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X-RAY STUDIES OF LIQUID CRYSTALS VI (*)
THE STRUCTURE OF THE SMECTIC A, C, Bn AND Bt PHASES
OF TRANS-1,4-CYCLOHEXANE-DI-N-OCTYLOXYBENZOATE (**) 

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Abstract. — The smectic A phase of trans-1,4-cyclohexane-di-n-octyloxybenzoate (TCOB) appears to be a tilted smectic A phase. The uniaxial character of this phase is not caused by an absence of tilt, but rather by an absence of long-range order of the direction of tilt. The C-A phase transition is marked by the disappearance of this long-range order.

The smectic B phases of TCOB are different from most other B phases because of an unusually large disorder in the alkyl end-chains of the molecule, the result of the large intermolecular distance caused by the cyclohexane ring in the center of the molecule. The disorder in the alkyl chains disrupts the coupling between adjacent layers. As a consequence, the tilted smectic B phase has no three-dimensional order.

1. Introduction. — Trans-1,4-cyclohexane-di-n-octyloxybenzoate (TCOB) exhibits the following phases [1] :

\[ \text{XI} \rightarrow \text{B}_t \rightarrow \text{B}_n \rightarrow \text{C} \rightarrow \text{A} \rightarrow \text{Is} \]

We have used x-ray diffraction to determine the smectic layer thickness \( d \) and the average distance \( D \) between the long axes of neighboring molecules in all four smectic phases.

The primary aim of our study was to obtain information about the tilt angle in the A and C phases of TCOB by measuring \( d \). The reason for this special interest was a long standing belief in the existence of tilted smectic A phases [2-4] and, consequently, of different kinds of A-C phase transitions [4] (see sections 2 and 5.3.2 below). Towards the end of our investigation it became apparent that the smectic B phases were also very interesting. By combining the data on \( d, D \), and the profile of the outer diffraction ring, it has been possible to draw definite conclusions about the special character of the B phases of TCOB, particularly regarding the relative degrees of order of the central part of the molecule on the one hand and the alkyl chains on the other (see section 5.3.1 below).

2. Different kinds of A and C phases. — It is usually assumed that in A phases the molecules are perpendicular to the smectic planes, and that in C phases they are tilted. As a consequence, one expects \( d's \) in the A phases to be about equal to the molecular lengths, but in the C phases to be much less than that. Compounds that exhibit both an A and a C phase are especially interesting. Two important features have now become apparent from the studies of such compounds: (1) No compound has been found in which \( d \) changes discontinuously at the A-C phase transition. (2) There are at least two distinctly different types of A-C phase transitions [4].

One type of A-C phase transition was first observed in TBBA, which has been very extensively studied (for a listing of papers see reference [5]). The x-ray work [6, 7] showed that \( d \) is essentially independent

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of temperature and approximately equal to the
molecular length in the A phase, and that there is no
change in \( d \) at the A-C transition. In the C phase,
however, there is a very significant decrease in \( d \) with
decreasing temperature.

It has been widely assumed that the behaviour
observed for TBBA represented the general pattern
for the A-C phase transition. As De Vries has pointed
out [2, 4], however, Diele, Brand and Sackmann [8]
in 1972 reported a number of compounds for which (1)
\( d \) was significantly less than the molecular length in
the A phase, and (2) \( d \) was essentially independent
of temperature in the C phase. Similar results have been
reported recently on three different compounds [4, 9,
10] and we now want to present the results of a more
detailed investigation [11] of yet another compound,
TCOB. All this evidence indicates that (1) these
compounds exhibit a different type of A-C transition
than TBBA and (2) they exhibit a tilted smectic A
phase. Wulf has developed a model for this type of
A-C transition [12].

3. Experimental procedures. — X-ray diffraction
photographs from samples in glass capillaries
(0.5 mm diameter) were recorded on flat film with
the camera described earlier [13], using Ni-filtered Cu
radiation. The temperature of the sample was deter-
mained with a thermometer calibrated using melting
point standards [14], and the distance from the
sample to the film was determined via the diffraction
patterns of aluminum powder samples [14].

All photographs were measured on the Optronics
P-1000 Photoscan. This instrument is a digital
densitometer which converts the photographic pattern
into numerical data stored on magnetic tape. These
data were then analyzed with a number of computer
programs developed at Kent State University for
this purpose.

4. Data Analysis. — 4.1 OUTER RING DIAMETER. —
Because we used the Optronics Photoscan, our
methods for analyzing the data are now quite different
from what they were before [14], and should be
explained in some detail. All work was done with
the numerical data on the tapes, described above.

