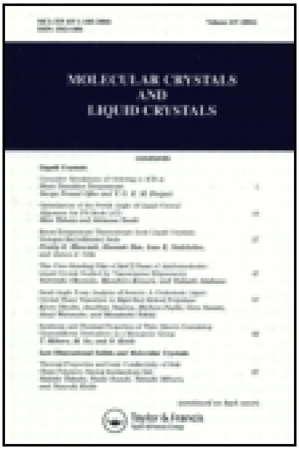

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# X-ray Photographic Studies of Liquid Crystals I. A Cybotactic Nematic Phase

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# X-ray Photographic Studies of Liquid Crystals
# I. A Cybotactic Nematic Phase†

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**Abstract**—The X-ray diffraction patterns of the nematic phase of bis-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine show major maxima at two diffraction angles. The ones at the larger angle are due to the interaction of neighboring, parallel molecules and the average distance between the long axes of the molecules can be calculated using the formula $2d \sin \theta = 1.117\lambda$. The maxima at the smaller diffraction angle are related to the length of the molecule; the observed diffraction pattern is explained by assuming that a part of the molecules are organized in groups (cybotactic groups) in such a way that the ends of the molecules lie in fairly well defined planes making an angle of about 45° with the direction of the long axis of the molecules. At lower temperatures the large majority of the molecules are arranged in these groups, and the groups appear to be fairly rigid. At higher temperatures the groups become less prominent, but they do not completely disappear.

## 1. Introduction

It is generally assumed that in a nematic liquid crystal the only restriction on the arrangement is that the molecules (which are long and rod-like) have a more or less parallel orientation with respect to their neighbors (" parallel " refers here to the long axes of the molecules).(3,9,14) It will be shown in this paper that this conception of the nematic phase, which one might call the classical nematic structure, is not an adequate description for the nematic phase of bis-(4′-*n*-octyloxybenzal)-2-chloro-1,4-phenylenediamine (BOCP for short), $H_{17}C_8O \cdot C_6H_4 \cdot CHN \cdot C_6H_3Cl \cdot NCH \cdot C_6H_4 \cdot OC_8H_{17}$, and that it will be necessary to assume that a substantial part of the molecules are regularly arranged in groups; in each group the centers of the

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molecules lie in a fairly well defined plane. Since these groups resemble strongly the cybotactic groups proposed by Stewart and Morrow(16) we shall call this kind of an arrangement a cybotactic nematic structure.

## 2. Experimental

X-ray diffraction patterns were recorded with a Picker Laue camera with a high temperature attachment and a modified collimating system. The samples were contained in thin walled glass capillaries (wall thickness 0.01 mm) of 0.5 mm diameter. The capillaries were held in a copper block which also served as collimator for the X-ray beam. The copper block was surrounded on five sides by an oil bath, on the sixth side (toward the film) by a set of plates with a thin (0.008 mm) glass window. The diameter of the X-ray beam (nickel-filtered Cu radiation) at the sample was about 0.5 mm and the temperature of the irradiated region of the capillary varied not more than a few tenths of a degree during each experiment (the exposure time for each photograph was 1 hr). The direction of the main axis of the capillary was perpendicular to the direction of the incident beam. The diffraction patterns were recorded on flat pieces of film, also perpendicular to the incident beam, 47.6 mm from the capillary.

The transition temperatures for the compound studied have been reported(1) as 59° for the crystal-nematic point (C-N point) and 179° for the nematic-isotropic liquid point (N-L point).

## 3. Discussion

For the description of the structure of a liquid crystalline phase, one has the choice of two approaches: the liquid crystal can be described as a disordered crystal, or it can be described as an ordered liquid. We have chosen here the second approach because we feel that nematic liquid crystals are in their structure much closer to a liquid than to a crystal.

We shall analyze first the diffraction pattern of the nematic phase at temperatures close to the crystal-nematic point. There are major diffraction maxima at two diffraction angles. We shall see that the one at the larger angle (the " outer ring ") can be ascribed to the interaction of neighboring, parallel molecules. The way in which this ring splits up when the molecules are aligned gives information about the mean direction of the long axes of the molecules. Next, it is shown that the maximum at the smaller diffraction angle (the " inner ring ") is related to the length of the molecule. The way in which *this* ring splits up for the aligned nematic phase indicates that the degree of order must be larger than generally assumed for a nematic phase.

## THE OUTER RING

When there is no preferred orientation in the sample, the most prominent features of the X-ray diffraction pattern of BOCP in the nematic state are two rings (Fig. 1a). The same was found to be true for several homologues of BOCP. When the diffraction angles for these rings were compared (Table 1), it was found that the angle for the outer ring was virtually the same for all these compounds, but that the angle for the inner ring decreased steadily with increasing length of the alkyl group. These results are completely analogous to those of Stewart and Morrow⁽¹⁶⁾ for liquid primary normal alcohols

