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X-Ray Diffraction by Cybotactic Nematics

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Several magnetically aligned liquid-crystal monodomains yielded x-ray diffraction photographs containing four intense maxima about the direct beam characteristic of cybotactic nematics. In the case of *p*-alkoxy benzoic acids, such maxima appear, both, when a smectic-C phase forms at lower temperatures and when the nematic transforms to the crystalline phase directly. The intensity distribution in reciprocal space for azoxybenzene and BOCF was found to lie along two interpenetrating rings whose common diameter is normal to the aligning magnetic field and for *p*-*n*-alkoxybenzoic acids along outwardly curving arcs. Four similarly intense maxima recorded in x-ray diffraction photographs of a thermotropic liquid-crystalline polymer were found to be part of two parallel rings lying in planes normal to the polymer axis.

INTRODUCTION

About fifteen years ago, an unusual x-ray diffraction diagram consisting of four intense maxima symmetrically disposed about the direct beam was obtained from an oriented monodomain of the nematic phase of *p*-*n*-azoxybenzene in Russia¹ and from BOCF in the United States.² The name *cybotactic nematic* was proposed by de Vries² who suggested that the molecules group themselves into isolated planar arrays resembling fragments of the layers formed by these mesomorphs in the smectic-C phase at lower temperatures. In a more recent review article, de Vries further suggested that such "skewed" cybotactic nematics are observed only if the liquid crystal exhibits both a nematic and a smectic-C phase.³ This model went unchallenged for ten years when Azároff argued that the de Vries model could not account adequately for all such diffraction data reported in the literature.⁴

In order to align the liquid-crystal molecules in a monodomain, it is usual to place the sample in an external magnetic field. When a conventional magnet is used for this purpose, it is most convenient to direct the incident x-ray beam at right angles to, both, the stationary magnetic field direction and the specimen holder. Such a normal-beam (Laue) arrangement limits the investigator's ability to explore the intensity distribution throughout reciprocal space, however, so that Azároff suggested in his review of the x-ray diffraction by liquid crystals⁵ that moving-film cameras should be used instead. In what follows, it will be shown that the intensity distribution observed with a Buerger precession camera equipped with an attached (moving) magnet is not consistent with any of the molecular arrays proposed to date. Based on a study of a series of odd and even $p - n$ -alkoxybenzoic acids, it will be shown further that similar diffraction intensities are observed in this series for liquid crystals that do not form smectic phases. Finally, an analogous intensity distribution recorded for a thermotropic liquid-crystalline polymer also will be described.

EXPERIMENTAL PROCEDURE

A Buerger precession camera⁶ is especially suited for the examination of liquid-crystal monodomains for a number of reasons: In its "zero" setting, the incident x-ray beam is normal to the flat-film cassette. The diffracting sample, therefore, is readily accessible to external heaters, chillers, and magnetic fields. Most importantly, the diffracted intensity distribution can be recorded at the "zero" level as well as in upper levels, i.e., throughout reciprocal space, without distortion except for a known 'magnification' factor. For these reasons, the Buerger precession camera shown in Fig. 1 is equipped with a permanent magnet ($H = 2,200$ gauss) attached to the specimen spindle so that it precesses with the sample during an x-ray exposure thereby maintaining the alignment of the liquid-crystal monodomain. A temperature-controlled stream of air passes over the sample (through the tube on the left in Fig. 1) and maintains it to within $\pm 1^\circ\text{K}$ as determined by a thermocouple placed adjacent to the glass capillary containing the liquid crystal. Filtered Co $K\alpha$ radiation is used throughout to obtain maximal dispersion of the diffraction maxima at optimal exposure times. (Occasionally, Cr $K\alpha$ radiation is used to increase the dispersion.) The centers of the x-ray reflections were determined with a film

