standing deposited 147 mg. (8%) of brick-red material, m. p. 177–180.5°. Recrystallization from methanol with the aid of charcoal gave 109 mg. light yellow needles, m. p. 180.5–181.5° whose mixed m. p. with an authentic sample of 2-methoxy-1,4-naphthoquinone of m. p. 181.2–182° was 180.5–181.7°.

Oxidation of VII.—A suspension of 40 mg. of VII, 200 mg. of silver oxide and some anhydrous magnesium sulfate in dioxane was warmed to facilitate solution. A brilliant deep magenta-purple was produced almost at once. After shaking for thirty minutes the suspension was heated to boiling and filtered. The deep magenta filtrate was concentrated to a small volume and set aside. An amorphous dark precipitate separated which was collected and washed with cold dioxane, yield 17 mg., m. p. 260–262°. When held above its melting point for a few minutes, the beautiful deep red melt fades to a yellow-brown. The material when dry possesses a deep greenish-bronze surface reflex. Its magenta-purple solution in dioxane on standing fades to a brown solution. A small amount in dioxane on treatment with dilute aqueous alkali fades through a tan to a light green-yellow solution. It dissolves in concentrated sulfuric acid with a deep green-black color. For analysis, the material was dried at 78° and 10^{-4} mm. for one hour.

Anal. Calcd. for $C_{32}H_{16}O_4$: C 76.73; H, 4.68; 2 OCH_3, 18.02. Found: C, 76.26; H, 4.79; OCH_3, 16.33.

Summary

1. Condensation reactions between 1,1-bis-(*p*-dimethylaminophenyl)-ethylene and α-naphthoquinone, β-naphthoquinone, naphthazarin, and naphthazarin diacetate as well as a similar condensation between 1,1-dianisylethylene and α-naphthoquinone have been described.

2. These condensations are those expected from a consideration of the electron donating capacity of the ethylene and the electron accepting capacity of the quinones involved. Present evidence indicates that the condensation is not catalyzed by acids or bases.

3. A discussion of certain points of interest in connection with the color and basicity of the condensation products is given.

BRYN MAWR, PENNSYLVANIA
RECEIVED SEPTEMBER 7, 1943

[CONTRIBUTION FROM THE IOWA AGRICULTURAL EXPERIMENT STATION]

The Structure of the "B" Modification of Starch from Film and Fiber Diffraction Diagrams[1]

BY R. E. RUNDLE, LESTER DAASCH AND DEXTER FRENCH

Introduction.—Of the unit cells proposed for the "A" (cereal) and "B" (tuber) modifications of a starch, those of Bear and French[2] are supported by the best diffraction data, and are altogether the most reasonable thus far proposed. Yet even their data, as they point out, were necessarily confined to those available from powder diagrams. Such data are not wholly adequate for the support of large unit cells for crystals of low symmetry, so that their results are left open to question.

Though the desirability of obtaining film and fiber diffraction diagrams for starch is obvious, attempts to prepare suitable films and fibers have been unsuccessful because whole starch was employed. The chief constituent of whole starch[3] is a highly branched component, amylopectin in Meyer's nomenclature,[4] where interruptions in the starch chains occur approximately every 20 glucose residues. The resulting unbranched portions of the chains are too short to produce satisfactory films or fibers.

Fortunately, it is now possible to isolate the unbranched (amylose) component present in most starches.[5] The unbranched chains in this component are probably in excess of 200 glucose units long,[6] and upon suitable treatment form both films and fibers. The production of these films and fibers and mention of the importance of their optical properties have been reported previously.[7] Recently Whistler and Hilbert have confirmed this property of amylose, finding that the acetate of this component of starch forms films with properties to be expected only for films of long, linear molecules.[8]

The diffraction diagrams from amylose retrograded at room temperature are quite like those from tuber starch granules and retrograded whole starch, so that the amylose component of starch can be used for the study of the crystalline portions of whole starch.

Preparation of the Samples.—A hot solution containing about 5% amylose is allowed to evaporate slowly, and the surface skins are removed carefully from time to time. The skins are allowed to dry on an aluminum sheet or ferrotype. Dry films thus prepared are only a few hundredths of a millimeter thick. The thicker films usually tend to curl or become distorted, but this can be overcome to some extent by doubling them while they are still wet.

