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Structure of the smectic D phase

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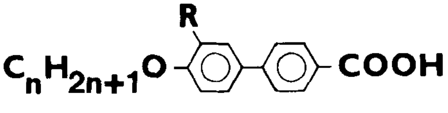
The so-called 'smectic' D phase of 4′-*n*-octadecyloxy-3′-cyanobiphenyl-4-carboxylic acid (one of only four materials known to exhibit this phase) has been shown unambiguously by X-ray diffraction to be characterized by a primitive cubic space group. The space group is either *P*23 or *Pm*3, and the lattice parameter a_0 is 86 Å. It is shown that data from previous studies of this phase may be re-intepreted to be consistent with these findings. In view of these conclusions it is clearly inappropriate to refer to the phase as smectic.

1. Introduction

At the present time, four materials are known to exhibit the 'smectic' D phase. These are the biphenyl carboxylic acids with the general formula



where n = 16 or 18 and R is either NO_2 or CN. For brevity, these materials will be referred to in the remainder of this paper simply by specifying n and R, and in the light of our conclusions we shall refer to the phase simply as the D phase. This phase was first observed in 16 : NO_2 and 18 : NO_2, by Gray and co-workers in 1957, although the phase was not defined as 'smectic D' until these acids were investigated by Demus *et al.* [1]. Subsequently, Pelzl and Sackmann [2] showed that the D phase is optically isotropic, and suggested that this indicated a structure possessing cubic symmetry.

Attempts to confirm this point using X-ray diffraction have been hampered because, in the relatively high temperature range where the D phase occurs, the 16 : NO_2 and 18 : NO_2 acids deteriorate quite rapidly. The D phases of 16 : CN and 18 : CN first observed by Goodby and Gray [3] have now been found to be appreciably more stable, and this paper reports the first X-ray diffraction measurements on a new preparation of one of these materials (18 : CN). This has the following phase behaviour:

$$\mathrm{K} \xrightarrow{131^{\circ}\mathrm{C}} \mathrm{S_C} \underset{138^{\circ}\mathrm{C}}{\overset{156^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{D} \underset{200^{\circ}\mathrm{C}}{\overset{201^{\circ}\mathrm{C}}{\rightleftharpoons}} \mathrm{I}.$$

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The CN and NO_2 compounds are completely miscible in the D phase so that it is clear that this phase is the same for all four compounds.

Two X-ray diffraction studies of the D phase of the NO_2 acids have been reported in the literature. In each of these studies, a weak and diffuse ring corresponding to a *d* spacing of ~4·5 Å was always observed, which presumably arises from liquid-like intermolecular ordering.

Diele *et al.* [4] examined the 16 : NO_2 and 18 : NO_2 using a flat film technique and, for the former, reported a non-regular hexagonal set of Bragg reflections at small scattering angles. They assumed a cubic unit cell and indexed these as {110} reflections, which would correspond to the [111] direction lying parallel to the incident beam. This yielded a lattice parameter of 61 Å. A structure was postulated in which spherical aggregations of the aromatic parts of molecules are packed in a cubic lattice, while disorder between hydrocarbon chains gives rise to the diffuse scattering.

Tardieu and Billard [5], on the other hand, made powder diffraction measurements of a 16 : NO_2 sample using the Debye–Scherrer method with a rotating sample. Six reflections were observed and were indexed assuming a cubic unit cell according to the a_0/d ratios $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{8}$, $\sqrt{10}$, and $\sqrt{11}$. Because of the presence in this series of $\sqrt{7}$, a body-centred cubic lattice was proposed (space group $Ia3d$) with the first reflection indexed as (211), giving a lattice parameter of 102 Å. By analogy with lipid–water systems (Luzzati and Spegt [6]), a model was proposed consisting of two interpenetrating infinite three-dimensional networks of interconnected rods, where the rods may represent either the positions of the aromatic groups or of the hydrocarbon chains. Tardieu and Billard appeared to favour the former option, although they did not discuss space-filling or X-ray intensities for either possibility.