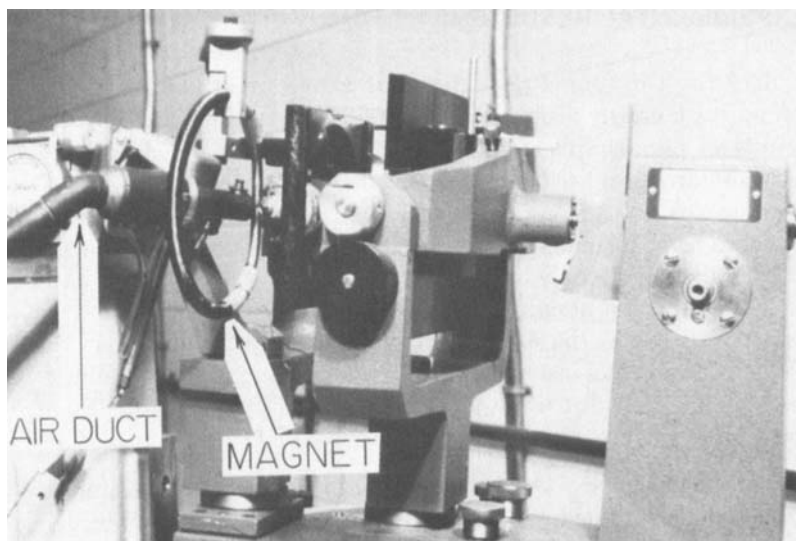


FIGURE 1 Buerger precession camera equipped with a permanent magnet. The temperature of the sample is controlled by a stream of heated (cooled) air passing through the tubing seen on the left.

reader as well as by locating their maximum optical densities with a Quantimet image analyzer.

Highly pure liquid crystals of 4,4'-dibutoxyazoxybenzene, bis-(4'-*n*-octyloxybenzal)-2-chloro-4,4'-phenylenediamine (BOCP), and of an odd and even series of *p*-*n*-alkoxybenzoic acids were obtained from a commercial supplier.⁷ These mesomorphs were placed in a cylindrical lindenman-glass capillary of 0.7 mm diameter oriented at right angles to the magnetic field lines and the incident x-ray beam at the "zero" camera setting. X-ray diffraction photographs were recorded using single and multiple-film packs for the zero level and an upper level ($\xi = 0.04$) at several temperatures ranging from just above the smectic-C transition temperature to the clearing-point temperature. A specimen of a thermotropic polyester with azoxybenzene mesogenic units and flexible spacers in the main chain, prealigned in the nematic range in a magnetic field of ~ 15 T, was provided by Professor A. Blumstein. This specimen had to be refrigerated subsequent to its alignment so that the air stream flowing over chunks cut from the sample (approx. $1 \times 1 \times 0.5$ mm) was maintained at 277°K. Since this specimen is solid at this temperature, the magnet shown in Fig. 1 was not required and considerably greater freedom existed in exploring the reciprocal space.

EXPERIMENTAL RESULTS

BOCP. The four x-ray reflections characteristic of a cybotactic nematic are clearly visible about the direct beam in Fig. 2 showing a zero-level photograph of BOCP, i.e., the plane in reciprocal space passing through the origin. When the layer-line screen and film position are set to record upper levels in reciprocal space parallel to this zero level, a similar photograph results except that the four inner reflections move symmetrically towards the direct beam. The centers of these reflection are indicated in Fig. 3 for $\zeta = 0.00, 0.04$, and 0.05 , respectively, where the size of the ellipses suggests the maximum value of the experimental error estimated by comparing manual readings to those obtained with the automated image analyzer. (ζ is the distance in reciprocal-space units normal to the zero level.)

***p*-azoxybenzene.** A zero-level photograph of 4,4'-dibutoxyazoxybenzene recorded with Cr $K\alpha$ about two years ago resembled Fig. 2. Because the moving magnet employed at that time was weaker ($H \sim 1,000$ gauss), the four spots are elongated along the horizontal, i.e., at right angles to the magnetic field. Although location of their centers, therefore, is less precise, a comparable progressive displacement of the reflections towards the film center (Fig. 3) was noted in upper levels recorded at $\zeta = 0.04, 0.05, 0.06$, and 0.07 , respectively.

***p*-*n*-alkoxybenzoic acids.** The transition temperatures for the various mesomorphs of *p*-alkoxybenzoic acids have been reported by Herbert.⁸ Although a special attempt to check these values was not made, they agree quite well with corresponding values noted in the present study. In the even-numbered series, a nematic to smectic-C transition is observed for $n = 8, 10$, and 12 , while for $n = 4$ and 6 the solid transforms directly to the nematic phase. Similarly, for the odd-membered series, a nematic to smectic-C transition is observed only for $n = 7, 9, 11$, and 13 .

