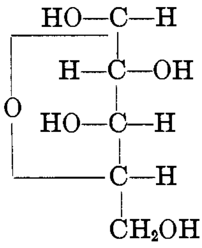
Another set of isomeric compounds having five carbon atoms which has been thoroughly investigated includes *α-l*-xylose, *α-d*-xylose, and *β-l*-arabinose. These have the following formulas:



α-l-xylose



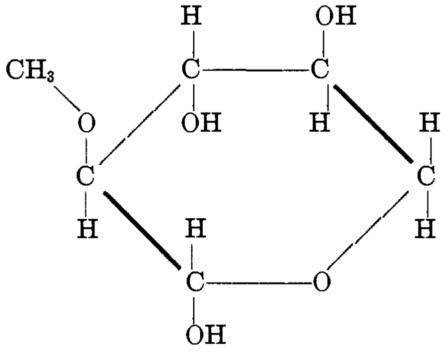
α-d-xylose



β-l-arabinose

All three form rhombic crystals with four molecules in the elementary cell. The molecules are asymmetric. From the intensity distribution of the scattered radiation it has been deduced that in each case the molecule is a ring with five links, having approximately the following dimensions: 6.5, 5.6, and 4.8 Å. This shows that we have to regard such sugar molecules as being elliptic plates, the thickness of which is slightly less (8, 30) than the smaller diameter. As will be mentioned later, this conception agrees completely with the chemical evidence on the structures of simple sugars (2, 8).

In addition to the xyloses, the *α*- and *β*-methylxylosides, having the formulas



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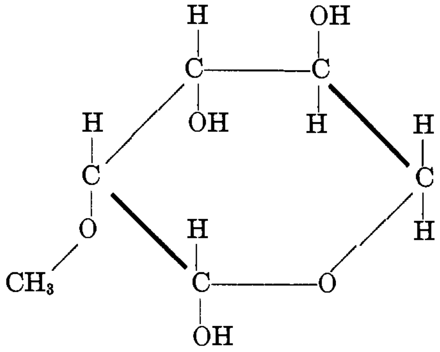

have been studied. Both form perfect monoclinic crystals, well-suited to x-ray investigation. In each case the molecule has the form of a ring with six links, containing five carbon atoms and one oxygen atom. The five carbon atoms lie very closely in one plane, while the oxygen atom which closes the ring lies about 0.8 Å. above this plane. This shows again that in building up structures of sugars we may rely firmly on the general rules concerning the diameters of carbon and oxygen atoms, but we have to consider certain deviations of the valence directions, a fact which will be discussed more in detail later.

After these preliminary remarks concerning sugars of low molecular weight, we turn now to the fundamental unit of cellulose, namely glucose, and its derivatives.

β-d-Glucose crystallizes in the rhombic system. The elementary cell contains four molecules. Consideration of the x-ray diagrams shows that the molecule has the shape of a ring with six links, being built up of five carbon atoms and one oxygen atom. No evidence regarding details of the ring is available (16).

An interesting investigation was carried out by Nowakowsky (39) with three esters of glucose: namely, *α*-acetylglucose, *α*-laurylglucose, and *α*-palmitylglucose. These compounds crystallize in needles which, bundled together, give more or less distinct fiber diagrams. This fact made it possible to determine the fiber period; it was found to be practically the same in all three cases, being 5.39, 5.36, and 5.38 Å., respectively. On the other hand, the edge lengths of the unit cells perpendicular to the fiber axis were entirely different and increased from the acetate over the laurate to the palmitate. This shows that in these structures the glucose ring runs parallel to the needle axis, as shown in figure 2, and that the substituent is extended perpendicular to this direction. The period of about 5.4 Å. coincides with the length of one diameter of the xylose ring mentioned above. It seems that the ring diameter between carbon atoms 1 and 4 corresponds to this distance. It will later be shown that the distance between the center of gravity of these two atoms is only about 3 Å. but the substituents allotted to them increase the dimensions of the ring in this direction to about 5.4 to 5.6 Å.