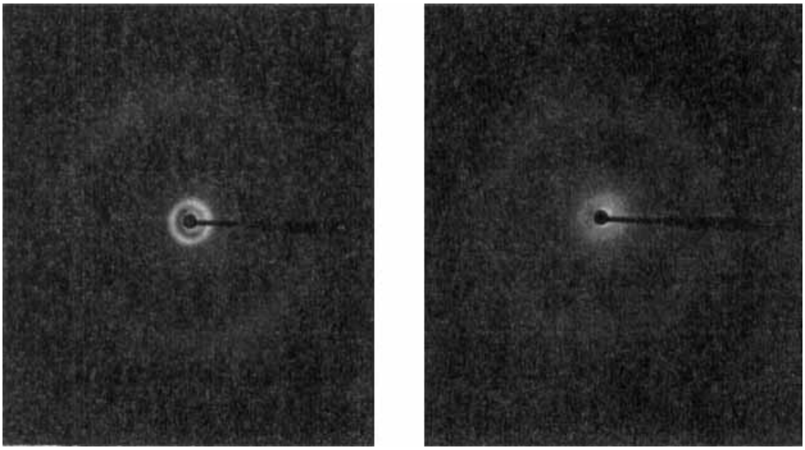

Figure 1. Diffraction patterns of (a) the nematic phase with little preferred orientation and (b) the liquid phase.

TABLE 1 Position of Inner and Outer Diffraction Ring for Several BACPs†

| | Inner ring | | Outer ring | | |
|---|---|---|---|---|---|
| $n$ | $2\theta$ | $d_1$ | $2\theta$ | $d_2$ | $t$ |
| 5 | 4.1° | 21.6Å | 20.3° | 4.89Å | 100 °C |
| 6 | 3.6 | 24.3 | 20.2 | 4.90 | 100 |
| 8 | 3.3 | 26.6 | 20.5 | 4.83 | 60 |
| 9 | 3.0 | 29.0 | 19.9 | 4.97 | 98 |
| 10 | 2.8 | 31.3 | 19.7 | 5.02 | 115 |
| 12 | 2.6 | 33.5 | 19.4 | 5.12 | 134 |

† Bis-(4′-$n$-alkoxybenzal)-2-chloro-1,4-phenylenediamines. The column headings have the following meaning:
$n$: *number of carbon atoms in the alkoxy chains*
$2\theta$: angle of diffraction
$d_1$: interplanar spacing
$d_2$: interplanar spacing multiplied by 1.117 (see Appendix)
$t$: temperature at which the photograph was taken

and of Morrow(12) for liquid normal monobasic fatty acids. These authors held that this type of behavior indicates that the outer diffraction ring is due to the interaction between neighboring parallel molecules and thus gives a measure of the average distance between adjacent molecules, while the inner ring is determined by the length of the molecules. We propose the same interpretation for the inner and outer diffraction rings of the BACPs and also for similar diffraction maxima of other compounds with rod-like molecules. This interpretation of the *outer ring* is supported by the following observations:

1. The position of this ring changes when the thickness of the molecule is changed: Chistyakov(4) found the outer maximum of cholesteryl caprate at an angle ($2\theta = 15.3°$) significantly smaller than the angles reported here, and we have been able to confirm this for other cholesterol derivatives.

2. It can be shown theoretically that a group of parallel linear molecules, perpendicular to the incident X-ray beam, gives diffraction maxima in a plane perpendicular to the long axes of these molecules (Refs. (7), and (10), p. 582). The position of the maxima in this plane is determined by the separation between the molecules (see Appendix). Experimentally it has been observed by several

authors (e.g. Ref. (8)) that, when a nematic material is aligned, the outer diffraction ring† splits up into two crescents, and that the direction in which the maxima of these crescents are found‡ is perpendicular to the mean direction of the long axis of the molecules. We have obtained diffraction patterns of BOCP in which the outer ring was split into two crescents (Fig. 2b).

From these data, and those presented in Table 1, it appears to be sufficiently well established that the outer diffraction ring from the nematic phase of BOCP, and the corresponding diffraction maxima for other compounds, are due to the interaction between neighboring parallel molecules, and that the position of these maxima gives us a measure of the average distance between adjacent molecules. This interpretation is also in agreement with that of a similar ring in the diffraction patterns of amorphous linear polymers, which is taken to be " due principally to interatomic vectors between adjacent chains " (Ref. (11), p. 633).

From the arguments presented above under point 2 it follows that a separation of the outer diffraction ring into two crescents, 180° apart (as in Fig. 2b), indicates an alignment of the molecules with the mean direction of their long axes perpendicular to the direction in which the crescents are found and also perpendicular to the direction of the incident beam.§ From the shape of the crescents in Fig. 2b, which are quite short as compared to those found in other cases, we can conclude that the alignment must be very strong in this case.

## THE INNER RING

The intensity of the inner ring is far greater in the nematic phase at temperatures close to the C-N point than in the nematic phase at temperatures close to the N-L point or in the liquid phase (Fig. 1).

From the values of the diffraction angle of this ring, given in

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† With " outer diffraction ring " we mean here the ring that corresponds in intensity and diffraction angle to the outer ring for BOCP.

‡ By " the direction in which a maximum is found " we mean the direction of the line from the center of the diffraction pattern to the center of the maximum.