All of the odd- and even-numbered compounds having a nematic and smectic-C phase were examined in the present study, both, by recording zero and upper-level photographs. The zero-level photographs resembled closely those recorded for BOCP (Fig. 2). Upper-level photographs recorded at $\zeta = 0.04$, however, showed that the reflections moved *outward* at right angles to the magnetic field while retaining their vertical separation (parallel to the magnetic field) virtually unchanged. Several compounds were examined at two or three temperatures spanning the nematic range and the four inner reflections were found to persist throughout this temperature range

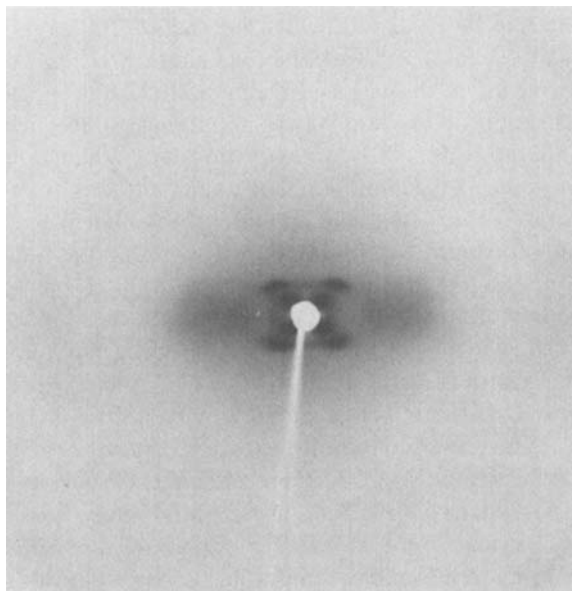


FIGURE 2 Zero-level precession photograph of BOCP (Co $K\alpha$, $\mu = 18^\circ$).

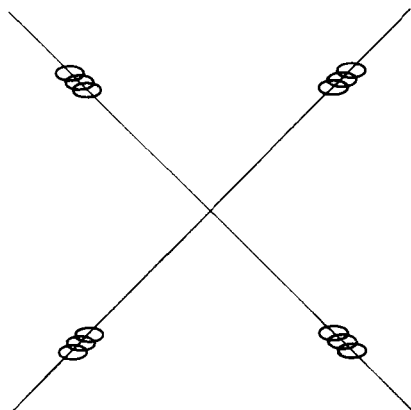


FIGURE 3 Locations of inner reflections of BOCP in zero level ($\zeta = 0.00$) and upper levels recorded at $\zeta = 0.04$ and 0.05 , respectively.

although they became elongated at right angles to the magnetic field. The effect of the magnetic field strength also was examined by recording the zero levels at full field strength ($\sim 2,200$ gauss) and half strength ($\sim 1,100$ gauss) and with the field shut off. The monodomain alignment persisted in the reduced magnetic field but vanished when the field was shut off. One sample was maintained subsequently at the nematic temperature for 48 hours with no field. When the magnetic field was turned on, the monodomain alignment was fully restored. This was done to verify that the alignment was due to the field and not a wall effect caused by the capillary containing the liquid crystal since such an alignment due to capillary wall effects had been observed in previous studies of BOCP.

To establish whether cybotactic nematics occurred only when a liquid crystal exhibits nematic *and* smectic-C phases, the nematic phases for $n = 4, 5$, and 6 were examined by recording their zero-level photographs. The four inner reflections characteristic of cybotactic nematics were observed in all of them although they were somewhat broadened, particularly for $n = 4$. These photographs were recorded at temperatures that were a few degrees above the solid-nematic transition temperature for that compound.

Thermotropic polyester. The alignment of the mesogenic units in a highly viscous liquid-crystalline polymer requires magnetic field strengths orders of magnitude larger than those attainable with the movable magnet shown in Fig. 1. Once such a polymer is aligned, however, the mobility of the mesogenic units is so small that the alignment can be maintained for very long times without requiring a magnetic field as long as the sample is maintained at temperatures below its glass transition temperature. This means that the sample can be examined without a magnet in the x-ray diffraction experiment so that a larger precession angle can be used in recording upper levels in reciprocal space and the sample can be positioned at will relative to the direct beam direction.

A zero-level photograph of such a polymer is shown in Fig. 4 and it resembles closely the normal-beam photograph previously reported by Blumstein et al.⁹ Upper-level photographs at $\zeta = 0.06$ and 0.10 also were recorded. The differences in these upper levels of interest to the present study are that the four inner reflections are displaced but not towards the film center (direct beam). Instead, they retain their separation along a direction parallel to the polymer axis but move towards each other, forming rings in planes normal to this direction as can be seen in Fig. 5.

