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J. Billard ^a, J. C. Dubois ^b, C. Vaucher ^b & A. M. Levelut ^c

^a Laboratoire de Physique de la Matière, Condensée Collège de France, 75231 Paris - Cédex, France and Laboratoire de Dynamique des Cristaux moléculaires, Université des Sciences and Techniques de Lille, 59655, Villeneuve D'Ascq, Cédex, France

^b Laboratoire central de Recherches, Thomson-C.S.F., Domaine de Corbeville, B.P. No. 10, 91401, Orsay, France

^c Laboratoire de Physique des Solides associé au C.N.R.S., Université de Paris-Sud-Bâtiment, 510, 91405, Orsay, France

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Structures of the Two Discophases of Rufigallol Hexa-*n*-Octanoate†

J. BILLARD

Laboratoire de Physique de la Matière Condensée‡ Collège de France – 75231 Paris – Cédex, France and Laboratoire de Dynamique des Cristaux moléculaires.‡ Université des Sciences and Techniques de Lille, 59655 Villeneuve D'Ascq – Cédex, France.

and

J. C. DUBOIS and C. VAUCHER

Laboratoire central de Recherches, Thomson-C.S.F., Domaine de Corbeville, B.P. No. 10, 91401, Orsay, France.

and

A. M. LEVELUT

Laboratoire de Physique des Solides associé au C.N.R.S. Université de Paris-Sud – Bâtiment 510, 91405, Orsay, France.

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X-ray diffraction experiments have been performed on the two mesophases \mathcal{D}_B and \mathcal{D}_C of the hexa-*n*-octanoate of rufigallol (RHO). The disk-like molecules form parallel columns, and the mean distance between two neighbouring cores has the largest value observed until now for a columnar mesophase. The structure of the \mathcal{D}_B phase is similar to that of the mesophase of the hexa-*n*-octanoate of triphenylene, whereas the structure of the monotropic \mathcal{D}_C phase is a new one in which three different orientations of the molecular core are present.

1 INTRODUCTION

Since the first paper reporting the existence of a thermotropic mesophase for a pure compound consisting of disk like molecules,¹ the list of the discogen materials has increased rapidly.

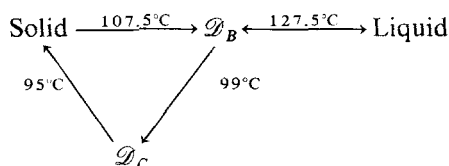
† Paper presented at the Eighth International Liquid Crystal Conference, Kyoto, Japan, June 30–July 4, 1980.

‡ Equipes associées au C.N.R.S.

During this time, knowledge of the structures of such mesophases has progressed.¹⁻⁵ These phases are generally formed by a regular packing of parallel and independent columns of molecules. An analogy can be drawn between these columnar mesophases and the smectic phases obtained with rod-like molecules. We may emphasize that up to now, five different structures are known and that a rich polymorphism is possible for these phases as well as for smectic phases.

The recently synthesized compound, the hexa-*n*-octanoate of rufigallol (RHO)⁶ (Figure 1) seems to be particularly interesting for several reasons:

- a) this compound is one of the rare discogens with molecules having a core of low symmetry (twofold axis);
- b) two mesophases \mathcal{D}_B and \mathcal{D}_C ⁷ have been observed for RHO



Polymorphism in disc-like mesogens does not occur very often;

- c) this compound is totally miscible with the hexa-*n*-octanoate of triphenylene in the \mathcal{D}_B state.⁶ This provides, up to today, a unique example of total miscibility in a discotic state for two compounds from two different chemical series. The structure of the discophase from the terphenylene derivative is known,⁴ and it is important to compare the structural parameters of the two components.