§ It can easily be shown theoretically that the crescents will no longer be 180° apart when the mean direction of the long axes is not perpendicular to the incident beam; this has also been experimentally confirmed by us.

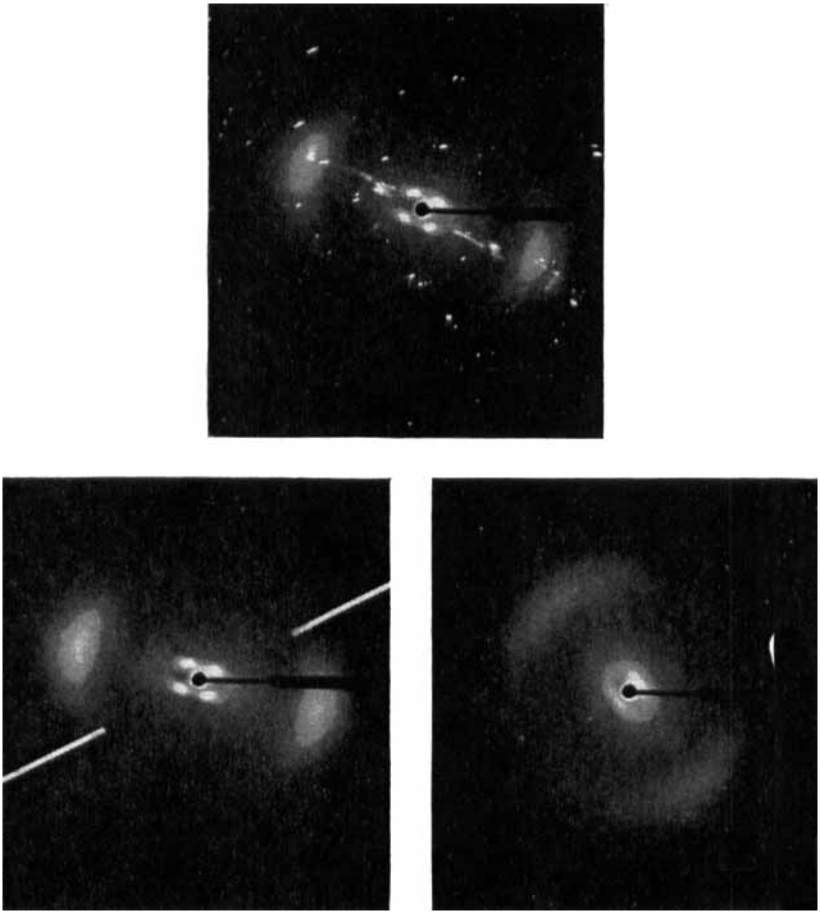

Figure 2. Diffraction patterns at different temperatures: (a) 59 °C, (b) 60 °C, and (c) 174 °C. At 59 °C part of the solid phase is still present; at the other temperatures the whole sample is in the nematic phase. The white lines in (b) indicate the direction of the capillary.

Table 1, and from the fact that they decrease steadily with increasing molecular length, there can be little doubt that for this ring, too, Stewart and Morrow's interpretation is correct in that it must be related to the length of the molecule. Additional information about the nature of this relationship was obtained by examining the diffraction pattern of the aligned nematic phase (Fig. 2b): the inner ring appears to be split up into four maxima, and the directions in which these maxima are found make angles $\alpha'$ (Fig. 3) with the directions in which the maxima in the outer ring are found.

We have found it impossible to explain this diffraction pattern with the classical theory of the nematic phase:† their presence requires a relationship between the positions of the centers of gravity of neighboring molecules,‡ and such a relationship is absent in the classical nematic phase. *From this it follows that the nematic phase of BOCP must be different from the classical nematic phase.*

† We do not agree with the explanation given recently by Chistyakov and Chaikovsky(5) (further referred to as CC) of a similar pattern which was obtained from samples aligned with a magnetic field. These authors hold that the inner ring " gives the mean spacing between centers of molecules along the axis of texture ". According to them the set of four maxima is " due to the fact that the molecules are lined up in the magnetic field, not parallel, but at a certain quite definite angle with respect to the lines of field forces "; this " distribution of molecules possesses a cylindrical symmetry ". In this explanation the authors appear to have completely overlooked the appearance of the maxima in the outer ring. According to their Fig. 2b the " quite definite angle " should be about 43° for 4,4′-*p*-ethoxyazoxybenzene. Thus, if the explanation of CC were correct, there would be molecules in the sample in all directions which make an angle of 43° with the direction of the magnetic field (neighboring molecules would, of course, always be essentially parallel to each other, according to the general definition of the nematic phase; so, in each of the molecular directions discussed here there would be groups of parallel molecules). Of these directions of the molecules there would be two that are perpendicular to the incident beam; the angle between these two directions would be $2 \times 43° = 86°$. As pointed out above in our discussion of the outer ring, a group of parallel molecules which are normal to the incident beam gives outer ring maxima in a plane perpendicular to the direction of the molecules. The angle of 86° between the two molecular directions would mean, therefore, that these differently oriented groups of molecules would give two sets of maxima in the outer ring which are 86° apart. It can be seen easily that the other molecules (i.e., those not perpendicular to the incident beam) would fill in the space between the maxima to give two crescent shaped maxima in the outer ring, each maximum extending over at least 86°. The actual extent of the maxima is only about 50° (CC, Table 2), and even this value is measured from the very tips of the reflection (CC, Fig. 1a). Thus, the outer ring maxima are far too narrow to allow the explanation proposed by CC; the same is true for the diffraction pattern presented in our paper.