The center of the outer diffraction ring is determined
with an iterative procedure. Scans along lines from
this center through the outer ring are made in a
large number of different directions \( \alpha \) (Fig. 1). In
each scan, the diffracted intensity \( I \) is determined as
a function of the distance \( R \) from the center of the
ring (Fig. 2). On either side of the peak, the inflection
point is determined (i.e. the point where \( \Delta I/\Delta R \)
is maximum; points 1 and 2 in figure 2), and a horizontal
line is drawn through the point half-way between the
two inflection points, from one side of the peak to
the other. The middle of this line is taken as the
peak position. The distance between the peak positions
for the angles \( \alpha \) and \( \alpha + 180^\circ \) is taken as the diameter
of the diffraction ring for the angle \( \alpha \).

Plotting these diameters as a function of \( \alpha \), we found
that none of the diffraction rings were true circles,
and that they were much more appropriately represent-
ed by ellipses (Fig. 3). We assumed that the diffraction
rings are elliptical because the plane of the film
cassette in the x-ray camera is not quite perpendicular
to the direction of the incident beam, but rather
somewhat tilted. The data from the aluminum
samples appeared to be the most accurate (the dif-
fraction maxima are sharper !), and we decided to
calculate the magnitude (4.70°) and direction of the
tilt of the film cassette from these data and then to
correct all data for the tilt so calculated (Fig. 3). For
each photograph, the corrected diffraction ring dia-
eters were averaged over all \( \alpha \) values, and this
average was taken as « the diameter » of the outer
diffraction ring on that photograph. This procedure
enabled us to make use of all available data. Also,
the random error in the measurement of the diameter is now less than the apparent variation in the sample-to-film distance, whereas previously [14, 15] the two were about equal.

4.2 INNER RING DIAMETER. — The diameters of the inner diffraction rings were determined in essentially the same manner as for the outer rings. In all cases the second-order maxima were used rather than the first-order ones, and the averaging of the diameters was limited to a small number of \( \alpha \) values for which the second-order maxima were well enough developed.

4.3 FORMULAS USED. — From the diffraction ring diameter one obtains the corresponding diffraction angle \( 2 \theta \). The diffraction angle of the second-order inner ring yields the spacing \( d \) of the smectic planes via the formula \( 2d \sin \theta = 2 \lambda \), where \( \lambda \) is the wavelength of the radiation used (1.5418 Å). The diffraction angle of the outer ring yields the intermolecular distance \( D \), but the formula depends on the model one uses for the molecular arrangement within the layer. If one assumes an ordered arrangement with a hexagonal lattice, the formula is \( 2D \sin \theta = 1.1547 \lambda \) [16]. If one assumes a disordered arrangement, the formula is \( 2D \sin \theta = 1.117 \lambda \) [13].

5. Results and Discussion. — 5.1 INTERMOLECULAR DISTANCE — THE OUTER RING DIAMETER. — The outer ring diameter as a function of temperature is given in figure 4. The data can be very well represented by two straight lines: one for the ordered phases \( (B_1 \) and \( B_n \)), another one for the disordered phases \( (C \) and \( A \)). The ring diameter does not appear to be influenced by tilt, but it does depend upon temperature.

The corresponding intermolecular distances are given in figure 5. The data can again be very well represented by separate straight lines for the ordered and for the disordered phases. The slopes of these lines are \( 2.22 \times 10^{-3} \text{Å}/\text{°C} \) for the ordered phases and \( 2.34 \times 10^{-3} \text{Å}/\text{°C} \) for the disordered phases, with standard deviations of \( 0.18 \times 10^{-3} \) and \( 0.15 \times 10^{-3} \), respectively. These slopes agree closely with the values determined by De Vries [15] for the isotropic phases of mesogenic compounds, indicating that the linear expansion coefficients are essentially the same. The standard deviation for the individual data points, determined from a least-squares analysis of the straight lines, is 0.002 Å for the ordered phases and 0.003 Å for the disordered phases. This represents a significant improvement over the value of 0.006 Å obtained with the old method of data analysis [15].

Figure 5 shows a significant decrease in \( D \) at the \( B-C \) transition, but it is not clear how this should be interpreted [16]. Beyond question, however, is the fact that in all phases the \( D \) values are much larger than for other compounds studied so far [16]: around 5.3 Å as compared to the usual 4.9-5.0 Å. Since TCOB has a cyclohexane ring in the molecule, and none of the other compounds [16] contains this group, we suspect the cyclohexane ring to be the cause of
the larger intermolecular distance. This hypothesis receives further support from two other observations. First, a cyclohexane ring is not planar like a benzene ring, and the carbon atoms of a cyclohexane ring carry two hydrogen atoms each whereas the carbon atoms of a benzene ring carry only one hydrogen atom each. Thus, one would indeed expect a cyclohexane ring to need more space than a benzene ring. Second, it can be calculated from the data on the crystal structure of the C₁ homologue of TCOB [17] that in this crystal structure, with molecules essentially parallel to each other, the distance between the long axes of neighboring molecules is 5.30 Å, in excellent agreement with the distances shown in figure 5.