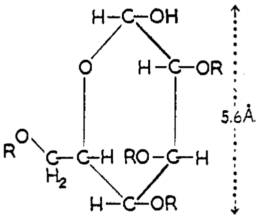

FIG. 2. Formula of the tetra esters of glucose

The fact that the substituting groups lie perpendicular to the glucose ring is significant and has been confirmed in the investigation of the different esters of cellulose.

One step closer to cellulose is *β-d*-cellobiose, the structure of which is shown in figure 3. This substance crystallizes in the monoclinic system.

The elementary cell contains two molecules. Owing to the existence of small but well-formed crystals, a comparatively careful investigation has been possible. It points to the fact that the cellobiose molecule is composed of two rings which are practically coplanar. They are held together by an oxygen atom which is about 0.8 Å. from the plane of the rings. This structure is closely related to that of the cellobiose residue in cellulose chains (16).

The transition from the molecular lattice of cellobiose to the main-valence chain lattice of cellulose is of great interest, and its careful experimental investigation would be very welcome. Unfortunately, cellobiose and its derivatives are the last sugars in the cellulose family which can be obtained in single crystals. The higher representatives of the cellodextrins are available only as crystal powders, a fact which prevents their complete x-ray investigation. Nevertheless, considerable work has been concentrated on them (9, 50, 53). First of all, it may be emphasized that the investigations of Willstätter, Zechmeister, and Toth have shown without a doubt that three well-defined sugars can be prepared: namely, cellotriose, cellotetrose, and cellohexose. They were separated by hydrolyzing cotton and fractionating the product yielded thereby. These sugars can be methylated and acetylated without destroying their structure.

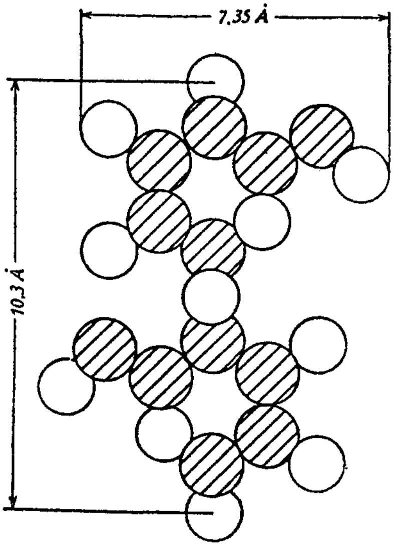

FIG. 3. Structure of β-*d*-cellobiose; hydrogen atoms are omitted

All chemical and physical investigations have led to the conviction that they are homogeneous, pure substances with three, four, and six glucose rings in the chain.

X-ray diagrams of the sugars themselves have furnished only powder diagrams which could not be interpreted. An investigation of the acetates, however, has yielded some results. From an x-ray study of glucose pentaacetate, cellobiose octaacetate, and cellotriose undecaacetate, the dimensions of the three elementary cells of these substances have been deduced (25, 55). The figures are given in table 1. They show that the first axis of the elementary cell is practically the same in all these three compounds. This distance must apparently be perpendicular to the chain direction and hence perpendicular to the glucose ring, as shown in figure 4. The second axis of the elementary cell is also practically constant; it is apparently related to one ring diameter perpendicular to the chain of cellobiose and cellotriose. This ring diameter would normally be equal to a distance of about 6.3 Å. Here, however, it is more than double this value, owing to the fact that all hydroxyl groups of the three sugars have been substituted with acetic acid. The third axis of the elementary cell shows an increase from glucose to cellobiose to cellotriose, the increment being about 18 Å. Apparently this is the direction in which the chain is developing, as roughly sketched in figure 4.