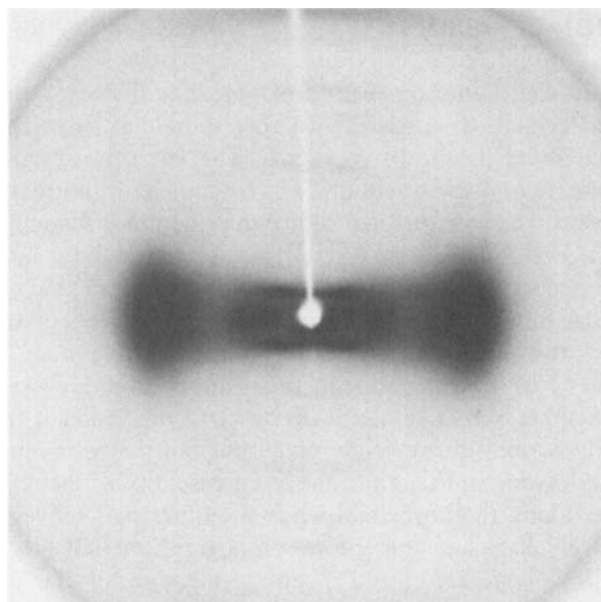


FIGURE 4 Zero-level precession photograph of a thermotropic polyester with azoxybenzene mesogenic units and flexible spacers (Co $K\alpha$, $\mu = 30^\circ$).

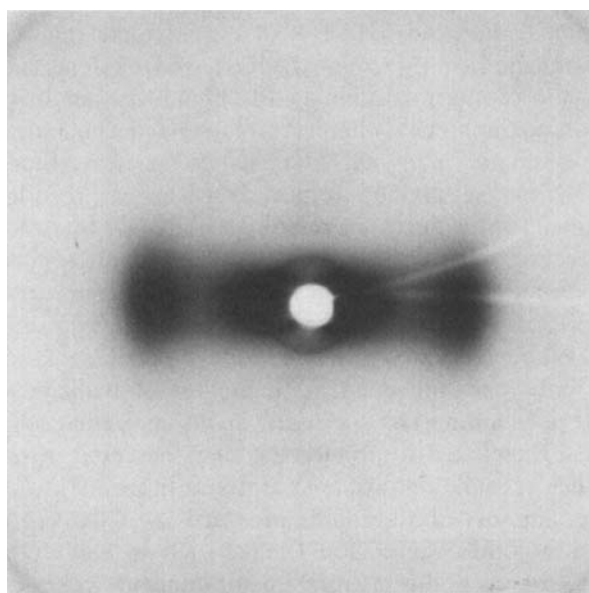


FIGURE 5 Upper-level precession photograph of the thermotropic polyester at $\zeta = 0.06$ (Co $K\alpha$, $\mu = 30^\circ$). (Same sample and orientation as in Fig. 4.)

DISCUSSION OF RESULTS

The intensity distribution in reciprocal space for the first two monomeric liquid crystals discussed above corresponds to two rings intersecting each other as shown in Fig. 6. The left side of this figure depicts these two rings when the magnetic field is normal to the incident beam which is directed along their common diameter. The right side of Fig. 6 depicts the same rings rotated about a horizontal axis which occurs when the magnetic field is tilted so that it is not perpendicular to the incident beam. The reciprocal-lattice plane passing through the origin intersects the interpenetrating rings in four symmetrical spots regardless of tilt. In an upper level, however, these four intersections move symmetrically towards the center if the magnetic field is normal to the origin plane but not if it is inclined to it (right-hand drawing in Fig. 6). In the latter case, two of the reflections move closer along the horizontal while the other pair moves further apart. Figure 7 shows an upper-level photograph of BOCP when the magnetic field is rotated by 25° about the axis of the capillary containing the liquid-crystal sample. The relative displacements of the pairs of reflections are clearly evident. (A confirming series of photographs was recorded with $\text{CrK}\alpha$ radiation which provided larger dispersion of the reflections.)

