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A new thermotropic smectic phase made of ribbons (*)

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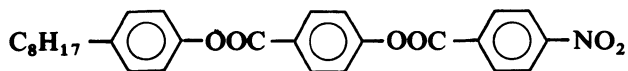
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Résumé. — L'étude des textures et de la structure des phases mésomorphes d'un nouveau composé polaire thermotrope, le nitrobenzoyloxybenzoate d'octylphényle nous a permis de mettre en évidence une nouvelle phase fluide constituée de rubans formant un réseau bidimensionnel oblique. Nous proposons un modèle simplifié basé sur un calcul de facteurs de structure.

Abstract. — From microscopical observations and structural studies on the mesophases of a new thermotropic polar compound — the nitrobenzoyloxybenzoate of octylphenyl — we have shown the existence of a novel fluid mesophase built with ribbons forming a two-dimensional oblique lattice. We propose a crude model based upon structure factor calculations.

1. Introduction. — It is known that mesogen compounds with a terminal cyano-end group can exhibit a rich polymorphism such as reentrant sequences [1] or S_A - S_A transitions [2]. The second sequence has been found only for the cyanobenzoyloxybenzoates of alkyl phenyl DB_n and for their mixtures with other mesogens [3, 4, 5]. A transition between two S_A phases corresponds to a change in the layer thickness of the smectic layer, the liquid-like order in a layer remains of the same kind. The substitution of the cyano group by a nitro group induces for the heptyl derivative (DB_7NO_2) [6] a new kind of phase in which a two-dimensional centred rectangular lattice is superimposed over a short range liquid-like order between adjacent molecules. We report here our investigations upon the polymorphism of the octyl nitro derivative (DB_8NO_2) which is shown to exhibit a new two-dimensional phase. The study of this compound has been made by microscopical observation, thermal analysis, magnetic susceptibility measurements and X-ray diffraction.

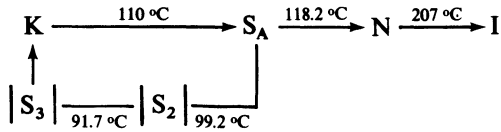
2. Preliminary study. — The « DB_8NO_2 » compound



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exhibits the following mesophases :



By decreasing temperature from a homeotropic domain of the S_A phase we observe at $T_{S_A S_2}$ the occurrence of a transient texture (Fig. 1b on left). This texture rapidly disappears giving a stable texture formed by polydomains (Fig. 1c on left). Just before the crystallization, at $T_{S_2 S_3}$ a homeotropic texture appears again. In the non homeotropic domains (Figs. 1a, 1b, 1c on right) one can see a mosaic texture in the S_2 temperature range (Figs. 1b, 1c on right). This sequence is corroborated by DSC measurements, in particular at $T_{S_A S_2}$ a narrow heat peak corresponding to a transition entropy $\Delta S_{S_A S_2} = 260 \text{ cal. mole}^{-1} \text{ K}^{-1}$ is detected.

Furthermore by Faraday's method [7] we have performed diamagnetic susceptibility measurements in a direction parallel to the magnetic field (χ_{\parallel}). At the $S_A \rightarrow S_2$ a dramatic increase of $|\chi_{\parallel}|$ is revealed. In good agreement with the microscopic observations this result seems to indicate that the S_2 phase is not uniaxial.

3. X-ray diffraction studies. — The sample was contained in a Lindemann glass tube, a 0.3 T magnetic field orienting the director in the nematic phase, the X-ray beam coming from a double-bent pyrolytic graphite and the diffracted beams being collected on a flat film.

In the nematic phase we observed the usual large angle diffuse ring at 4.5 \AA and two diffuse spots aligned along the direction of the magnetic field, the two corresponding scattering vectors are $q_{1z} = \frac{2\pi}{51.6} \text{ \AA}^{-1}$ and $q_{2z} = \frac{2\pi}{29.5} \text{ \AA}^{-1}$. Cooling down in the S_A phase the first diffuse spot becomes a Bragg spot while the second remains diffuse. From the position of the Bragg spot we can assert that we have a partially bilayer S_A phase with a layer thickness $d \simeq 44.5, 45 \text{ \AA} \gg L$ (L molecular length obtained from stereomodel : 31 \AA) [4, 5].

The diffuse spot takes the shape of a thin disc in the reciprocal space with a component along the director $q_{1z} = \frac{2\pi}{28.7} \text{ \AA}^{-1}$ at $116 \text{ }^\circ\text{C}$ and $q_{1z} = \frac{2\pi}{28} \text{ \AA}^{-1}$ at $105 \text{ }^\circ\text{C}$. This diffuse scattering comes from a short range order of periodic columns constituted with strings of molecules, thus the longitudinal period in the column is approximately equal to the molecular length.

At $T < 99 \text{ }^\circ\text{C}$ in the S_2 phase the small angle part of the X-ray pattern shows an important modification while the large angle diffuse ring remains unchanged (Fig. 2).

