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X-ray Diffraction and Polymorphism of Smectic Liquid Crystals. II. D and E Modifications†

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Abstract—The X-ray patterns of two new smectic modifications (smectic D and smectic E) are investigated. The D-modification is optically isotropic. A cubic structure is presumed. In the E-modification the pattern exhibits three sharp outer rings besides the inner ring, which points to a higher order compared with the A, B and C-Phases.

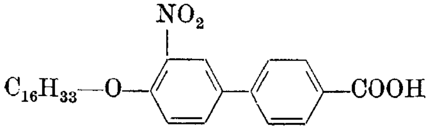
1. Introduction

The great majority of smetic liquid-crystalline forms are modifications of type A, B and C (see Table 1 of Part I(1)). Some forms are found which could not be associated with these modifications by their miscibility. They are designated as D and E. Now we have looked into the question whether these modifications exhibit characteristic features in their X-ray diffraction patterns.

2. The Smectic D-Modification

SUBSTANCES

No. 1: 4′-*n*-Hexadecyloxy-3′-nitrodiphenyl-4-carboxylic acid



$$\text{solid} \xleftrightarrow{126.8} s_C \xleftrightarrow{171.0} s_D \xleftrightarrow{197.2} s_A \xleftrightarrow{201.9} \text{isotropic}$$

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† Presented at the Third International Liquid Crystal Conference in Berlin, August 1970.

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No. 2: 4′-*n*-Octadecyloxy-3′-nitrodiphenyl-4-carboxylic acid

$$\text{solid II} \xleftrightarrow{85} \text{solid I} \xleftrightarrow{124.6} s_C \xleftrightarrow{158.9} s_D \xleftrightarrow{195.0} \text{isotropic}$$

The two homologues of the nitrodiphenyl-4-carboxylic acid show a new liquid crystalline modification D. This modification occurs in substance No. 1 between the smectic A and C types and in substance No. 2 as a high-temperature form in addition to the C-modification. Some details of the description of the modifications are found in Ref. 2. Frequently, modification D originates as an isotropic, polygonal form in miscroscopic observations. In liquid-crystalline modifications " pseudo-isotropy " caused by a spontaneous orientation of the sample is often found.(3) Also, the D-modification was considered as pseudo-isotropic at first. Investigations for the double refraction have established the optical isotropy of modification D. This modification is not double-refracting.(4)

The X-ray patterns are recorded by the flat-film method (see Part I).(1) The sample placed into a heated glass capillary tube was irradiated perpendicular to the cylinder axis with Ni-filtered Cu K_α radiation. The electric furnace does not permit rotation of the sample about the cylinder axis.

The patterns of the C- and A-modifications show the usual picture:(1) an inner sharp ring and an outer ring. The outer ring is weak and blurred.

In the D-modification a very weak and blurred ring is also found in a Bragg-angle range of about 10°. The inner ring degenerates into spot-like interferences (appearing at a Bragg-angle of about 1°). Their number and position may be different (Fig. 1, the arrow indicates the direction of the cylinder axis of the sample). However in substance No. 1 it was possible to get diagrams with a clearly hexagonal arrangement of the reflections (Fig. 2). Figure 3 gives a schematic graph. The open circles represent the hexagonally arranged interference spots at 1°. The filled circles (dots) indicate very weak reflections visible on the original. The very weak and blurred ring at 10° is sketched on the figure.

The interpretation of the results as a fibre-texture with a hexagonal symmetry must be eliminated because the formation of such a texture, vertical to the cylinder axis, is hardly conceivable.

The existence of the spot-like reflexes with a hexagonal arrangement,

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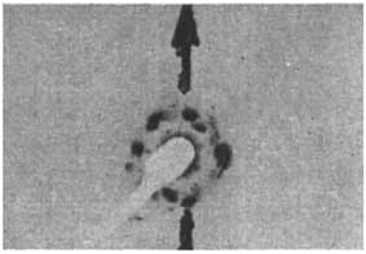

Figure 1. Substance No. 1. $T = 175$ °C, smectic D, the arrow indicates the direction of the sample.

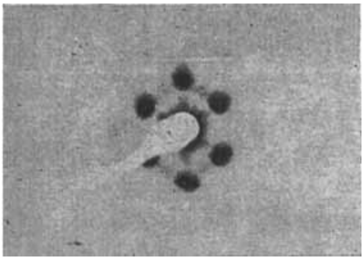

Figure 2. Substance No. 1. $T = 182$ °C, smectic D.

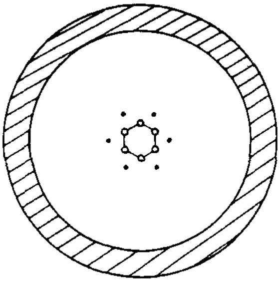

Figure 3. Schematic graph of the reflexions from Fig. 2.

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in addition to the liquid-like outer interference, requires a model which contains well-ordered parts and statistically distributed ones. Layer-structures are incompatible with the optical isotropy.

Thus an attempt has been made to describe the patterns on the basis of a cubic model. On the formation of the modification, small irregularly distributed parts with a defined arrangement of the molecules occur, giving rise to a pattern like Fig. 1. Some of these parts grow to a liquid crystalline " single crystal " in the viscous melt. In Fig. 2 such a " single crystal " was examined, whose size is equal to or greater than the irradiated volume, and whose body-diagonal was in this case nearly parallel to the incident beam. An exact evaluation of the Bragg angle from Fig. 2 is not possible because the interference spots which have different shapes and a noticeable width, do not form a regular hexagon. For the calculation we have used a Bragg-angle $\theta = 1.03°$, but we must take into account an error of $\pm 0.08°$. If we assume these are $(\bar{1}10)$-reflections, we obtain for the lattice distance $a = 61$ Å. So far we do not know the density of this modification. For the present we have used the following model: the lattice points are formed by spheres (micelles) existing of the aromatic parts of several molecules. But the hydrocarbon chains should be distributed irregularly to cause the weak ring at large angles. But more detailed investigations are necessary to confirm these speculations.