TABLE 1

Dimensions of the elementary cells of three acetates

SUBSTANCE	NUMBER OF MOLECULES IN THE ELEMENTARY CELL	IDENTITY PERIODS OF THE ELEMENTARY CELL		
		a	*b*	*c*
		Å.	*Å.*	*Å.*
Glucose pentaacetate...........	4	5.65	14.9	24
Cellobiose octaacetate..........	4	5.7	15	42
Cellotriose undecaacetate......	4	5.7	15	60

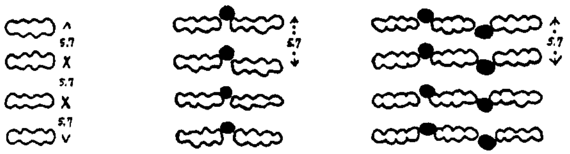

FIG. 4. Comparison of the structures of the acetates of glucose, cellobiose, and cellotriose

These three acetates crystallize in needles. From a bundle of the needles one obtains comparatively good fiber diagrams, from which the identity period along the needle axis is calculated to be 5.72 Å. in the case of glucose and 5.59 Å. in the case of cellobiose. These distances coincide, within experimental error, with the identity periods in the *a* direction (table 1), indicating that the needle axis is perpendicular to the direction in which the chains develop and perpendicular to the plane of the glucose ring. This is in good agreement with our knowledge of the structure of other organic crystals, e.g., fatty acids, naphthalene, anthracene, etc., showing again that as long as normal molecular lattices are prevailing, the direction of the largest development of the crystals (in this case the needle axis) is perpendicular to the direction of the largest development of the molecule (in this case the chain axis). The same conclusion has been reached in studies of fatty acids; in these compounds the molecular chains lie perpendicular to the plane of the flat crystal sheets.

In compounds containing a main-valence lattice, on the other hand, the chain axes of the molecules are parallel to the fiber axis of the sample.

Although there is no visible similarity between the diagram of cellulose on one hand and that of cellobiose and glucose on the other, the investigation of a mixture of higher cellodextrins which had been produced by hydrolyzing cotton showed their x-ray diagrams to be completely analogous to those of mercerized cellulose. It is easy to see that, if one has long chains bundled together into a lattice-like arrangement, the ends of the chains will be distributed irregularly all over the crystallized areas and hence will not contribute anything to the interference phenomenon. Whether such a structure is composed of long or short chains will not affect the character of the x-ray reflections in any respect. However, as soon as all the chains are of identical length a normal molecular lattice is built up and the chain ends are all concentrated in certain lattice planes. As a consequence, new x-ray reflections appear and a different diagram is observed. (Figure 5 shows diagrammatically the difference between a substance with chains of equal length forming a normal molecular lattice, in which the chains are perpendicular to the fiber axis, and a material which has a main-valence chain lattice, in which the chains run parallel to the fiber.)

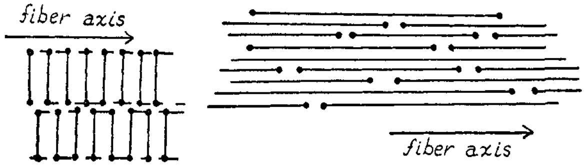

FIG. 5. a, molecular lattice, with chains of identical length; b, chain lattice, with molecules of different length

Summarizing we may say: All x-ray investigations on well crystallizing carbohydrates show that in the lattices of these substances the atomic distance rules are maintained, although there may be considerable distortions of the directions of the valence forces. All carbohydrates and their derivatives which have been investigated have normal molecular lattices. The lower sugars, including glucose and cellobiose, have ring structures. The dimensions of the rings have been determined. The x-ray study of cellotriose, cellotetrose, cellohexose, and some other dextrins has led to a reasonable picture for the transition from a normal molecular lattice to a structure built up of chains of irregular length which are held together by intermolecular forces.

IV. X-RAY INVESTIGATIONS OF CELLULOSE

The fact that cellulose gives a definite x-ray diagram was first detected in 1913 by Nishikawa and Ono (37). In 1918 Scherrer (46) investigated cellulose with x-rays and reported a fiber diagram in 1920 (47). It was clear that at that time no attempt to evaluate these diagrams could be successful, because our general knowledge of crystal structure and x-ray scattering was much too incomplete. As a matter of fact, Nishikawa, Ono, and Scherrer confined themselves to the statement that natural fibers show a very interesting x-ray scattering effect, indicating the presence of small oriented crystals.

