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F. Hardouin, Nguyen Huu Tinh, A.M. Levelut

J. Physique — LETTRES **43** (1982) L-779 - L-784 15 NOVEMBRE **1982**, PAGE L-779

Classification
Physics Abstracts
61.30E — 64.70E

Novel biaxial bilayered fluid mesophases

F. Hardouin, Nguyen Huu Tinh

Centre de Recherche Paul Pascal, Université de Bordeaux I,
Domaine Universitaire, 33405 Talence Cedex, France

and A. M. Levelut

Laboratoire de Physique des Solides (*), Université de Paris-Sud, Bât. 510, 91405 Orsay, France

(*Reçu le 19 juillet 1982, accepté le 23 septembre 1982*)

Résumé. — La substitution d'un chlore sur le noyau central d'un cyanobenzoyloxybenzoate d'alkylphényle offre un matériau qui permet de généraliser aux milieux fluides biaxes les anomalies de périodicité rencontrées initialement dans les phases nématique et smectique A de la série non substituée (« DB_n »). En effet par analyse structurale RX, observations microscopiques, analyse enthalpique différentielle et mesures magnétiques, nous révélons une nouvelle séquence mésomorphe nématique-smectique A_2-smectique C_2-smectique$_?$. Dans les trois phases smectiques les couches sont liquides (même à courte portée) avec une période de modulation proche de deux fois la longueur moléculaire. La phase smectique basse température apparaît comme une nouvelle structure lamellaire avec des couches bien séparées.

Abstract. — In a substance with a substituted chlorine on the central ring of an alkylphenyl cyanobenzoyloxybenzoate we obtain evidence in a biaxial fluid medium for anomalies of periodicity similar to those initially found in the nematic and smectic A phases of the unsubstituted series (« DB_n »). From X-ray studies, microscopic observations, D.S.C. recordings and magnetic measurements, a new mesomorphic nematic-smectic A_2-smectic C_2-smectic$_?$ sequence is reported. In the three smectic modifications there is a liquid-like order within the layers (even at short-range) and the layer thickness is close to two molecular lengths. The lowest temperature smectic phase seems to be a new lamellar structure with well defined layers.

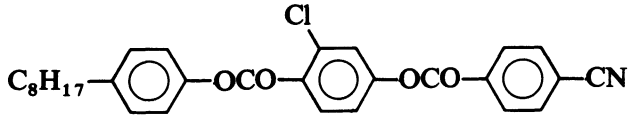
1. **Introduction.** — From the X-ray studies of the homologous compounds of the alkylphenyl cyanobenzoyloxybenzoate series (« DB_n » for short), it is known that two collinear wave vectors coexist in the nematic and smectic A phases [1-3]. They are related to two modulation periods of the layers : one the density wave is connected to the molecular length, the other is schematically connected to dipolar pairs of molecules with a weak overlapping [4, 5].

For the short aliphatic chains with $n = 5$ or 6, the two periods appear commensurated with a ratio of 2. Decreasing the temperature from the nematic phase leads to a « bilayer » smectic A_2 phase through the condensation of a periodicity close to twice the molecular length. In this case ($n = 5, 6$) only the very unusual intensity of the Bragg spots 002 gives evidence for establishing two characteristic wave vectors [1, 3].

(*) Laboratoire associé au C.N.R.S.

So far, these anomalies of unidimensional condensation (1D) in three dimensional fluids involve only optically uniaxial media, except partial bilayer S_C in some reentrant systems [6, 7]. Can these proporties exist in fluid media with optical biaxiality ? The results presented here give a positive answer to this question.

This result has been achieved by synthesizing a cyano compound similar to those of the DB_n series but with a lateral substituted chlorine and by conducting some primary physico-chemical observations. The formula of this substance octyl-phenyl 2-chloro-4-(p-cyanobenzoyloxy) benzoate is the following :



(labelled « DB_8 Cl » here after).

2. **Experimental results.** — By means of polarizing microscopy and D.S.C. measurements, four mesophases which are enantiotropic are detected in DB_8 Cl.

Below a nematic state, the mesophase II between 155 °C and 117 °C (Fig. 1) is a uniaxial medium as indicated by large homeotropic areas with some fan shaped textures (Fig. 2*a*). The X-ray analysis of an aligned sample cooled down from the nematic phase in a magnetic field of 0.3 T provides the characteristic patterns of a smectic A_2 phase with an increase of the intensity of the 002 reflection as the temperature decreases (Figs. 3*a* and *b*).

Over the temperature interval of 117 °C-107 °C (Fig. 1) the mesophase III gives rise to schlieren textures in the homeotropic parts indicative of a biaxiality, while broken fan shaped textures are observed elsewhere (Fig. 2*b*). In addition to the fact that the order is liquid-like within the layers, the X-ray patterns of this phase corroborate the fact that the planes are no longer normal to the director. We conclude that this phase is a smectic C in which the commensurate lock-in occurring in the S_{A_2} is retained (Fig. 3*c*). In particular the first and second order layering reflections always have similar intensities and the layer spacing $d = d_{S_{A_2}}.\cos\theta$, θ : tilt angle which varies from 0° to 30° as the temperature decreases (Fig. 4).