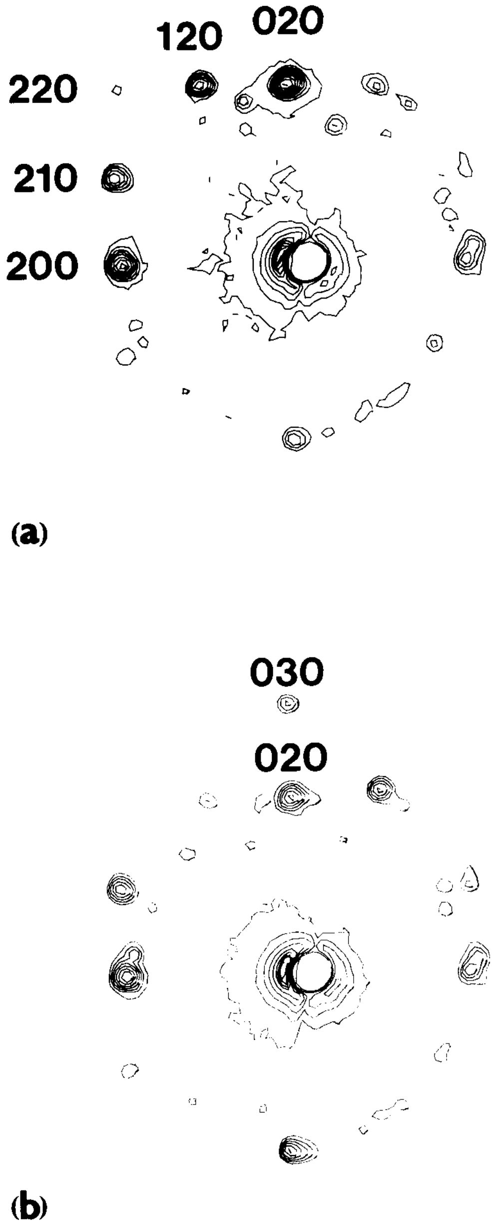
2. Experiment

The sample of the 18 : CN acid was tightly sealed in a cylindrical beryllium cell of 1·0 mm i.d. and 3·0 mm o.d. which was mounted on a modified and automated Hilger–Watts four-circle diffractometer. Diffraction patterns were measured using a multi-wire position-sensitive area detector. Data were acquired in the form of a 400 × 400 array with a position resolution of ~0·5 mm. A similar detector system has been described in detail by Bateman *et al.* [7, 8]. With a sample to detector distance of about 1·1 m, a scattering angle range of 0·5° to 5° was covered, giving a minimum *d*-spacing of approximately 17 Å, using $\lambda = 1{\cdot}54$ Å.

Initial measurements on the D phase showed a large number of reflections at all sample orientations, characteristic of randomly oriented domains but not of a good powder sample. The sample was held at a temperature of 175°C in the D phase for 3 weeks, during which time the number of domains decreased and the domain size increased. By suitably orienting the sample, it was then possible to identify particular reflections from a major domain, although the diffraction patterns still contained reflections from neighbouring domains.

3. Results

The figure shows diffraction patterns measured at two sample orientations. The diffuse ring at $d \sim 4.5$ Å is outside the range of the detector for these measurements, although it was observed in measurements made with a smaller sample to detector distance. The peaks shown can be indexed unambiguously as the (200), (210), (220),



Contour map of the diffraction pattern of the D phase of the 18 : CN acid, (*a*) showing (200) and (210) reflections, plus a (220) spot. (*b*) showing a (030) reflection. Contours at the centre of the pattern result from scattering by the beam stop.

(120), (020) and (030) reflections of a cubic unit cell, from a single domain. Other measurements which are not presented here show the {111} and {211} reflections from the same domain. Note that the figure does not give a true representation of relative intensities because it was taken with a fixed sample orientation chosen simply to show the maximum number of reflections. The lattice parameter is 86 ± 2 Å. The calculated and observed parameters for these peaks are compared in the table.

Indexing parameters.

hkl	Measured *d* spacing/Å	Calculated lattice parameter/Å	Measured χ/deg	Calculated χ/deg
020	42·9	85·8	92·9	92·0
120	37·8	84·5	118·8	118·6
220	30·4	86·0	136·4	137·0
210	37·9	84·7	156·0	155·4
200	43·4	86·8	182·3	182·0
030	28·1	84·3	92·9	92·0

χ is the angle in the plane of the detector which a reflection subtends with the horizontal line intersecting the position of the incident beam. χ values are calculated assuming that the [200] direction is inclined at 2° to the horizontal.

For $(h^2 + k^2 + l^2) < 9$, only the {100} and {110} sets of reflections have intensities below the measurement limit. The absence of these reflections does not correspond to any of the possible sets of systematic absences, and it must be concluded that these intensities are non-zero, but less than the experimental detection limit.

Because of the lack of systematic absences, the space group must be one of the five primitive cubic space groups, *P*23, *Pm*3, *P*432, $P\bar{4}3m$ and *Pm*3*m*. These space groups can be further differentiated because in general the (*hkl*) and (*khl*) intensities differ only for *P*23 and *Pm*3, since these space groups do not possess four-fold axes of symmetry. The inequality only applies when $h \neq k \neq l$, so that, of the reflections measured, only the intensities of the {210} and {120} sets of reflections might be found to be unequal. The intensities of all except two of the twenty-four {210}/{120} reflections were measured, giving relative values of 7·8 and 5·2 with standard deviations of 19 per cent and 15 per cent respectively. In comparison, the intensities of all eight {111} reflections were measured with a standard deviation of 12 per cent. Thus although the distributions of the {210}/{120} intensities are broader than would be expected from the counting statistics, it seems clear that these intensities are different and that the space group is almost certainly either *P*23 or *Pm*3. Because the presence or absence of a centre of symmetry cannot be detected on the basis of diffraction measurements (Friedel's Law), the space group determination cannot be taken further using X-ray methods since *Pm*3 is equivalent to *P*23 with the addition of a centre of symmetry.