Beginning in 1919, this problem was attacked experimentally by Herzog and Jancke (17). These workers confirmed Scherrer's first statement and started a series of systematic investigations with different kinds of cellulose fibers. They discovered a new type of x-ray diagram, consisting of a group of symmetrically distributed points or stripes. This they called a "fiber diagram." It was first interpreted theoretically by Polanyi (40), who was later aided in his work by Weissenberg (42). In this way an important experimental and theoretical advance was made, which encouraged the drawing of some conclusions concerning the structure of the investigated material from the new experimental evidence. Without chemical help reliable deductions were clearly impossible; the assumption was therefore made that cellulose is built up from glucose residues and that cellobiose exists to a certain extent in the lattice.

These considerations did not lead to entirely definite results, but offered three different possibilities for the structure of cellulose. It is very interesting and certainly should be clearly emphasized that one of the structures proposed by Herzog (18) and Polanyi (41) was a continuous chain of glucose residues very similar to the solution which is regarded today as being the best. It is quite evident that at that early date (1921) it was impossible to choose definitely between the different models deduced from the x-ray studies without the aid of arguments coming from another type of investigation.

It is interesting to note that in the same year, 1921, such an argument was in fact brought forward by Freudenberg as a result of chemical experiments with methylcellulose (10). He came to the conclusion that, according to the results of methylation and degradation, cellulose should be composed of long chain-like molecules.

In this way both organochemical and physicochemical measurements pointed in the same direction but no successful combination of these results was attempted at that time. This may be explained by the fact that the deductions from the x-ray measurements were published very cautiously and tentatively, without emphasizing the possibility of long chain molecules and by the fact that at the same time other chemical investigations seemed to point more in the direction of small ring-shaped units in the cellulose lattice.

It was necessary that the chemical situation undergo a more complete clarification and that our general knowledge regarding the structure of organic crystals be increased. Progress was soon made in both these directions. Of special importance was Haworth's definite establishment of a structural formula for the glucose residue. It was shown to be a ring built up from five carbon atoms and one oxygen atom (13, 14). At the same time cellobiose was shown to be built up of two glucose units linked together by a 1,4-glucosidic main-valence bond.

As a result of many x-ray investigations of other organic substances, the atomic diameters of the carbon and oxygen atoms could be determined. In particular, W. H. and W. L. Bragg proposed that in all organic lattices the carbon atom has a diameter of about 1.5 Å. and the oxygen atom of about 1.4 Å. If one combines these values with the ideas of stereochemistry it is possible to build up molecular models which not only show diagrammatically the shape of the particle but which give a true picture of the dimensions and the form of a given organic molecule. This was successfully carried out in several cases, as with naphthalene, anthracene, fatty acids, etc.

It was obvious that application of the recently acquired knowledge of sugar chemistry (Haworth), together with the new information about molecular dimensions (W. L. Bragg), to the cellulose problem as left in 1921 (Freudenberg, Herzog, Polanyi) would have a good chance of leading to a successful solution of the problem of cellulose structure.

Such an attempt was, in fact, made by Sponsler and Dore in 1926 (49). These authors gave the first spatial molecular model of cellulose based upon the possibility of infinitely long glucose chains. Unfortunately, they selected a type of linkage which did not agree with the chemical evidence. However, as shown by Meyer and Mark (32), the original model of Sponsler and Dore could easily be changed so as to make it satisfy all physical and chemical requirements.

This finished the first step in the development of a suitable structural formula for cellulose and established the fundamental principle of its structure. The crystallized regions are composed of long main-valence chains of glucose residues linked together by 1,4-glucosidic bonds. This statement has never met any experimental opposition but, on the contrary, may be regarded as being supported by all the evidence available up to the present time.

After this achievement a second period of cellulose structure work in the x-ray field started. It was evident that the models proposed by Polanyi, Sponsler and Dore, and Meyer and Mark had to be regarded as first approximations. The next task was to work out as accurately as possible the positions of all the atoms in the elementary cell of native cellulose.