We report here X-ray investigations for the two discophases of RHO

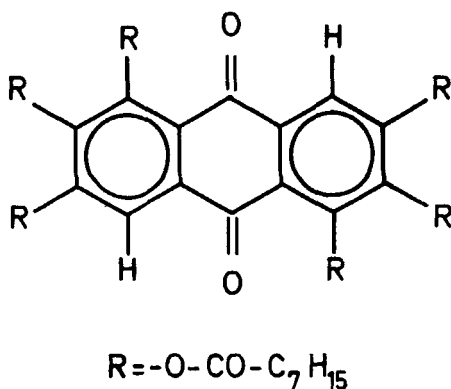


FIGURE 1 The molecule of the hexa-*n*-octanoate of rufigallol (RHO).

2 EXPERIMENTAL

Two kinds of diffraction experiments have been performed :

1) the sample was held in a Lindemann glass tube (diameter 1.5 mm) and illuminated with a monochromatic, point-focussing X-ray beam ($\text{CuK}\alpha$). The diffracted X-rays were collected on a flat film, 40 mm from the sample ;

2) a Guinier camera (diameter 114 mm) equipped with a heating stage was used. The sample was put on a platinum mesh and could be rotated in its plane.

With this second equipment, we used $\text{CoK}\alpha_1$ radiation, and we could obtain the lattice parameter with good accuracy, whereas in the first case we could detect more easily features of the pattern having low intensity.

3 RESULTS

The diffraction patterns obtained with a capillary tube sample holder are shown in Figure 2 for the isotropic liquid (A), the high temperature enantiotropic mesophase (B) and the monotropic low temperature mesophase (C).

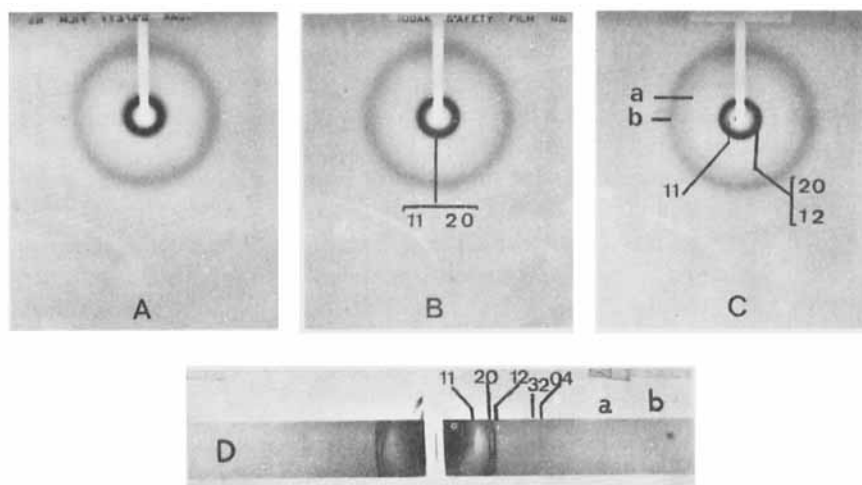


FIGURE 2 X-rays patterns obtained using a sample in a capillary tube (A, B, C) and with the Guinier camera (D). A—Isotropic liquid, B— \mathcal{D}_B phase, C and D— \mathcal{D}_C phase. (a) Diffuse ring characteristic of the core order (b) Diffuse ring characteristic of the chain order (the intensity of the diffuse ring (a) increases as the temperature decreases and it is more visible at lower temperature than here, even in the \mathcal{D}_B phase).

An example of a Debye-Scherrer pattern obtained with the Guinier camera is shown in (D) for the \mathcal{D}_C phase.

A Isotropic liquid

The diffraction pattern is similar to the diffraction pattern of all discogens in the isotropic liquid state: there are two diffuse rings. The outer ring lies at $d \simeq 4.5$ Å, while the inner ring which is of higher intensity corresponds to $d \simeq 18.6$ Å for RHO. We can compare these values with those obtained in the case of the hexa-*n*-octanoate of triphenylene for which we find an inner ring with $d \simeq 19$ Å and an outer ring with $d \simeq 4.5$ Å. We can thus conclude that the order in the isotropic state is not much affected by the change in the core symmetry which occurs when an anthraquinone core is substituted for a triphenylene core.