4. Discussion

4.1. *Structural considerations*

An estimate of the density of 18 : CN indicates that a cubic unit cell with a lattice parameter of 86 Å must contain approximately 700 molecules. Since intensity measurements have been made for only nine independent reflections (including (100) and (110)), it is obvious that a complete and unique structural determination cannot be made. The number of intensity measurements is limited by the rapid decrease in intensity with increasing scattering angle, so that the amount of structural information derivable from diffraction studies is inherently limited. Therefore, in order to attempt a structural interpretation of the diffraction data, it is necessary to make some simplifying assumptions.

The simplest starting structural model is based on micelles and was first proposed in general terms by Diele *et al.* [4]. The simplest approach in the light of the findings presented here is to site micelles, made up of the aromatic regions of the 18 : CN molecules, on the equivalent positions of *P*23 or *Pm*3. Furthermore, in order for the model to predict very low relative intensities for the {100} and {110} reflections, the micelles must be sited on the special positions for which the fractional co-ordinates are given by $x = y = z = 1/4$. It is implicit in this siting that the micelles can no longer be spherical but must have three-fold point symmetry, since otherwise a space group of higher symmetry would result.

In the *P*23 space group these special positions lie at the corners of a regular tetrahedron within the unit cell, while for *Pm*3, a cubic arrangement results. For this type of model, space filling considerations indicate that *P*23 is more likely for the following reasons. The maximum (fully extended) molecular length for 18 : CN is about 35 Å, and it is highly likely that these molecules are dimerized across the carboxylic acid groups, giving a maximum dimer length of 70 Å. The latter dimension may be taken as a rough estimate of the size of a micelle. In the micellar model based on *P*23, the distance between micelle centres for a unit cell of 86 Å is 60 Å which is reasonable for interpenetrating and partially melted tails. For *Pm*3, however, the inter-micelle distance would be 43 Å, which seems unreasonably short. Detailed modelling calculations based on these considerations are in progress.

4.2. *Comparison with previous diffraction studies*

While this study has shown that the D phase of 18 : CN is almost certainly characterized by the space group *P*23 (or *Pm*3) with a lattice parameter of 86 Å, the two diffraction studies of the D phase of the 16 : NO_2 acid discussed earlier came to different conclusions. Although it may be conceivable that the space group of the 'D' phase may be different for the different acids, it is interesting to see how the data of these earlier studies can be interpreted in the light of the present findings.

4.2.1. *Diele* et al. *[4]*

Figure 2 of [4] shows six reflections, which were indexed as (110) reflections. However, an alternative indexing scheme is possible. If the [110] direction is assumed to lie in the direction of the incident beam, then two reflections may be re-indexed as (200), while the remaining four may be re-indexed as (111). This indexing has the advantage that it explains the non-regularity of the hexagonal arrangement of Bragg reflections which is apparent in the figure. As a check, *d* spacing ratios were measured from an enlargement of figure 2 of [4], and were found to be within 5 per cent of those expected from this indexing, while the angles between the (200) and (111) reflections are within 4° of the values expected. This re-indexing gives a new lattice parameter of 74·7 Å. Direct comparison with the lattice parameter determined in this study for 18 : CN is not valid, but the value is not unreasonable given the 3 Å difference in molecular lengths which corresponds to a difference in lattice parameter of about 9 Å for the simple micelle model which we have discussed.

4.2.2. *Tardieu and Billard [5]*

Tardieu and Billard indexed their power diffraction data according to the $\sqrt{(h^2 + k^2 + l^2)}$ sequence: $\sqrt{3}$, $\sqrt{4}$, $\sqrt{7}$, $\sqrt{8}$, $\sqrt{10}$ and $\sqrt{11}$. In comparison, the data presented here are indexed in the sequence: $\sqrt{3}$, $\sqrt{4}$, $\sqrt{5}$, $\sqrt{6}$, $\sqrt{8}$ and $\sqrt{9}$. Clearly, it is possible to re-index the first two reflections quoted by Tardieu and Billard as (111) and (200) but the remainder are not in agreement with our data. However, since they gave no actual data but only a schematic representation of their powder diffraction results, with no values of *d* spacings, it is not possible to resolve this point. Indexing the first and second peaks as (111) and (200), a lattice parameter of 72·1 Å is obtained, which is again a reasonable value.

Thus, when allowance is made for the difficulty in indexing poor powder diffraction data, it can be seen that the data from the two previous diffraction studies can be reinterpreted to be consistent with the results presented here.

5. Conclusions

The structure of the D phase of 4′-*n*-octadecyloxy-3′-cyanobiphenyl-4-carboxylic acid is based on a primitive cubic space group which is almost certainly either *P*23 or *Pm*3. If a model of the micelle type is assumed, then the available evidence suggests that the space group is *P*23. While diffraction techniques are not capable of differentiating between the two space groups, this can be done in principle through measurements of optical second harmonic generation on which work is now in progress, together with detailed calculations on structural models.

The D phase is now clearly established as having three-dimensional periodicity and is definitely cubic. It should not therefore be called a smectic phase but it will be conventient for identification purposes to continue to refer to it as the D phase.

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