Fibers which produce a "B" diffraction diagram are very difficult to prepare, and none that we have produced is of particularly high quality. The chief difficulty lies in the fact that plasticizers which can be used to aid in stretching produce fibers corresponding to new crystalline modifications of starch. These, of course, are of interest in

(1) Journal Paper No. J-1129 of the Iowa Agricultural Experiment Station, Ames, Iowa. Project 639. Supported in part by a grant from the Corn Industries Research Foundation.

(2) R. S. Bear and D. French, THIS JOURNAL, **63**, 2298 (1941).

(3) F. Bates, D. French and R. Rundle, *ibid.*, **65**, 142 (1943).

(4) K. Meyer, "Advances in Colloid Science," Interscience Publishers, Inc., New York, N. Y., 1942, pp. 142–162.

(5) T. J. Schoch, THIS JOURNAL, **64**, 2957 (1942). For an analysis of the component isolated by Schoch, and a discussion of structure, see (3).

(6) J. Foster and R. Hixon, *ibid.*, **65**, 618 (1943).

(7) R. Rundle and D. French, *ibid.*, **65**, 559 (1943).

(8) R. Whistler and G. Hilbert, "The Film-Forming Properties of the Acetates of Fractionated Starch," read before the Division of Sugar Chemistry, Am. Chem. Soc. convention, Detroit, 1943.

themselves, and are reported in another paper.[9] Without plasticizers, amylose films are brittle and cannot be stretched enough to produce a high degree of orientation. So far we have been able to use only water with the starch if a "B" diffraction diagram is to be obtained.

The following method is effective for the preparation of "B" type fibers. A 3% amylose solution is allowed to evaporate near the boiling point until it becomes quite viscous. At this point a wire frame with one side movable is dipped into the solution, and a film is prepared by extending the area of the film as much as possible without breaking the film. The film is then allowed to dry in the frame. Though very thin, the dry film can be removed from the frame and narrow strips cut from it. The strips can be stretched when moistened with water. Those which have been extended 50% or more show definite fiber orientation by X-ray diffraction. Similar techniques can be used with plasticizers added to the solution. Better orientation can then be produced in the fibers, but the plasticizers thus far employed alter the diffraction diagram of the amylose.[9]

Optical Properties.—The amylose films are highly birefringent, both wet and dry, and in convergent polarized light they show a typically uniaxial, optically negative, interference pattern. Fibers produced from the strips of amylose film retard light most if its electric vector is along the fiber axis. Optically the fibers are quite like cellulose and protein fibers in this respect. It is now certain that in the "B" modification the direction of greatest polarizability of the starch molecule is along its greatest length.[10]

X-Ray Diffraction Diagrams.—Diffraction diagrams of both films and fibers were made using Cu K radiation, Ni filtered. The amylose films were mounted with the normal to the film at right angles to the X-ray beam. Patterns of the fibers were made with the fiber axis normal to the beam. The patterns are not so sharp as those obtained from wet starch granules, probably because the samples were too dry to produce the best diffraction patterns. Both films and fibers become rather weak and gummy and hard to handle when moist, and wet fibers could not be kept under tension.

Indexing of the Diffraction Diagrams.—The layer line separation of the fiber diagram gives a fiber spacing of about 10.6 Å. This corresponds to none of the dimensions of the unit suggested by Bear and French.[2] Indeed the fiber spacing is not at all explained by any previous cells suggested for starch, yet the maxima are clearly those of the "B" modification of starch (Table I). In indexing the fiber and film patterns, and in the determination of the unit cell for the "B" modification, reference was made to the powder patterns of "B" starch, since on it diffuse maxima could be located with much greater accuracy than on the oriented patterns.

In Table I, column 3, values of $(2 \sin \theta/\lambda)^2 \times 10^4$ were obtained by measurement of patterns from wet potato starch, taken according to the technique suggested by Bear and French.[2] Cu $K\alpha$ radiation was used. At angles greater than those which they list $[(2 \sin \theta/\lambda)^2 \times 10^4 = 860]$ the maxima are rather diffuse and many are quite weak in intensity. It is probable, therefore, that not all maxima have been observed to the largest spacing given in Table I. However, the more intense maxima in this region can be measured with considerable accuracy on good powder diagrams and are included in the table.