The alignment direction (director) of the monomer molecules lies along the magnetic field direction which is orthogonal, i.e., normal to the axis of the capillary containing the liquid crystal. In order to determine photographically whether the cybotactic nematic has the cylindrical symmetry of a normal nematic, therefore, requires the rotation of the magnet about a vertical axis. This can be done in the arrangement shown in Fig. 1 by rotating the magnet by $\sim 20^\circ$ about the field direction. The resulting series of photographs confirmed the intensity distribution reproduced in Fig. 6 thereby demonstrating that such cylindrical symmetry is absent. It nevertheless is difficult to deduce what the molecular array is in the cybotactic nematics examined since only one 'independent' reflection is available for this purpose. (It is tempting to speculate about molecular alignments along conical directions to produce the rings observed in reciprocal space but such speculations are not fruitful at this time.)

The larger number of reflections provided by a liquid-crystalline polymer, on the other hand, should make such an analysis possible. In this case, however, the intensity distribution in reciprocal space corresponds to two parallel circles lying in planes that are normal to the polymer axis. Unlike the monomers, the intensity distribution for

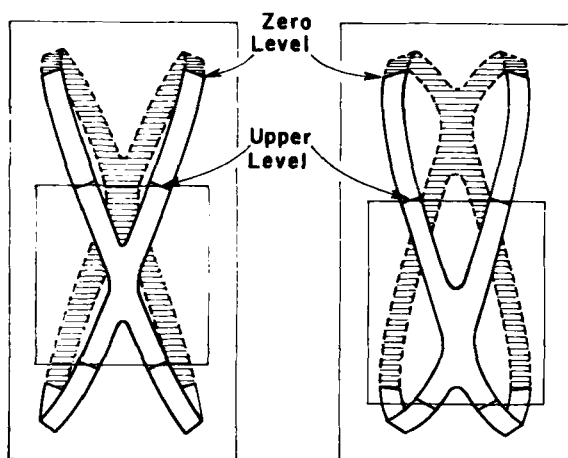


FIGURE 6 Intensity distribution in reciprocal space for the innermost reflections from BOCP. The plane of the magnetic field is drawn normal to the incident x-ray beam on the left and tilted on the right.

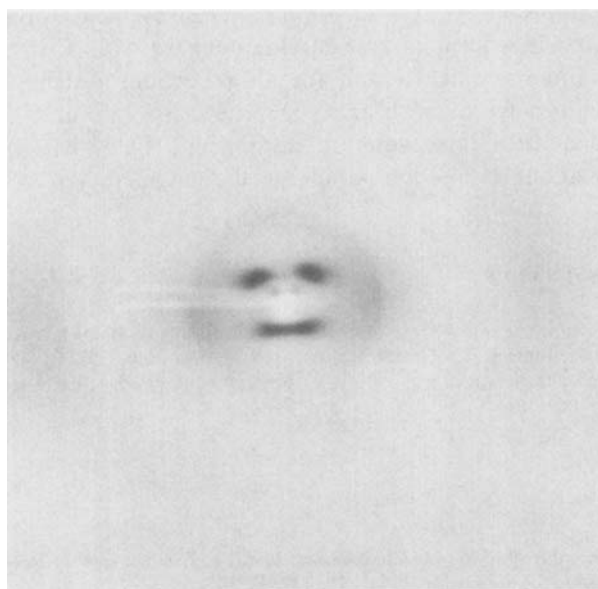


FIGURE 7 Upper-level precession photograph of BOCP ($\xi = 0.04$) with the magnetic field tilted by 25° from normal to the incident beam (Co $K\alpha$, $\mu = 18^\circ$).

all recorded reflections of the polymer has cylindrical symmetry about a direction parallel to the polymer axis. Whether the intense inner reflections in such a polymer provide evidence of the formation of a cybotactic nematic array, as has been suggested,⁹ remains to be determined. A more thorough study of such polymers is currently in progress and its results will be reported elsewhere.

CONCLUSIONS

Although it is not yet possible to propose a unique molecular model for a cybotactic nematic, several conclusions can be drawn from the present study:

1. The molecular array in a monodomain produced by placing a cybotactic nematic in a magnetic field lacks the cylindrical symmetry of a regular nematic domain.
2. Instead, the molecular arrays in *p*-azoxybenzene and BOCF produce a diffracted intensity distribution in reciprocal space that lies along two interpenetrating circles whose common diameter is normal to the magnetic field.
3. The molecular arrays in *p*-*n*-alkoxybenzoic acids produce diffracted intensities forming arcs curving outward.
4. The intensity distribution for all reflections obtained from a thermotropic polyester with azoxybenzene mesogenic units and flexible spacers, after orientation in a magnetic field, has cylindrical symmetry about a direction parallel to the polymer axis.

Acknowledgements

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