This elementary cell had first been assumed to be rhombic (Polanyi; Sponsler and Dore). Later a monoclinic cell was proposed (Meyer and Mark), and another monoclinic cell has been considered by Sauter (45). From the experimental point of view, the most important factor is the use of highly oriented preparations which not only show fiber structure but which are also oriented in respect to the other two crystallographic axes. Using the most highly oriented material available and the technique most appropriate for the purpose, Gross and Clark (12) have obtained what may be regarded as a final solution of this important question. They conclude that a monoclinic cell with the dimensions a = 8.35 Å., b = 10.3 Å., c = 7.95 Å., and $\beta = 84°$ is in best agreement with all experimental evidence to date.

The space group of cellulose can also be regarded as definitely settled; it is C_2^2.

In this group there are two sets of twofold screw axes parallel to the b-axis. These are independent of each other. The two parallel sets of glucose chains which run through the elementary cell can therefore be disposed in two different ways: (*a*) they may be oriented in the same direction, or (*b*) they may be oriented in opposite directions. To choose between these possibilities, a very careful study of the intensity distribution in the x-ray diagrams is necessary. This was made by Mark and v. Susich (27), and their work was extended by Andress (1). These authors showed that the assumption that all the chains are oriented similarly was in satisfactory agreement with the experimental evidence then available. Later, new experiments showed that there was more probability for arrangement *b*, with the two sets of main-valence chains running in opposite directions. In conformity with this conclusion, Meyer and Misch (34) proposed for cellulose the model represented in figures 6, 7, 8, and 9.

It seems to be reasonable to discuss this model briefly and to consider to what extent it meets our present requirements from chemical and physical points of view.

(*a*) *Optical behavior.* This model explains the double refraction and the rotatory power of cellulose in a qualitative way, owing to the fact that its anisotropy is that of a uniaxial crystal.

(*b*) *Mechanical behavior.* The fact that the main-valence chains are parallel to the fiber axis explains the high tensile strength in this direction and the smaller strength perpendicular to it. The modulus of elasticity of cellulose, as determined by Meyer and Lotmar (31), is in good agreement with this model. The thermal expansion, which has been measured by Hengstenberg, agrees equally well (33).

(*c*) *X-ray behavior.* All observed x-ray interference spots can be completely explained, in respect to their position, intensity, and width. No exception has yet been found.

(*d*) *Swelling.* The anisotropy in swelling confirms the main-valence chain model of cellulose and has recently led to important progress concerning the process of mechanical deformation.

The question of intramicellar swelling leads to the problem of the nature of the forces by which the lattice of the cellulose is kept together. It is well known that cellulose (as well as other high molecular compounds) has the peculiar quality of reacting with different chemical substances without losing its lattice structure. This topochemical reactivity must have some connection with the lattice structure and the forces which keep this structure together.

From an examination of figures 6 to 9 we can derive the following conclusions: In the direction of the *b*-axis the main-valence chains are kept together by 1,4-glucosidic bonds, the strength of which may be regarded as being of the order of magnitude of 50,000 calories per mole (see especially figures 8 and 9).

Considering the forces which hold the structure together in the other two directions we first concentrate our attention on figure 7. This shows that along the *a*-axis the glucose rings are in rather close proximity to each other. As a matter of fact, the centers of the two nearest oxygen atoms of two such groups approach each other to about 2.5 Å. It is well known from our general knowledge of organic crystal structures that two oxygen atoms belonging to different molecules should not approach nearer than 3.0 Å. if there are only van der Waals' forces acting between them. The two oxygen atoms of the glucose residues in the cellulose lattice are much closer. This arouses the suspicion that stronger forces are acting between them in the lattice of cellulose. It seems to be reasonable to assume that a hydrogen bond is established between these two oxygen atoms. According to Huggins (20) this would correspond to a strength of about 15,000 calories