Examination of the equatorial reflections of the fiber pattern indicated that they could be indexed by the equation

$$\sin^2 \theta_{(h0l)} = 0.00230h^2 + 0.00705l^2 \qquad (1)$$

This corresponds well with the equation for reflection $(hk0)$ of the Bear and French unit.[2] It was observed that differences in the $\sin^2 \theta$ values of the powder diagram frequently involved 0.00525 and 0.02100, corresponding to $\lambda^2/4b_0^2$ and λ^2/b_0^2, where b_0 is the fiber axis determined by layer line measurement. The equation

$$\sin^2 \theta_{(hkl)} = 0.00230h^2 + 0.00525k^2 + 0.00705l^2 \qquad (2)$$

was then tested, both against the measurable reflections of the powder diagrams and the intensifications noted on film and fiber diagrams. The results are recorded in Table I.

The film and fiber diagrams provide the severest test of the indexing. From the fiber diagram the middle index can be determined beyond question, since $k = 0$ in the equator, $k = 1$ in the first layer line, etc.

A film corresponds to rotation of a fiber about a normal to the fiber axis. If b_0 is again taken as the fiber axis the type of intensification of the various planes (hkl) about what would be the powder arcs permits the evaluation of k. On the film diagrams it was possible to note the intensification only for the low order reflections, where $k = 0$ or 1. For reflections $(h0l)$, the intensification is greatest in the equator (Fig. 1). Doublets, with a plane (hkl) and a plane $(h0l)$, showed no

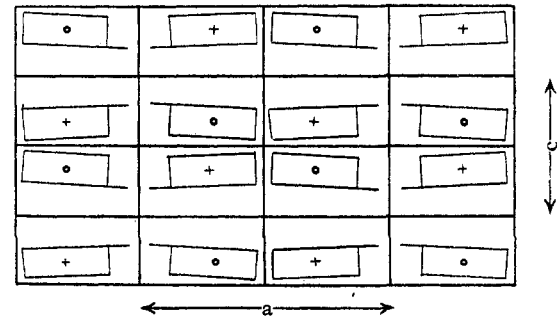

Fig. 1.—Symmetry requirements of space groups D_2^1 and D_2^2: Small circle indicates a chain running in one direction, across the other. For space group D_2^1 all chains running in the same direction are superimposable by translation along a_0 and c_0, together with rotation about b_0. D_2^2 differs only in that alternate chains running in the same direction are also transposed $1/2$ along b_0.

(9) R. E. Rundle and L. Daasch, *ibid.*, **65**, 2261 (1943).

(10) This statement has to be limited to certain modifications of starch, for in the "V" or helical configuration the greatest polarizability of the starch molecule is normal to its greatest length. See (7) and R. Rundle and R. Baldwin, *ibid.*, **65**, 554 (1943).

TABLE I

X-RAY DATA FROM POWDER, FILM AND FIBER DIAGRAMS

No.[a]	Indices	$\left(\frac{2 \sin \theta}{\lambda}\right)^2 \times 10^4$ (Calcd.)	(Powder)	(Film)	(Fiber)	h-Obsd.	Intensity[b] (Powder)	(Film or fiber)
1	(100)	38.8	38.2	38.8	..	0-(film)	s	vs
	(010)	..		...	..	....	...	...
2a	(001)	119	123	...	..	....	...	...
	(110)	.128		129	..	1-(film)	f	f
2b	(200)	155	157	159	..	0-(film)	vf	vf
	(101)	158						
	(011)	207	(196)	...	..	....	vvf	...
3a	(210)	244	244	244	244	1	m	m
	(111)	247						
3b	(201)	274	282	281	274	0	ms	ms
	(300)	350		345	345	0		s
4a	(020)	355	358	...	..	....	s	...
	(211)	363		361	358	1		vs
	(120)	393	..	...	..	....	...	...
	(310)	438	..	...	..	....	...	...
5a	(301)	469	478	462	473	0	f	f
	(002)	476						
	(220)	510						
5b	(121)	513	517	...	..	....	vvf	...
	(102)	515						
	(311)	557	..	...	..	....	...	...
	(012)	565						
					591	1-(fiber)		m
6a	(112)	604	598	(591)	621	0-(fiber)	ms	f
	(400)	621						
	(320)	704		...	701	2-(fiber)	ms	m
6b	(410)	710	713	...	?	?	ms	...
	(212)	720		...			ms	...
	(321)	823		...	..	....		...
7	(302)	826	832	...	..	....	m	...
	(411)	829		...	..	....		...
	(022)	831		...	..	....		...
	(420)	976	978	...	..	....	f	...
	(422)	986						
	(003)	1072	1067	...	..	....	f	...
	(322)	1180	1184	..	1182	2-(fiber)	m	f
	(132)	1320	1319	...	..	....	vf	...
	(023)	1426	1429	...	..	....	m	...