‡ This conclusion is supported by what James (1954, p. 584) says in his discussion of the packing of straight rows of points: " It may be stated generally that if definite interference spots occur on layer lines other than the equatorial one, it is very strong evidence that the individual crystallites consist of more than one row of points, and that the rows are in a lattice-like array ".

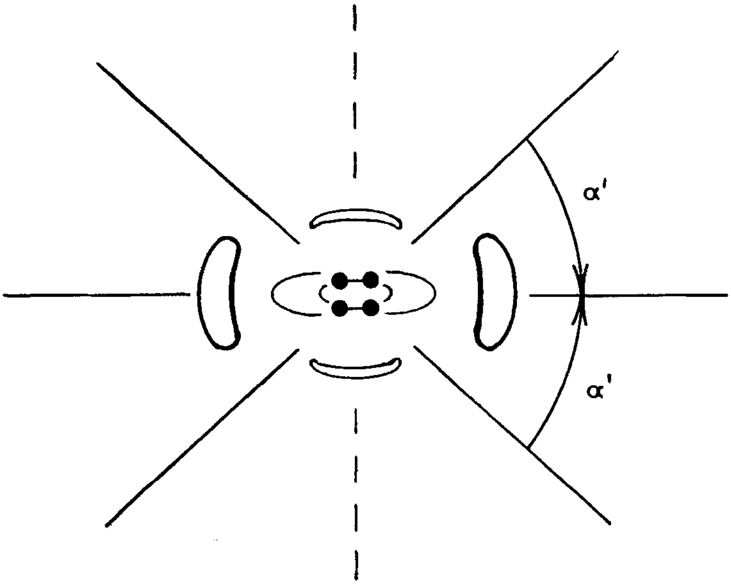

Figure 3. Schematic representation of the diffraction pattern of the nematic phase with strong preferred orientation. The direction of the incident beam is perpendicular to the plane of the paper. The broken line indicates the mean direction of the long axes of the molecules.

The simplest model that can account for the observed diffraction pattern is an arrangement of the molecules in groups, in such a way that the centers of the molecules in each group lie in a fairly well defined plane which makes an angle $\alpha$ with the direction of the molecules (Fig. 4). With such an arrangement the boundary planes of a group (indicated in Fig. 4) would be loci of low electron density, since they are the regions where hydrogen atoms of different molecules come in van der Waals contact with each other. The dimensions of the groups are not known and it is also possible that several groups are stacked together (having boundary planes in common) so as to form larger units. The sharpness of the inner maxima in Fig. 2b suggests, in fact, that these larger units are present at 60 °C, whereas the much vaguer maxima in Fig. 2c may indicate that the units are much smaller at 174 °C. The basic building block, however, would always be a single-layered group as indicated in Fig. 4. We shall call these groups of molecules cybotactic groups, a name used by Stewart and Morrow⁽¹⁶⁾ for quite similar groups which they postulated to explain the diffraction patterns of the normal alcohols.

These cybotactic groups can explain the diffraction pattern as follows. The mean direction of the long axes of the molecules we shall call " the direction of alignment ". The direction of the incident X-ray beam will be taken perpendicular to this direction of alignment. For the sake of the argument we shall assume here that the long axes of the molecules are all strictly parallel to the direction of alignment (indicated in Fig. 3), and that the angles $\alpha$ of all cybotactic groups are exactly equal. The boundary planes of the cybotactic groups will then all make an angle $\alpha$ with the direction of alignment, but otherwise their orientation is arbitrary. In other words, all boundary planes will be tangent to cones which have the direction of alignment as axis and a vertical angle of $2\alpha$. Of all the planes in all these possible orientations, however, only those which have the proper orientation with respect to the incident beam will give maximum reflected intensity. It is well known from the theory of X-ray diffraction in crystals that the conditions for reflection from a set of parallel equidistant lattice planes are: (1) the angle between the incident beam and the reflecting plane is equal to the angle between the reflected beam and the reflecting plane; (2) using the symbol $\theta$ for this angle, $\theta$ is defined by $2d \sin \theta = \lambda$, where $d$ is the distance between neighboring planes (we consider here first order diffraction effects only); (3) the incident beam and the reflected beam lie in a plane normal to the reflecting plane. In the case of the boundary planes of a cybotactic group there are only two parallel planes, and they are probably not as well defined as lattice planes, so we will have to relax the above mentioned reflection conditions. It will still be true, however, that *maximum* reflected intensity is obtained only when the angle between the boundary planes and the incident beam is $\theta$ ($\theta$ as defined above). There are four orientations of the boundary planes which meet this requirement, each giving rise to one of the four inner diffraction maxima. The *directions* in which these maxima are found on the film are determined by the third condition for reflection mentioned above: that incident and