Let us call Oz and Ox two rectangular axes with Oz parallel to the magnetic field. Increasing q_z we see sharp spots lying respectively at :

$$\mp q_x, q_{1z}; \quad 0, q_{2z}; \quad \mp q_x, q_{3z}; \quad 0, 2q_{2z}; \quad \mp q_x, q_{4z}.$$

Depending on the sample, the spots $\mp q_x, q_z$ have not the same intensity and sometimes only one set of spots is visible. Thus the Oz axis is not a symmetry axis of the reciprocal lattice, we have an oblique $2d$ lattice and a few single crystals are seen simultaneously. This observation confirms the biaxial behaviour previously observed. We can index the spots as $\bar{1}1$; 01 ; $\bar{1}2$; 02 ; $\bar{1}3$. The 10 and 12 spots are not visible, the $\bar{1}1$ spot is merely seen on the diffuse scattering background surrounding the intense 01 peak, the $\bar{1}3$ spot can be seen only on highly exposed films. From the values of the scattering vectors we can deduce the lattice constants :

$$a = 106 \text{ \AA}, \quad c = 58 \text{ \AA}, \quad \beta = 120^\circ$$

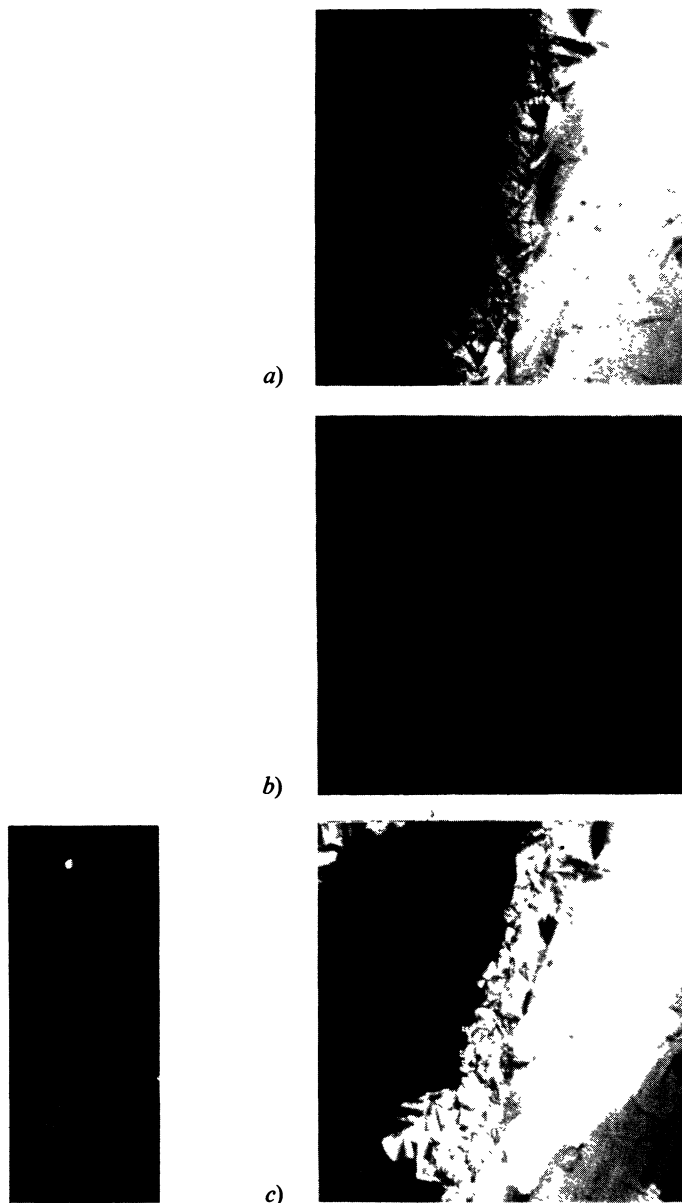


Fig. 1. — *a*) DB_8NO_2 , smectic A, homeotropic domain on left, $T = 99.3^\circ\text{C}$ ($\times 200$). *b*) DB_8NO_2 , S_2 phase : transient texture on left, mosaic texture on right ; $T = 99.2^\circ\text{C}$ ($\times 200$). *c*) DB_8NO_2 , S_2 phase : the transient texture disappears giving a stable texture (on left), mosaic texture on right ; $T = 99^\circ\text{C}$ ($\times 200$).

the a axis is perpendicular to the magnetic field while the c axis makes a 30° angle with the magnetic field. A similar structure has already been described by A. Tardieu [8] for some mesophases of synthetic lecithines. Such a phase was named the $P_{\beta'}$ phase and it is formed by asymmetrically undulated layers. In the case of the $P_{\beta'}$ phase the paraffinic chains are rigid and form a hexagonal bidimensional array in the layers. On the other hand the centre of mass of the molecules in the S_2 phase are randomly distributed within planes perpendicular to the director but we can keep the image of undulated layers. In order to have a better insight into the structure we have performed

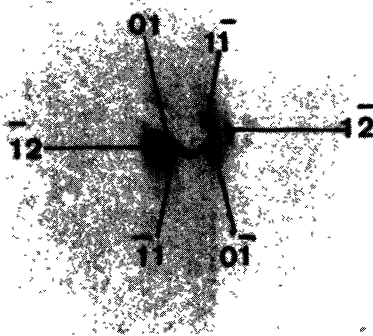


Fig. 2. — X-ray pattern of the S_2 phase (central part).

a structure factor calculation on a simplified model since we have just an idea of the order of magnitude of the diffracted intensities.