A discussion of the consequences of this large intermolecular distance and the confirmation of these consequences by other data from our current investigation follows in section 5.3.

5.2 Smectic Layer Thickness — The Inner Ring Diameter. — The smectic layer thickness d, calculated from the diameter of the inner diffraction ring (see section 4.3), is given in figure 6. Further investigations have indicated to us that the first point in the Bₙ phase in figure 6 represents a pre-transition effect of the approaching Bₙ phase. Disregarding this data point, the following general observations can be made from figure 6.

1. In the Bₙ phase d is significantly larger than in any other phase.
2. In the C phase the change in d with temperature is small and approximately linear.
3. In the A phase there is no apparent change in d with temperature, and there also is no apparent change in d at the C-A phase transition.
4. In the Bₙ phase d is less than in the C phase, but this could easily be the result of a continued slight decrease of d with decreasing temperature, extrapolated through the Bₙ phase (broken line in figure 6).

Behaviour similar to this has been reported for three other compounds [4, 9, 10], and we are convinced that this behaviour is characteristic for most — if not all — compounds with the phase sequence A-C-Bₙ-Bₙ and also for compounds with the phase sequence A-C-Bₙ if one disregards, of course, the observation on the Bₙ phase. The explanation for this behaviour is given below in section 5.3.2.

5.3 Molecular Length and Tilt in the Layers. —

5.3.1 The B phases. — We have calculated the length of a fully extended molecule of TCOB by combining the length of the central part of the C₁ homologue (obtained from the crystal structure [17]) with the length of the alkyl chains, using standard bond lengths and angles. This gives a total length l = 41.9 Å. Consequently, even in the Bₙ phase d is still about 4 Å shorter than l, a difference much larger than found by De Vries for smectic phases with molecules perpendicular to the layers [15]. The reason for this, we believe, is not tilt but rather the large intermolecular distance between the molecules in the smectic layer (see section 5.1). Because of this large distance, the alkyl chains are packed very loosely and are no longer predominantly in the extended conformation as they are in most other compounds.

The statement has often been made (see, e.g., reference [18], p. 285) that the alkyl chains in smectic layers can be considered as fluid. We believe that such a statement is misleading for most compounds because the lack of space between the molecules constrains the alkyl chains to a predominantly extended conformation, with neighboring chains essentially parallel to each other. TCOB, however, appears to be a compound for which the concept of fluid chains is appropriate. The shape of the outer diffraction maximum (Fig. 7) further confirms this. For a disordered phase (Fig. 7d) there is a single broad maximum; for an ordered phase (Fig. 7a) there is a single sharp maximum; but for the Bₙ and Bₙ phases of TCOB (Figs 7b and 7c) there is a relatively sharp maximum (caused by the ordered central parts of the molecules) superimposed on a broad maximum (caused by the disordered tails).

In the Bₙ phase the much smaller d value (Fig. 6) indicates a considerable tilt of the molecules. The overall molecular conformation stays the same, as indicated by the absence of any discontinuity at the Bₙ-Bₙ transition in the D versus t graph (Fig. 5). Other phases have in the literature been assigned the symbol Bₙ on the basis of miscibility studies, but we feel that this is structurally inappropriate because all these phases show three-dimensional order, and the identification B should be reserved for phases with only two-dimensional order [19]. The Bₙ phase of TCOB appears to be a true tilted B phase: the x-ray
Determinations of the layer-thickness in a number of compounds [15] are in agreement with this supposition. In TCOB, however, and in other compounds with the phase sequence $A-C-B_\infty$ [4, 9, 10], the layer thickness in the $A$ phase is significantly less than in the $B_\infty$ phase (Fig. 6). Doucet and Levelut [10] have explained this by assuming that in the $A$ phase the alkyl chains have more kinks than in the $B$ phase, but we believe this explanation to be incorrect. In TCOB, as in the other compounds [4, 9, 10], the layer thickness within the $A$ phase is essentially independent of temperature, indicating that the number of kinks in the chains is also essentially independent of temperature. Since the structure of $A$ and $C$ phases is basically very similar, one can conclude that in the $C$ phase the number of kinks will also remain essentially the same. This would mean that any significant difference between the number of kinks in the $A$ and $B$ phases would have to be introduced at the $B_\infty-C$ transition. This would indeed be the logical place for it, since this is the transition from the ordered to the disordered regime. There are two independent pieces of evidence, however, that argue against any significant increase in the number of kinks at the $B-C$ transition.