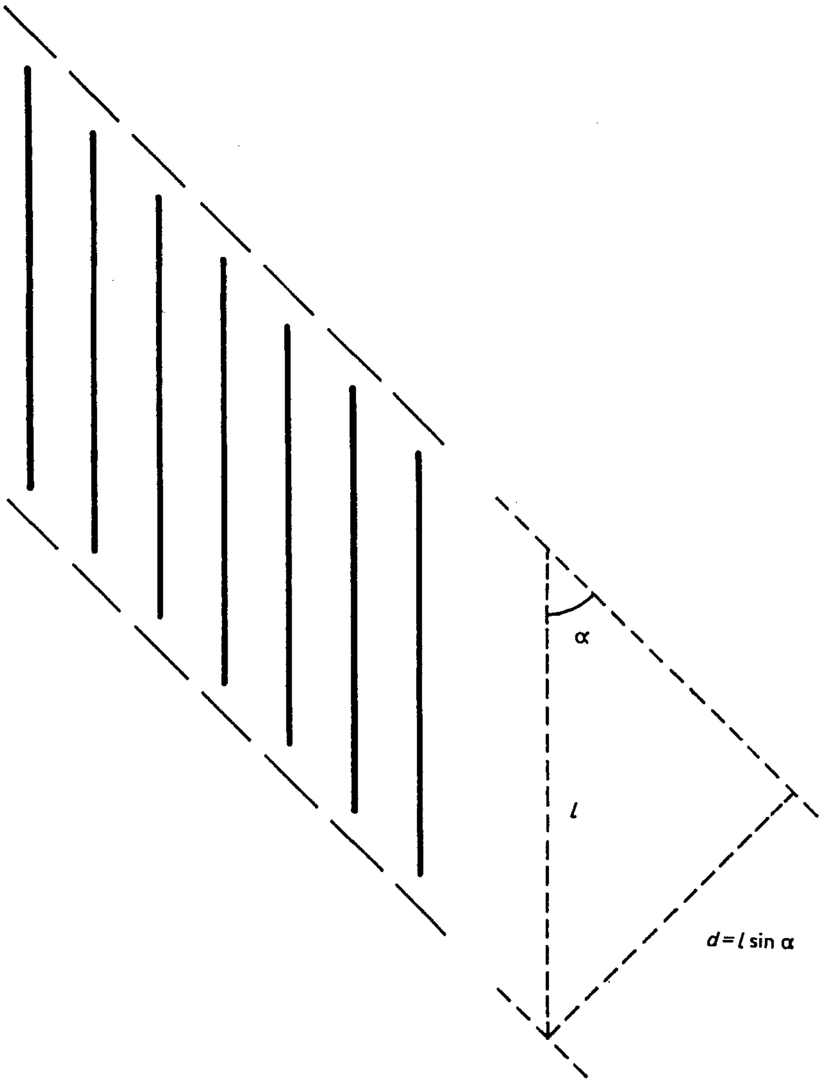

Figure 4. Schematic representation of a cybotactic group. The full lines indicate the molecules; the (coarse) broken lines give the positions of the boundary planes. The group is supposed to extend perpendicular to the plane of the paper.

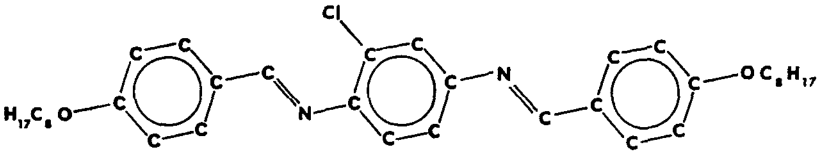

Figure 5. Structure of the molecule (the hydrogens on the benzene rings have been left out).

reflected beam should lie in a plane perpendicular to the reflecting plane (Fig. 6). These directions in which the maxima are found give a measure for the angle $\alpha$ of the cybotactic groups. In the limit of $\theta$ going to zero, the angle $\alpha'$ (Fig. 3) is equal to the angle $\alpha$ (Fig. 4). With $\theta$-values as found for BOCP the difference between $\alpha$ and $\alpha'$ is about 0.02°, as can be shown easily, and since the error in the measurement of $\alpha'$ is about 1° we can neglect this difference.

Cybotactic groups can thus explain the observed diffraction pattern in a qualitative way, but there are several additional reasons for believing that this model is correct. First, there is good agreement (Table 2) between the values of $\alpha$ that can be obtained

TABLE 2 Some Angles and Distances from Photographs at Various Temperatures

| | Angular positions† | | | | | |
|---|---|---|---|---|---|---|
| Temp. | Outer maxima | Bisectrix of inner maxima | $\alpha'$ | $\alpha$‡ | Inter-planar spacing§ | Inter-molecular spacing‖ |
| 60 °C | 40° | 43° | 43° | 42.1° | 26.2Å | 4.85Å |
| 79 | 44 | 45 | 44 | 42.1 | 26.2 | 4.85 |
| 98 | 45 | 46 | 45 | 43.1 | 26.7 | 4.91 |
| 117 | 48 | 49 | 46 | 44.2 | 27.2 | 4.98 |
| 136 | 56 | 54 | 47.5 | 47.3 | 28.5 | 5.04 |
| 155 | 69 | 70 | 48.5 | 47.9 | 28.8 | 5.08 |
| 174 | 78 | 78 | 50 | 54.2 | 31.2 | 5.13 |

† The direction of the capillary axis has been taken as 0°. The agreement between the two columns shows that the error in the measurements is not more than a few degrees.