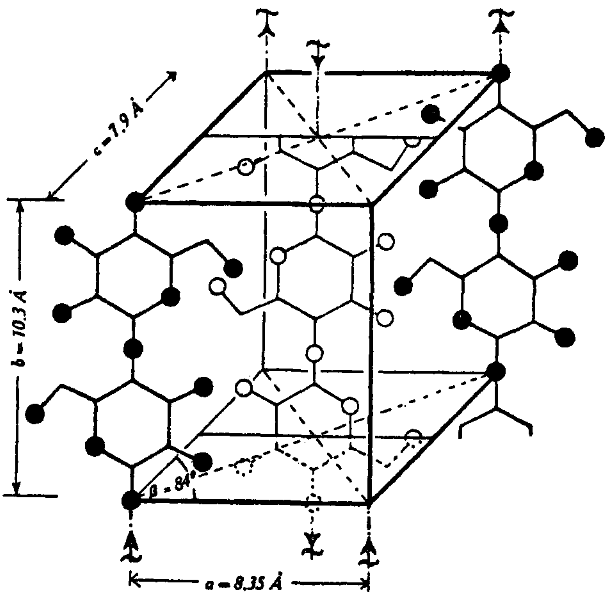

FIG. 6. Representation of the monoclinic elementary cell of cellulose (according to Meyer and Misch). Three chains of glucose units are shown, running parallel to the *b*-axis (fiber axis).

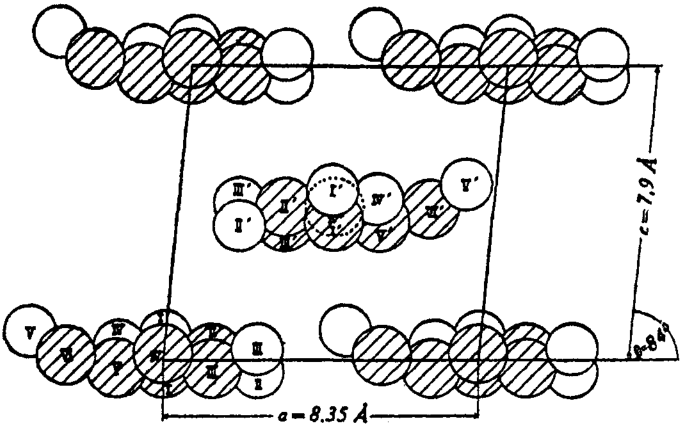

FIG. 7. View of the elementary cell of cellulose along the main-valence chains (*b*-axis). One sees the projections of the glucose groups on the *a*-*c* plane. Hydrogen atoms are omitted.

per mole. This would explain the comparatively tight packing in the *a*-*b* plane in the direction of the *a*-axis and would, at the same time, offer an explanation for the fact that more highly oriented structures can be

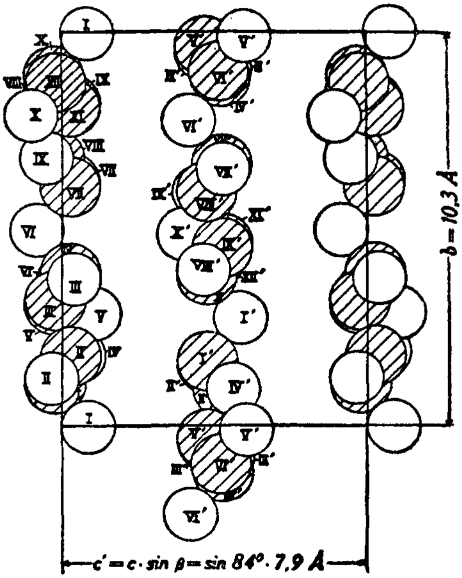

FIG. 8. View of the elementary cell of cellulose along the *a*-axis. One sees the chains from the side and observes that rather large spaces are between them. Hydrogen atoms are omitted.