B The enantiotropic \mathcal{D}_B phase

By cooling our sample, we obtained the \mathcal{D}_B phase, but we were not able to obtain an orientated sample. Nevertheless, we can assert that the phase is constituted by columns of molecules: several sharp inner rings are seen and characterize the two-dimensional lattice formed by parallel columns. From the Debye-Scherrer pattern obtained with the Guinier camera, we can deduce a *Pgg* rectangular lattice (Figure 3 and Table I) $a = 34.8$ Å, $b = 18.1$ Å.

Let us notice that the 21 line, which is of zero intensity in a *Cm* lattice and not in a *Pgg* lattice, is here a line with a very low intensity and can just be seen only in the pattern obtained with a tube sample holder.

The intense inner ring seen for the isotropic liquid has shifted towards the high angle region in the mesophase temperature range; this ring is in fact the doublet 20,11 which is not clearly separated in Figure 2(b). Such a shift has not been observed in the case of a triphenylene derivative. In fact one can easily see that the distance between neighbouring columns is shorter than the mean lateral distance between molecules in the liquid state. The area for a column is 314 Å² and the specific area $A/M = 1.78 \cdot 10^7$ cm² g⁻¹.

In the case of the hexa-*n*-octanoate of triphenylene, we have measured a specific area of $2.52 \cdot 10^7$ cm² g⁻¹.

The rectangular lattice is such that the columns form a pseudo-hexagonal array. The distortion from a regular hexagon is measured by the relative difference between the reticular distances 20 and 11: $2(d_{20} - d_{11})/d_{20} + d_{11}$. This distortion is equal to 9% for RHO while it is about -1% for the triphenylene hexa-esters. This greater distortion is related to the shape of the molecular core, while the distortion observed in the case of triphenylene

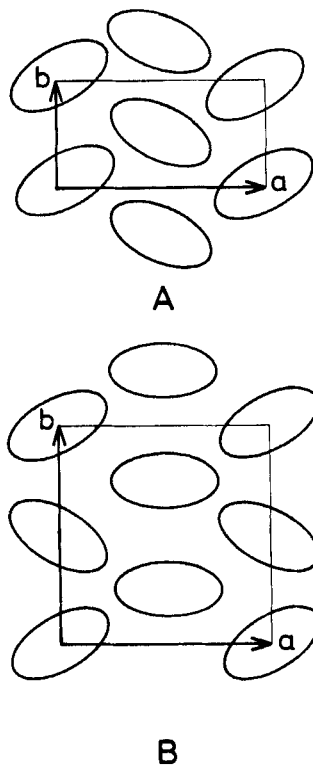


FIGURE 3 Schematic representation of the lattice formed by the columns. (A) \mathcal{D}_B phase, (B) \mathcal{D}_C phase (the ellipses represent the molecular cores).

TABLE I

\mathcal{D}_B	Reticular Distances	
	Measured	Calculated (\AA)
*20	17.4	
*11	16.1	
21		12.54
*31	9.35	9.40
*02		9.05

* High intensity: $h + k = 2n$

Extinction rule $\begin{cases} h0 & h = 2n + 1 \\ 0k & k = 2n + 1 \end{cases}$

derivatives probably comes from the tendency for chains to be parallel to each other. This tendency is enhanced when lateral phenyl groups are attached to the triphenylene core, since a distortion of -6% is observed in the columnar phase of triphenylene hexa-*n*-undecyloxybenzoate which has the same rectangular structure.

When we look at the large angle region of the X-ray pattern, we now observe two broad rings (the separation between the two rings is more evident when a Guinier camera film is used). The outer ring lies at $d \simeq 4.5$ Å and is related to paraffinic chains in a fluid state. The inner is sharper and corresponds to a mean distance of 5.6 Å. The distance is the distance between two neighbouring molecules along a column. Along the column we have a liquid-like order and the large value of 5.6 Å is consistent with the small value of the area of a column. Such a value suggests that the double-bonded oxygens of the carboxylate groups lie out of the anthraquinone plane. A large distance between cores (4.6 Å) is also observed in the case of the hexa-alkanoates of benzene.² On the contrary, the esters of triphenylene exhibit a mean core to core distance of 4 Å, and we suppose that in this last case an interdigitation of the double-bonded oxygens takes place. The small area per molecule implies that the chains are not extended in the plane of the core, while in the isotropic range, the probability of an extended planar configuration should be more important.