‡ Calculated from the interplanar spacing using a molecular length of 38Å (planar molecule, cog-wheel arrangement of the alkoxy chains).

§ Calculated from the average diffraction angle of the four inner maxima using $2d \sin \theta = \lambda$.

‖ Calculated from the average diffraction angle of the outer maxima using $2d \sin \theta = 1.117\lambda$; the " intermolecular spacing " is the average distance between the long axes of the neighboring parallel molecules.

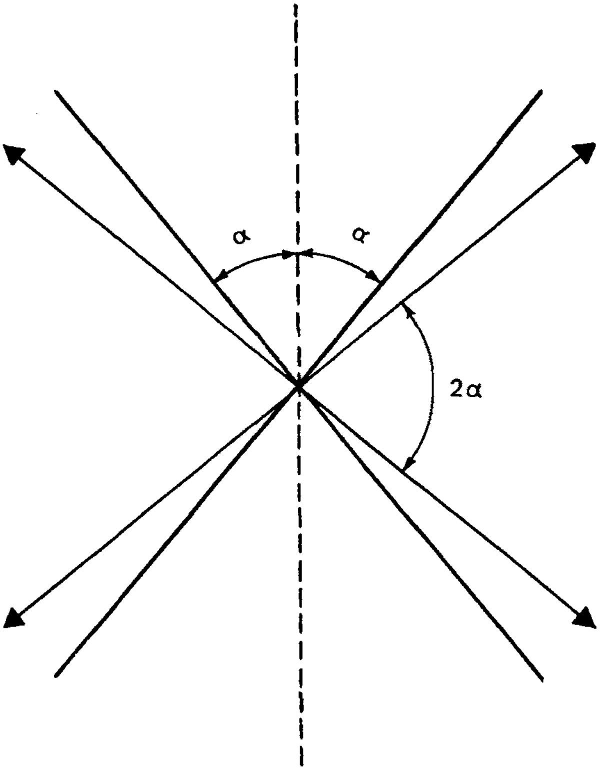

Figure 6. Schematic drawing showing the relation between the boundary planes of the cybotactic groups and the directions of the diffracted X-ray beams, in the limit of $\theta$ going to zero. The incident beam is considered to be perpendicular to the plane of the drawing. The full lines indicate the two orientations of boundary planes that satisfy the reflection conditions (in the limit of $\theta$ going to zero there are only two of these orientations instead of four); the planes are perpendicular to the plane of the drawing. The vertical dashed line is the direction of alignment. The four arrows (which are perpendicular to the full lines) give the directions in which the four maxima in the inner ring will be found.

from the diffraction pattern in two ways: the value of $\alpha$ measured directly from the film ($\alpha'$), and the value of $\alpha$ calculated from the diffraction angle $2\theta$ of the inner maxima through the relations $2d \sin \theta = \lambda$ and $d = l \sin \alpha$.

Second, when the capillary was rotated around its axis (which was not parallel to the mean direction of the long axes of the molecules), the observed changes in the inner maxima (they move a little closer together in pairs) were in agreement with what would be expected for an arrangement of cybotactic groups as described above.

Third, there are two homologous series of compounds for which a nematic diffraction pattern as shown in Fig. 2b has been found so far: the BACPs (Ref. (6), and this paper) and the 4,4′-di-*n*-alkoxyazoxybenzenes,(5) and in both series several compounds have a smectic phase in addition to their nematic phase. The diffraction patterns of these smectic phases for both series show that the molecules in a smectic layer do not stand perpendicular to the boundary plane of the layer but at an angle. The cybotactic model here presented for the nematic phase of the BACPs would, therefore, simply mean that the molecular arrangement which is present in the smectic layers is maintained to a certain degree when the material goes over into the nematic phase, although the layers probably break up into smaller pieces.

It appears, therefore, that the cybotactic group model is a quite satisfactory model for the nematic phase of the BACPs.

## OTHER FEATURES OF THE DIFFRACTION PATTERN

The major features of Fig. 2b now accounted for, there are two minor features that warrant some discussion. First, although the four maxima in the inner ring are very strong, there are no corresponding second order maxima visible. The reason for this is that the structure of the molecule (in particular the presence of the Cl atom on the central benzene ring; Fig. 5) is such that the projection of the electron density of the molecule on its long axis has a maximum near the center. This maximum will reinforce the first order diffraction maximum caused by the electron density minima at the ends of the molecules, but it will reduce the second order maximum (the same effect has been found with layers of the longer fatty acids)(2,13).