[a] Line numbers are those used by Bear and French[2] and correspond to the original numbering of the lines by Katz and van Itallie, *Z. physik. Chem.*, A150, 90 (1930). [b] Intensity notation—s, strong; m, moderate; f, faint and v, very.

identifiable intensification on the film patterns, but indices could be checked on the fiber patterns. It will be noted that the indexing explains the intensification on both film and fiber patterns.

Reflections occurring at small angles on the fiber diagrams are not given in Table I. This is an unfortunate omission, occasioned by the fact that fibers with satisfactory orientation were produced in but a few of many attempts, and the diffraction diagrams obtained from them happen to be very intense, with reflections at low angles obscured by the heavy background. Fortunately, the film patterns obtained are quite satisfactory for settling the middle index of these reflections.

The Unit Cell.—The unit cell dimensions, determined from the coefficients in equation (2), are

$a_0 = 16.0$ Å. $b_0 = 10.6$ Å. $c_0 = 9.2$ Å.

The cell is, within the limits of our observation, orthorhombic. The possibility cannot be excluded that the unit is monoclinic or triclinic with the angles between the axes very nearly 90°.

Two of the above dimensions, a_0 and c_0, are just those of the unit suggested by Bear and French.[2] Here, however, they are more unambiguously determined by the equatorial reflections on the fiber diagram. The fiber spacing, b_0, results directly from measurement of the layer-line spacings on the fiber diagram.

The volume of the unit cell of "B" starch is 1566×10^{-24} cc. If the density and water content assumed by Bear and French[2] are adopted, the carbohydrate density for starch is 1.23 g./cc. There are then 7.25 glucose residues per unit. The density, 1.50 g./cc., assumed by Bear and

French, corresponds to the bulk density of starch. It seems far more likely that the X-ray density of a substance as porous as starch should materially exceed its bulk density. If it be assumed that there are eight glucose residues per unit cell, the X-ray carbohydrate density is 1.36 g./cc., and if it be assumed that tuber starches contain about 15% water, the X-ray density for starch is about 1.60 g./cc., as contrasted with 1.50 g./cc. for bulk starch. It appears entirely reasonable that the X-ray density should exceed the bulk density of starch by this amount.

It is worthy of note, too, that granular starch is by no means 100% crystalline material. Whole starch, from whatever source, contains a branched component, the branch points of which cannot be within the starch crystallites. Preliminary experiments indicate that the crystalline portions of most ordinary, granular starches constitute about 50–60% of the total granule. One would expect the amorphous parts of the starch granule to be less dense than the crystalline regions, so for this reason too the average starch density should be less than the X-ray density reported here.

The Structure of the "B" Modification.—The present fiber patterns from starch are not yet of a quality to be compared with those obtained from cellulose and other naturally occurring fibers, so that any structure proposed for the "B" modification of starch must remain more tentative in nature than those proposed for chitin, cellulose, etc. Nevertheless, the dimensions of the unit cell and the apparent symmetry of the cell suggest the gross aspects of the structure.

Most important is the fiber spacing. It is very surprising to find this spacing perhaps even larger than that for cellulose.[11] Space models of starch using the usual strainless configurations of the pyranose ring or the semiplanar Cox model[12] would make it appear that the starch chains should be far more crumpled than those of cellulose, resulting in a much shorter fiber spacing. Regardless of the validity of the rest of the unit cell, however, the fiber spacing of the "B" modification can no longer be in doubt by more than a few tenths of an Å., and must be very closely equal to that of cellulose. It would appear that closer attention to the special arrangement of the ring than that afforded by building space-filling models is deserved.