C Structure of the monotropic discophase

When we reach the supercooled region, a transformation occurs and the main change in the X-ray pattern is the occurrence of an extra sharp ring at a small angle inside the 11,20 doublet ring (Figure 2(c)). The large angle region remains unchanged, apart from a narrowing of the 5.6 halo. The \mathcal{D}_c phase is formed of the same columns of molecules as the \mathcal{D}_B phase, but the two-dimensional lattice of the column is different. The existence of a new ring implies that the b lattice parameter is twice the b parameter of the \mathcal{D}_B phase; $a = 34.9$ Å, $b = 36$ Å. Thus we have four columns per unit cell. Since the intense doublet remains unchanged, the columns are probably in a pseudo-hexagonal array, but now at least three different orientations of the molecules are required to take into account the change in the lattice area. Thus we propose a structure of Pmg symmetry (Figure 3(b)); this structure implies extinction rules only on $0k$ lines, $k = 2n + 1$. Table II gives the observed lines compared with the calculated reticular distances. We notice that several lines are not observed on our X-ray patterns, but we can group the lines into three categories:

— the lines corresponding to the pseudo-hexagonal lattice are of high intensity, since the main part of the sample contributes to the diffraction. These are the 20, 12, 32, 04 lines and they give an idea of the molecular structure factor;

— the hk lines, such that $h + k$ is even; the contribution to these lines is due to half of the sample (that is to say $1/4$ of the intensity), since the molecules having their axes parallel to a do not contribute to the diffraction in this case;

— the hk lines, such that $h + k$ is odd are of intermediate intensity. A more precise study of their intensity should give the angle between the molecular axes and the symmetry axes.

TABLE II

\mathcal{D}_c	Reticular Distances	
	Measured	Calculated (Å)
10		34.90
11	24.96	25.06
02		18.00
*20	17.47	17.45
*12	16.00	16.00
21		15.70
22		12.54
30		11.63
31		11.67
*32	9.76	9.77
*04	8.98	9.00

* High intensity: $k = 2k'$ $h + k' = 2n$
 Extinction rule $0k$ $k = 2k' + 1$

4 CONCLUSION

This X-ray study of the mesophases of a rufigallol ester confirms the results obtained by the miscibility method. Moreover, the study of the anthraquinone derivative underlines the influence of the central part of the molecules upon the main parameters of the structure. An important variation of the mean distance between neighbouring molecules is found, contrary to the case for smectic phases (the core distance varies from 3.6 for the triphenylene ether to 5.6 for the rufigallol derivative). Nevertheless, a large difference between the core distances does not hinder total miscibility. The constancy of the inter-paraffinic distance should also be pointed out. The lack of connection which appears between the order of the central parts and that of the

chains is a consequence of the more or less planar configuration of the molecule, while in the linear configuration the order of the cores and the chains must necessarily fit them altogether. In the isotropic liquid, the distinction between the inter-chain and inter-core distance disappears, and simultaneously the difference between the RHO and the triphenylene derivative becomes less obvious.

Finally, a new phase is described in which one finds three different, possible orientations of the biaxial column. The structure of this last phase raises some questions about the structure of the \mathcal{D}_0 phase of the hexa-*n*-alkanoates of triphenylene.⁸ The \mathcal{D}_0 phase appears in the super-cooled range of the highest homologues of this series and follows a rectangular *Pgg* phase. We did not succeed in obtaining X-ray patterns of this phase, because of purity problems with the material. The column lattice of this phase should be either a rectangular lattice with four columns or a hexagonal lattice with two columns per lattice, in which different orientations of the molecular core can exist. Further studies of the textures obtained for the \mathcal{D}_0 phase, as well as structural studies, should allow us to be more precise about the nature of this phase.

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