3. The Smectic-E-Modification

SUBSTANCES

No. 1: Diethyl-*p*-terphenyl-4, 4″-carboxylate[5]

$$\text{solid} \xleftrightarrow{173.0} s_E \xleftrightarrow{188.5} s_A \xleftrightarrow{259.0} \text{isotropic}$$

No. 2: Dipropyl-*p*-terphenyl-4, 4″-carboxylate[5]

$$\text{solid} \xleftrightarrow{122.0} s_E \xleftrightarrow{137.1} s_A \xleftrightarrow{239.2} \text{isotropic}$$

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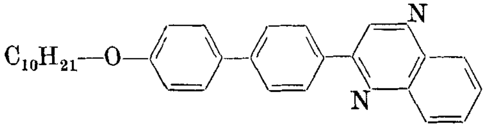
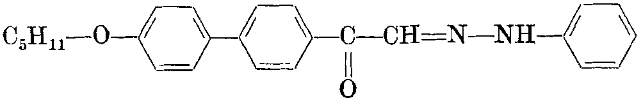
No. 3: 2-(4-*n*-decyloxydiphenyl)-quinoxalline[6]



$$\text{solid} \xleftrightarrow{97/98} s_E \xleftrightarrow{120} s_A \xleftrightarrow{194} \text{isotropic}$$

No. 4: 1-(4-*n*-pentyloxydiphenyl-(4′)-glyoxal-2-phenylhydrazine[6]



$$\text{solid} \xleftrightarrow{130} s_E \xleftrightarrow{165} s_A \xleftrightarrow{253} \text{isotropic}$$

In the substances named, a low-temperature form besides the smectic high-temperature for A is observed. The investigations of miscibility carried out so far⁽⁵⁾ show the existence of a new smectic modification, which has been given the designation E.

The X-ray patterns obtained in non-oriented samples of the four substances in modification E show the characteristics in Fig. 4. The diagrams were obtained with a Gunier camera using CuK_α radiation (monochromatized with a cut and curved quartz crystal). Besides a sharp interference at small angles (and its second order) three sharp interferences are found at large angles. The inner ring indicates the existence of the smectic layers.

An X-ray pattern from substance No. 1 in the crystalline phase at room temperature is shown in Fig. 5. A band structure of the reflections is visible. Such a band structure is found in molecular lattices, unit cells of which exhibit in one direction a significantly larger dimension than in the other directions (for example in the case

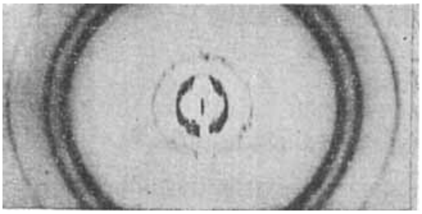


Figure 4. Substance No. 2. $T = 129$ °C, smectic E.

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of paraffins). This band structure is diminished on the pattern of modification E. This observation suggests that the three-dimensional order is largely removed.

A unique interpretation of the three reflections based upon a two-dimensional lattice with a quadratic or a hexagonal net was not possible. For the determination of an oblique cell further reflexes are necessary.

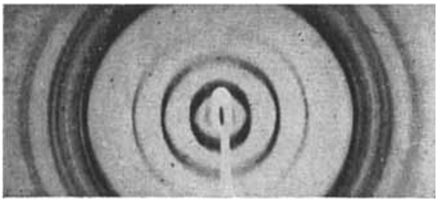

Figure 5. Substance No. 1. Room temperature, crystalline phase.

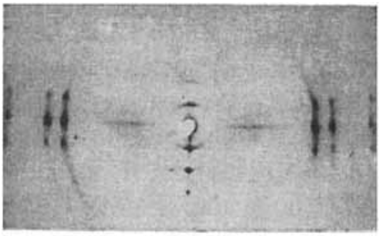

Figure 6. Oriented sample of substance No. 2. $T = 124$ °C, smectic E.

The X-ray pattern of a sample oriented in a magnetic field(1) and recorded the flat-film method (see Sec. 2) is shown in Fig. 6. Layer line reflections on the meridian are found up to the third order. The reflections at large angles are only visible up to the first layer-line. This could be a hint that the order in the third dimension is not well marked.

4. X-ray Diffraction and Polymorphism

The investigations of X-ray diffraction in the smectic modifications A, B, C, D and E presented in a previous paper (Part I) and in this paper confirm the characterization obtained by investigations of the

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miscibility in binary systems. The modifications designated in this way exhibit X-ray patterns in each case which tally in their essential characteristics. The new results found for F and G modifications(7) seem to prove this statement. It follows that the described modifications in each case also exhibit the same structure.

The well known concept of the basic structure of smectic modifications formed by layers of molecules is true of the A, B and C-modifications. The results show that the A modification is distinguished by a largely parallel arrangement of molecules standing vertically in the layers. The distribution of the molecular axes within the layers is largely statistical in the A modification.

In the B modification a rigid arrangement should be assumed. At present it is not possible to discern special characteristics of the structure of the B modification from our experiments. In the C modifications some investigations of oriented samples point to an inclination of the molecular axes to the layer. But the difference in the X-ray patterns of several investigators should be pointed out.

In the D and E modifications indications of a more highly ordered structure exist. For the D modification a cubic structure must be considered. This raises the question whether the designation " smectic " for the D modification is allowed. In the E modification a higher order of the molecules within the layers must be assumed. In this modification signs are present that the order goes beyond that within single layers.

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