The dimensions of the unit cell are quite similar to those of the chitin unit cell,[13] except that the 16 Å. spacing is increased to 19 Å. in chitin. In chitin the glucose residues are arranged with the planes of the glucose rings nearly parallel to the 19 Å. axis, the normals to the rings approximately parallel to the 9 Å. spacing. The width of the chitin unit is about 9.5 Å. It is interesting to note that it decreases to about 8.5 Å. when half the acetyl groups are removed from the residues, as in chitosan.[14] A width of 8 Å., or just half the 16 Å. spacing, would be expected for the glucose unit in starch. It is noteworthy that the periodicity of the starch helix in the starch–iodine complex is 8 Å.[15] It is presumed that this corresponds to the width of the glucose residue.

The thickness of the glucose residue appears to be about 4.5 Å. in both chitin and starch and in the carbohydrates in general; this is half the 9 Å. spacing reported here. The gross structure of starch in the "B" modification probably resembles the chitin structure, in that the planes of the glucose residues are probably parallel to the largest spacing of the cell (Fig. 2).

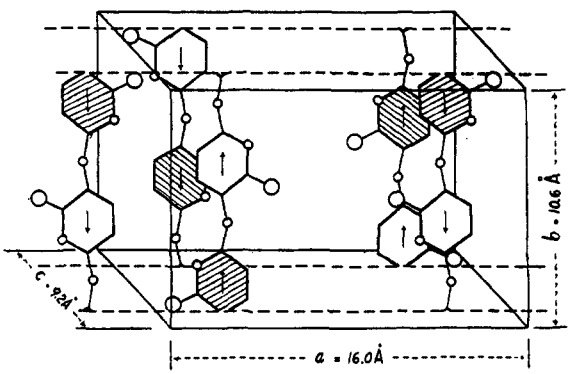

Fig. 2.—Structure of the "B" modification of starch: This structure is based on the space group D_2^1. An equally likely structure based on D_2^2 would differ only in having chains running the same direction in the unit cell translated with respect to each other $1/2$ along b_0.

If the starch structure is orthorhombic, as appears likely, then the space group must be isomorphous with the point group D_2, since all other point groups of the orthorhombic system contain planes of symmetry, not allowable to the optically active starch chains.

Of the space groups isomorphous with D_2, only D_2^1–P222 and D_2^2–$P22_12$ are permitted by the observed reflections. The first requires that there be a two-fold axis parallel to the chains, the second that there be a two-fold screw axis in this direction. The failure to observe reflections (010) and (030) is not sufficient to establish the latter as more than a possibility. In either case the two-fold axes normal to the chains must run between the chains, and in either case half the chains will be running in one direction, half in the other, as indicated in Figs. 1 and 2. The only difference is that for the space group D_2^2 a translation $1/2$ along b_0 is also required. In cellulose fibers,[16] chitin fibers,[13] etc., it has been found that half the

(11) O. Sponsler and W. Dore, "Fourth Colloid Symposium Monograph," Chem. Catalog Co., Reinhold Publ. Corp., New York, N. Y., pp. 174–202.

(12) E. Cox, T. Goodwin and A. Wagstaff, *J. Chem. Soc.*, 1495 (1935).

(13) K. Meyer and G. Pankow, *Helv. Chim. Acta*, **18**, 589 (1935).

(14) G. Clark and A. Smith, *J. Chem. Phys.*, **40**, 863 (1936).

(15) R. Rundle and D. French, THIS JOURNAL, **65**, 1707 (1943).

(16) K. Meyer and L. Misch, *Helv. Chim. Acta*, **20**, 232 (1937).

chains run in one direction, half in the other direction. This is most probably the case with starch too, and one of the above arrangements of the chains is probably approximately correct even if the starch structure is only pseudo-orthorhombic.

If adjacent glucose residues along the starch chain are identical in their configurations, the periodicity along the chain requires that adjacent glucose residues be rotated about b_0, so that the (CH_2OH) groups on adjacent glucose residues are *trans* to each other (Fig. 2). (This is also found to be the case in cellulose[16] and chitin,[13] where the glucosidic link is β.) The *trans* arrangement for starch in the "B" modification does not necessitate this arrangement in the "V" modification, where the chains assume a helical configuration.[15] Indeed, it is probable that a rotation about the glucosidic bond to the *cis* configuration accounts for the very different shape of the chains in these modifications of starch.