Second, there are weak lines connecting the four inner maxima in pairs. The direction in which these maxima are found is perpendiular to that in which the outer maxima are found. These maxima are indicated by short lines in Fig. 3 and they may also be discernable in Fig. 2b (in the original photograph they were clearly visible). Their appearance suggests that they are not just a continuation of the four inner maxima, but rather a separate diffraction effect. The diffraction angle for these maxima is so small ($2\theta \approx 2°$) that it could not be measured accurately, but it appears to agree well with an interplanar spacing equal to the length of the molecule. These maxima suggest that a small fraction of the molecules is either free, as in the classical nematic phase, or arranged in groups in which the centers of the molecules lie in planes *perpendicular* to the long axes of the molecules.

## THE CHANGE IN THE DIFFRACTION PATTERN WITH TEMPERATURE

Diffraction patterns were obtained from one sample at a series of temperatures ranging from just above the C-N point to just below the N-L point (the first and last patterns of this series are reproduced in Fig. 2b and 2c). Three changes in the pattern were immediately noticeable. First, the direction in which the maxima are found changes gradually (see also Table 2), showing that the mean direction of the molecules became closer to the direction of the capillary as the temperature increased.† Upon subsequent cooling the pattern did not rotate back. This suggests that the particular orientation shown by Fig. 2b was not caused by external forces, but rather had been dictated by the solid from which this nematic phase was formed (note also the direction of the streaks in the diffraction pattern of the solid, Fig. 2a).

Second, the inner maxima get weaker with increasing temperature, whereas the lines connecting them in pairs become stronger, until at the highest temperature there is hardly any distinction between them any more. Also, all maxima become more vague at higher temperatures. Factors contributing to these effects may be: increase in thermal motion, decrease of the size of the cybotactic groups, decrease of the order within the cybotactic groups, decrease of the degree of preferred orientation in the sample.

Apart from these changes there are some other ones which are not obvious from the photographs, but which become apparent upon inspection of Table 2. First, there is the slight but consistent increase (with temperature) in the intermolecular spacing (compare also the

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† It should be pointed out here that, since these photographs were made in one uninterrupted series, with not much time passing between consecutive photographs, this gradual change in the angular positions may just as well be a time effect as a temperature effect (the material is very viscous at the lower temperatures).

last two columns in Table 1). Second, there is a gradual increase in the angles $\alpha'$ and $\alpha$. This increase might be an artifact, however, caused by the increasing fuzziness of the maxima.

## 4. Conclusions

From the evidence presented in this paper it appears quite certain that in the nematic phase of bis-(4'-*n*-octyloxybenzal)-2-chloro-1, 4-phenylenediamine a part of the molecules are organized in cybotactic groups in such a way that the ends of the molecules lie in planes making an angle of about 45° with the direction of the long axis of the molecules. At lower temperatures the large majority of the molecules are arranged in these cybotactic groups, and the groups appear to be fairly rigid. At higher temperatures the groups become less prominent but they do not completely disappear, not even at only a few degrees below the nematic-isotropic transition point.

## Acknowledgements

The author gratefully acknowledges the interest and support given this work by Professor Glenn H. Brown. He is indebted to Mr. Paul Norton for making the high temperature attachment for the X-ray camera and to Dr. Sardari L. Arora for furnishing samples of the compounds studied.

## Appendix

In this paper two different formulas have been used for the calculation of the corresponding spacing from the diffraction angle of an intensity maximum. Since one of these formulas is new, we shall treat here briefly some of the different cases which may be encountered, and formulas for these cases. For the purpose of this discussion we define an axis $c$ in the sample, perpendicular to the incident beam; the intersection of the photographic film with the plane through the incident beam and perpendicular to the $c$ axis will be called the equator.

First, we consider the scattering from a pair of atoms. For a pair of point atoms, with an interatomic distance $d$ which is perpendicular to the incident beam and to the $c$ axis, the position of the first diffraction maximum along the equator is given by

$$d \sin 2\theta = \lambda.$$

If we allow the distance $d$ to rotate around the $c$ axis, while remaining perpendicular to it, it can easily be shown that the positions of the maxima along the equator are given by the positions of the maxima of the function $J_0(x) = \int_0^{2\pi} \cos(x \cos \alpha) d\alpha$, where $x = (4\pi/\lambda) d \sin \theta$. For the position of the first maximum this yields

$$2d \sin \theta = 1.117\lambda.$$

Allowing completely free rotation of $d$, one obtains for the position of the first maximum the Keesom formula (Refs. (10), p. 484, and (17))

$$2d \sin \theta = 1.229\lambda.$$

This formula has been used often in studies of liquids and amorphous materials (Refs. (11) p. 632, and (15) p. 507).

Another kind of interference effect, which should be quite important for liquid crystals and other materials containing long molecules, is the scattering from a pair of parallel, elongated molecules. As a model for this we take a pair of parallel linear chains of point atoms, a distance $d$ apart. James (Ref. (10) p. 575) has shown that, if these chains are parallel to the $c$ axis and are free to rotate around each other, the positions of the maxima along the equator are determined by the same function $J_0(x)$ mentioned above. For the position of the first maximum one therefore obtains again

$$2d \sin \theta = 1.117\lambda.$$

This formula has, to our knowledge, never been used yet, but it would appear to be the correct formula to be applied to the diffraction maxima attributed to interference between parallel molecules which are perpendicular to the incident beam. We have used it, therefore, for the calculation of the intermolecular spacing from those photographs (listed in Table 2 at 60 °C and 79 °C and shown in Fig. 2b) which indicated a very strong preferred orientation of the molecules perpendicular to the incident beam.