Taking into account earlier studies on DB_n and DB_nNO_2 series [3-6], we assume that the molecule form pairs which remain parallel to the magnetic field since there is no change in the large angle ring. If the centres of the pairs are on a plane $z = ux$ in reduced units the amplitude of the diffracted X-ray is given by :

$$F(h, l) = F_{\text{pair}}(q_z) \cdot \frac{\sin(\pi(h + ul))}{\pi(h + ul)}$$

where h and l are the indices of the Bragg spots, F_{pair} is the form factor of a pair of molecule, q_z is the projection of the scattering vector along c^* . The length of the pair is deduced from the values of c , β and u .

In table I we have reported the experimental and calculated values for the reticular distances and also the diffracted intensities, using $u = 0.6$ which corresponds to the best fit. In figure 3 we give a schematic model for this structure. The layers are broken in ribbons of bimolecular pairs with periodic stacking faults. The amplitude of the displacement between two adjacent ribbons is 0.8 molecular length. In fact we can also describe this phase as a regular stacking of bimolecular tilted regions and regions in which the order of two adjacent ribbons are interlaced. The relative importance of the two regions depends on the β value. We can compare this phase with the two-dimensional phase of $DB_7NO_2(S_{\lambda})$ [4]. In this latter case the lattice is centred rectangular (in the

Table I. — Reticular spacing and intensity of visible spots.

h, k reflections	Reticular spacing (\AA)		Intensity (arbitrary unit) calculated
	experimental	calculated	
—	—	—	—
$\overline{10}$	—	—	0
$\overline{11}$	55.05	58.65	7 700
01	49.15	49.15	1 700
$\overline{11}$	—	35.57	490
$\overline{12}$	27.92	27.92	720
02	24.58	24.58	120
$\overline{12}$	—	20.93	19
$\overline{13}$	17.84	17.95	75

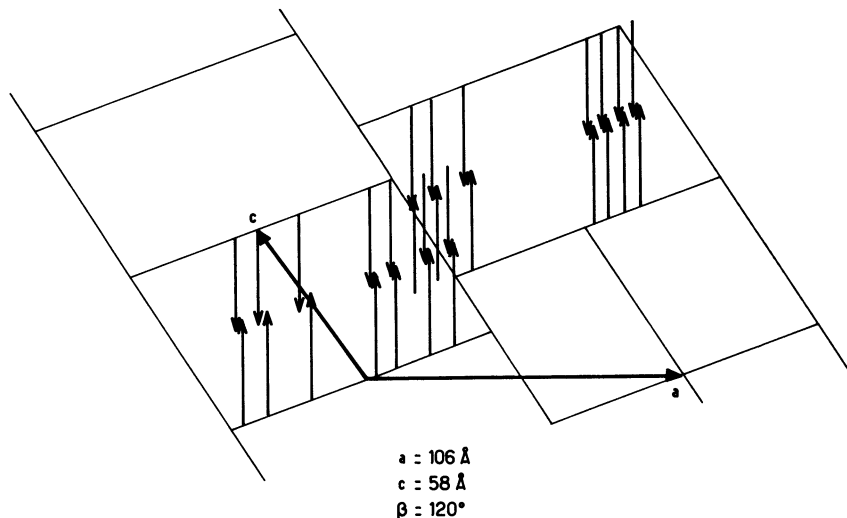


Fig. 3. — Schematic model for the structure of the S_2 phase.

limit of accuracy of our X-ray measurements). In accordance with the symmetry of the lattice we have proposed for DB_7NO_2 a ribbon structure in which the ribbon of bimolecular pairs has a rectangular section. The centred rectangular array of such a ribbon is equivalent to a bilayered structure broken periodically by defects walls. The two sides of the wall are translated by one half of the layer thickness, i.e. one molecular length. The $S_{\bar{\lambda}}$ phase is similar to the antiphase observed in some alloys. Therefore the difference between the two-dimensional phases of DB_7NO_2 and DB_8NO_2 comes from the difference in the respective orientations of the walls, director and layers. In DB_7NO_2 the director is parallel to the walls and perpendicular to the layers while the direction of both the walls and the layers are oblique with respect to the director in DB_8NO_2 . We have also to note that the thickness of each wall is important compared to the width of each ribbon since no high order of reflection has been observed in planes perpendicular to the director in DB_7NO_2 as well as in DB_8NO_2 . That assumption is consistent with our model of the structure of the S_2 phase of DB_8NO_2 . By analogy with the antiphase we propose to name this *serrated phase* a $S_{\bar{c}}$ phase. This nomenclature underlines the fact that this two-dimensional fluid structure is a tilted one.

Unfortunately, before crystallization we cannot detect by X-ray experiments the metastable S_3 phase.

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