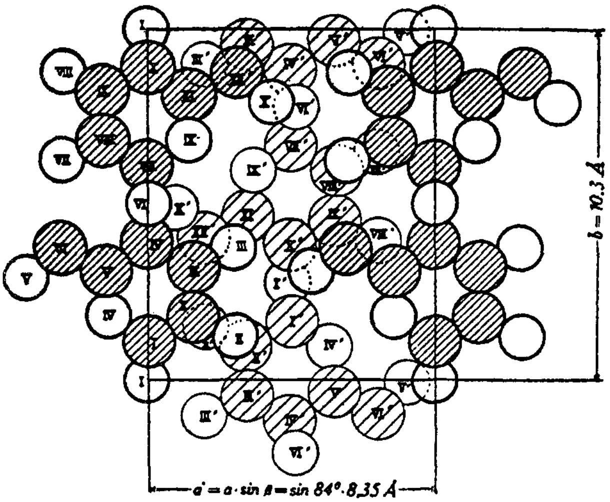

FIG. 9. View of the elementary cell of cellulose along the *c*-axis. One looks at the main-valence chains from their broad side. Hydrogen atoms are omitted.

obtained by mechanical treatment. Such an arrangement would be, at the same time, in agreement with the expectations of Bernal (3), starting from the discussion of the structure of ice.

We finally ask what forces hold together the lattice along the *c*-axis. According to figures 7 and 8, the nearest distance of atomic centers in this direction is about 3.1 Å. (This is the distance between a carbon atom of one chain and an oxygen atom of the other. The nearest distance between hydroxyls is 3.8 Å.) This corresponds closely to the distance to be expected if van der Waals' forces hold the lattice together in this direction. Such forces correspond to an energy of about 8000 calories per mole.

From this point of view, the lattice of cellulose may be regarded as a combination of a *chain lattice* and a *layer lattice.* The strongest forces act along the *b*-axis, but the forces along the *a*-axis are also comparatively large. There are main-valence chains along the *b*-axis and hydrogen bond nets in the *a-b* plane. Perpendicular to this plane, however, weak forces are acting and the spacing between these planes is large. This permits chemical reagents to penetrate easily into the lattice and to react with the hydroxyl groups of cellulose.

It would be premature to propose further and more detailed consequences of this viewpoint, but it might not be too far-reaching to say that the fact that cellulose is held together by three different kinds of forces in three different directions of space is responsible for the interesting and important properties which this substance exhibits during its reactions in the solid state.

V. X-RAY INVESTIGATIONS OF STARCH

Although no conclusive quantitative results could be derived from x-ray measurements on starch, this short report on x-ray investigations of carbohydrates would be incomplete if a few words and some literature references were not added concerning the structure of starch.

Starch has frequently been investigated with x-rays, but the results have not been very encouraging. One always obtains either a diagram which can only be called an amorphous halo or a few interference rings showing that there is some crystalline or micellar structure prevailing in the investigated sample.

However no attempt to evaluate these diagrams quantitatively has been successful hitherto, the main reason being that in spite of all efforts no oriented sample could be obtained which would allow a reliable calculation of the elementary cell. One is confined to measuring and evaluating a few diffused interference rings without having any other indication regarding the symmetry and dimensions of the lattice.

In the last few years systematic experiments have been carried out by Katz (22, 23, 44) concerning the changes which the x-ray diagram of starch undergoes if the sample is treated in different ways. He distinguishes between a crystallized and an amorphous diagram and shows that they can be converted into each other under certain conditions.

The only result which can be derived from the x-ray investigation of starch is a negative one. The impossibility of getting fiber diagrams, even after extreme mechanical treatment of the samples, indicates that apparently there are no long unbranched chain molecules present in starch. In this respect the x-ray investigations point in the same direction which has been furnished with very much stronger arguments in the last few years by chemical considerations.

The methylation and subsequent degradation of starch has led Hirst (19) to the conclusion that particles of starch consist of a highly branched chain system, in which the average individual length of the branches corresponds to a molecular weight of about 4500. X-ray measurements to date cannot supply any quantitative additional knowledge to this picture, but it can be stated that they are not contrary to it.

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