First, if compounds with the phase sequence $A-C-B$ have significantly more kinks in the $A$ phase than in the $B$ phase, then the molecules in other $A$ phases would probably also have a significant number of kinks. However, in studies of other smectic $A$ phases, the molecules appear to be predominantly in the extended conformation [15]. Second, NMR data has been interpreted as showing that the preferred conformation of molecules remains unchanged throughout all liquid crystal phases and phase transitions investigated [21, 22], and that there is no significant effect of mesophase structure on the kink statistics [23].

We find supporting evidence for this in our data on TCOB. First, more kinks would cause an increase in the intermolecular distance, but no indication is found for such an increase (section 5.1). Second, the data points for the layer thickness in the $B_\infty$ and $C$ phases appear to be part of one continuous curve (the broken line in figure 6).

For these reasons, we propose that in TCOB, as in other compounds which show similar behaviour [4, 9, 10], the molecular configurations in the $A$ and $C$ phases are essentially the same as in the $B_\infty$ phase. The difference in layer thickness is caused by a significant tilt in the $A$ and $C$ phases. This tilt persists through the $C-A$ transition and throughout the $A$ phase [4]. If we take the layer thickness of the $B_\infty$ phase as the effective length of the molecule and calculate the tilt angle as $\alpha = \cos^{-1}(d/d(B_\infty))$, we find the values indicated in figure 8, ranging from 21° in the $B_\infty$ phase to 17° in the $A$ phase. In the $B_\infty$ phase the tilt is zero, except for the one point affected by pre-transition effects. The difference between the $A$ and the $C$ phase of TCOB, then, is not a difference in the

diffraction pattern shows a total absence of any indication of three-dimensional order. This absence is perfectly understandable on the basis of the model given above for its structure: the fluidity of the alkyl chains prevents correlation between the two-dimensional lattices of the individual layers. This model bears some resemblance to the model of De Gennes and Sarma (reference [20] and reference [18], p. 287) for the smectic $B$ phase, but there is also a difference: De Gennes and Sarma predict that the outer maximum is not a Bragg peak, but we find that it is fairly sharp.

A further consequence of the large intermolecular distance and the fluidity of the alkyl chains is that in both $B$ phases even the two-dimensional order within the layers is less well developed than in the $B$ phases of other compounds, as evidenced by the relatively broad profile of the corresponding diffraction maxima (Fig. 7b and 7c).

5.3.2 The $A$ and $C$ phases. — In the $A$ phase the molecules have generally been supposed to be perpendicular to the smectic layer, as in the $B_\infty$ phase.
magnitude of the tilt angle, but rather a difference in the long-range order of the direction of tilt. In the C phase the direction of tilt has long-range order within the layers as well as between the layers, but in the A phase the direction of tilt has no long-range order [3, 4, 11, 12]. This difference between the C-A transition of TCOB and similar compounds on the one hand, and that of TBBA [6] and its homologues [7] on the other hand—in TBB and its homologues—the tilt angle does go to zero at the C-A transition—is further confirmed by the difference in temperature dependence of d in the C phase: in TCOB it is much smaller (Fig. 6) than in TBBA and its homologues [7].

6. Conclusions. In terms of the subdivision of smectic A and C phases proposed by De Vries [2, 4], the A and C phases of TCOB can be classified as follows:

The smectic A phase of TCOB is a smectic A3 phase: the molecules are tilted with respect to the normal to the layer, with a tilt angle of about 17°, and the uniaxial character of the phase is caused by the absence of long-range order of the direction of tilt.

The smectic C phase of TCOB is a smectic C4 phase: the tilt angle is rather small, about 18°, and varies only slightly with temperature, from 17° to 19°.

The cyclohexane ring in the center of the TCOB molecule appears to cause the molecules to be further apart from each other than in other compounds, and, as a result of this, the alkyl chains at the ends of the molecule are much more disordered. This has the following consequences for the A phases:

In the smectic B* phase of TCOB the molecules are perpendicular to the layers, but the thickness of the layers is reduced because of the disorder in the chains. It will probably not be possible in this B* phase to obtain large ordered domains in which the lattices of adjacent layers are all parallel, because the disorder in the chains reduces the coupling between the layers which is present in most other B* phases [24].

In the smectic B phase of TCOB the reduced coupling between the layers, caused by the disorder in the alkyl chains, apparently removes the possibility of the development of any kind of three-dimensional order. As a consequence, the overall order in the B phase of TCOB is significantly less than in the B phase of TBBA.

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Fig. 8. — Tilt angle as function of temperature (see also legend of figure 6).