For the case of a nematic or smectic phase with no preferred orientation of the molecules (and also for isotropic liquids consisting of long rod-like molecules), a suitable model would be the same pair of parallel linear chains used above, but now allowing them to take up any orientation with equal probability. Although no formulas are available for this case, we can draw some conclusions from an examination of the interference function (for a definition of the interference function see James$^{(10)}$; roughly, it is equivalent to a weighted reciprocal lattice). When the chains are always parallel to the $c$ axis, the maxima of the interference function form a set of concentric rings around the $c$ axis in a plane through the origin and perpendicular to the $c$ axis (this is the part of the interference function which determines the diffraction pattern along the equator; the remainder of the interference function is not relevant to this discussion) (Ref. (10) pp. 574–8, 582–4). These maxima are rather broad within the plane, but quite narrow perpendicular to the plane. When all orientations of the chains are allowed, the maxima of the interference function, which were ring shaped before, become spheres (spherical shells) around the origin. The radius of each sphere depends not only on the *radius* of the corresponding ring but also upon the *thickness* of this ring perpendicular to the plane of the rings. For very long chains of atoms, the rings are very thin and the radius of a sphere equals the radius of the corresponding ring; thus, the formula $2d \sin \theta = 1.117\lambda$ still holds for the first maximum along the equator. For shorter chains the rings are thicker, the radius of each sphere is larger than the radius of the corresponding ring, and the maxima along the equator are farther apart. In the limit of "chains" of only one atom long, we have again the case of a pair of atoms and the position of the first maximum is given by $2d \sin \theta = 1.229\lambda$. So, the factor with which $\lambda$ is multiplied varies from 1.117 to 1.229, depending upon the length of atom chains. Since the molecules of compounds that form liquid crystals are always fairly long (BOCP is 28 atoms long), the proper factor will be close to 1.117 for these compounds.

For BOCP and its homologues we have experimental evidence that this factor is indeed quite close to 1.117. In Table 2 we find a value of 4.85 Å for the intermolecular spacing in a very well aligned sample at 60 °C, using the factor of 1.117. In Table 1 we find a value of 4.83 Å for the same compound at the same temperature and using the same formula, but for a sample which showed much less alignment; the agreement between these two values is very good. Had we used the factor of 1.229 in the latter case, however, we would have obtained a value of 5.38 Å, and the agreement would have been very bad. Further, the intermolecular spacings in Table 2 (all calculated with the same factor) show the slight increase with temperature one would expect, notwithstanding the considerable decrease in the degree of alignment. Again, the values for the intermolecular spacings in Table 1 vary only slightly from one compound to the next, although the different compounds showed quite different degrees of alignment; comparing Tables 1 and 2, most of the variation in $d_2$ in Table 1 appears to be attributable to the variation in temperature. All this evidence suggests that the same formula should be used for all BACPs and regardless of the degree of alignment. We feel justified, therefore, in using the formula $2d \sin \theta = 1.117\lambda$ for the calculation of all intermolecular spacings in this paper.

## REFERENCES

1. Arora, S. L., Fergason, J. L. and Saupe, A., *Mol. Cryst. and Liq. Cryst.* (1970), to be published.
2. Bijvoet, J. M., Kolkmeyer, N. H. and MacGillavry, C. H., *Röntgenanalyse van Kristallen*, p. 199. Amsterdam: Centen (1948).
3. Brown, G. H. and Shaw, W. G., *Chem. Rev.* **57**, 1049 (1957).
4. Chistyakov, I. G., *Soviet Phys.—Cryst.* **8**, 691 (1964).
5. Chistyakov, I. G. and Chaikowsky, W. M., *Mol. Cryst. and Liq. Cryst.* **7**, 269 (1969).
6. De Vries, A., *Acta Cryst.* **A25**, S135 (1969).
7. Falgueirettes, J., *Bull. Soc. franç. Minér. Crist.* **82**, 171 (1959).
8. Glamann, P. W., Herrmann, K. and Krummacher, A. H., *Z. Krist. A.* **74**, 73 (1930).
9. Gray, G. W., *Molecular Structure and the Properties of Liquid Crystals*, London: Academic Press (1962).
10. James, R. W., *The Optical Principles of the Diffraction of X-rays*, London: Bell and Sons (1958).
11. Klug, H. P. and Alexander, L. E., *X-ray Diffraction Procedures*, New York: John Wiley and Sons (1954).
12. Morrow, R. M., *Phys. Rev.* **31**, 10 (1928).
13. Prins, J. A., *Physica* **6**, 305 (1926).
14. Saupe, A., *Mol. Cryst.* **1**, 527 (1967).
15. Sproull, W. T., *X-rays in Practice*, New York: McGraw-Hill (1946).
16. Stewart, G. W. and Morrow, R. M., *Phys. Rev.* **30**, 232 (1927).
17. Warren, B. E., *Phys. Rev.* **44**, 969 (1933).