In contrast to the case of chitin,[14] odd-ordered reflections ($h00$), ($00l$) and (hOl) are quite intense on the "B" diffraction patterns. This must mean that the chains are unequally spaced along a_0 and c_0 (Figs. 1 and 2).

Chains running in opposite directions through the unit may be displaced with respect to each other in arbitrary amount along b_0. The reflection (020) appears to be very weak or missing, since it does not appear on the fiber diagram. It is likely, then, that the displacement is approximately $^1/_4\ b_0$.

The structure shown in Fig. 2 is in accord with these qualitative observations of intensities. It is based on the space group D_2^1, but a similar structure, based on D_2^2, with every other chain translated $^1/_2$ along b_0 is equally likely. Even if the structure is not truly orthorhombic the spacing and orientation of the chains should approximate, in its gross aspects, the structure shown in Fig. 2.

Bear and French[2] have established a close relationship between the "A," "B" and "C" modifications of starch. This relationship is independent of the validity of their unit cells, so that it should be found that the "A" and "C" unit cells resemble closely that reported here for the "B" modification.

It seems well to point out that in contrast to cellulose, the configuration of the starch chain depends upon how the starch is treated. The chains, fully extended in the "B" modification, become helices in the "V" modification and the starch–iodine complex, and assume an intermediate, crumpled form in the fibers prepared by the use of certain plasticizers.[9]

Summary

1. Methods for preparing films and fibers of the "B" modification of starch are outlined.

2. Film and fiber diffraction patterns of the "B" modification of starch have been prepared. The fiber axis is 10.6 Å.

3. A new unit cell for the "B" modification has been found, with $a_0 = 16.0$, $b_0 = 10.6$, $c_0 = 9.2$ Å. The structure is probably orthorhombic. There are 8 glucose residues per unit; the density of the crystalline portion of starch is about 1.6 g./cc.

4. A rough structure of the "B" modification of starch has been proposed on the basis of the unit cell dimensions and qualitative consideration of the intensities (Fig. 2).

5. It is pointed out that plasticizers useful in producing starch fibers generally alter the starch structure materially, and unlike the case of cellulose, the fiber spacing of starch is easily altered by treatment of the starch.

AMES, IA. RECEIVED JUNE 18, 1943

[CONTRIBUTION FROM THE AVERY LABORATORY OF CHEMISTRY OF THE UNIVERSITY OF NEBRASKA]

α,β-Diamino Ketones. I. Reactions of Heterocyclic Secondary Amines with α-Bromo-β-aminoketones[1]

BY NORMAN H. CROMWELL, CHARLES E. HARRIS AND DONALD J. CRAM

The reactions of α-bromo-α,β-unsaturated ketones with primary and secondary amines have been the subjects of several investigations in this Laboratory.[2] The development of an excellent method of preparing mixed α,β-diamino ketones from α-bromo-α,β-unsaturated ketones is one of the results of these investigations. From a knowledge of the mechanisms[2f] of these reactions it is possible to arrange the conditions in such a manner as to allow the preparation of many specific mixed diamino ketones of possible chemotherapeutic interest.

α-Bromo-β-morpholinobenzylacetone[2c] reacted readily with tetrahydroquinoline (which is a weaker base than morpholine) to give good yields of the expected α-morpholino-β-tetrahydroquinolinobenzylacetone (I). The structure of (I) was established by hydrolysis to give α-morpholinoacetone, isolated as its oxime. This same bromo amino ketone reacted in dry ether with piperidine (which is a stronger base than morpholine) to give very poor yields of α-morpholino-β-piperidino-

(1) Presented before the Division of Organic Chemistry, American Chemical Society, Pittsburgh, Pa., September 6, 1943.

(2) (a) Cromwell, *et al.*, THIS JOURNAL, **62**, 1672 (1940); (b) **62**, 2897 (1940); (c) **62**, 3470 (1940); (d) **63**, 837 (1941); (e) **63**, 2984 (1941); (f) **65**, 301 (1943); (g) **65**, 308 (1943); (h) **65**, 312 (1943).