Thus, this is a « bilayer » smectic C noted S_{C_2} by analogy with S_{A_2}.

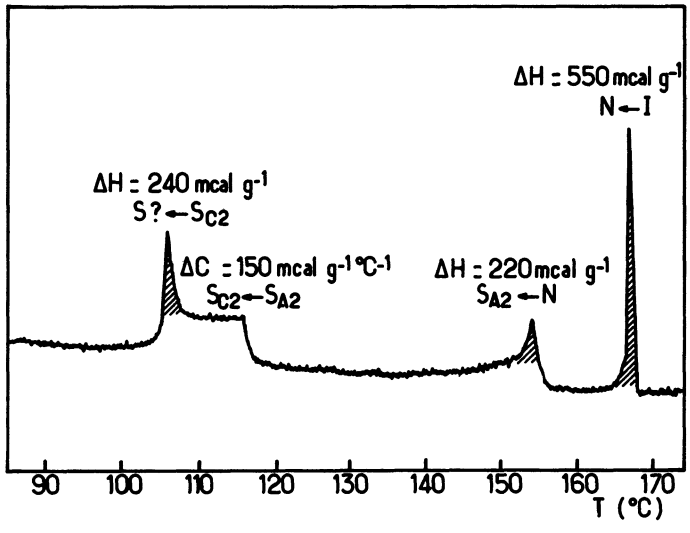


Fig. 1. — D.S.C. thermogram for DB_8 Cl.

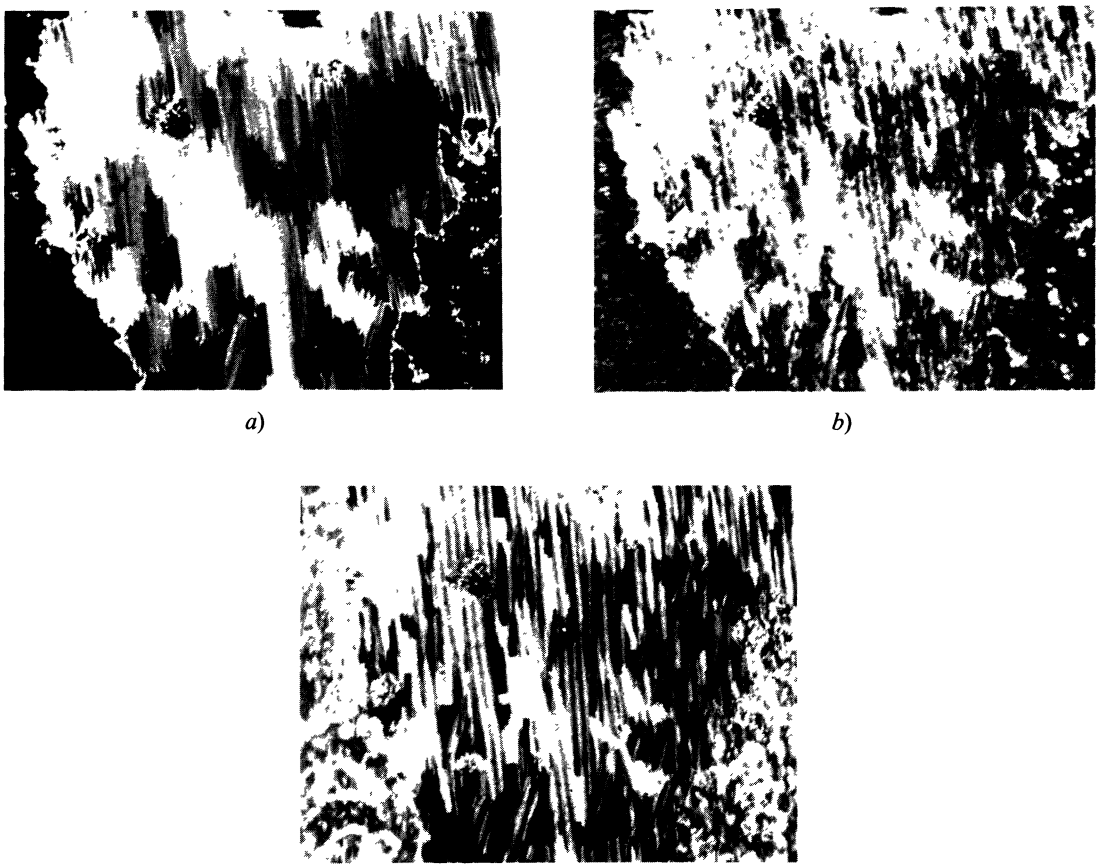


Fig. 2. — Optical textures of DB_8 Cl between crossed polarizers (× 250) : *a*) smectic A_2 (black areas are homeotropic); *b*) smectic C_2 (same area); *c*) smectic$_?$ (same area).

At 107 °C a sudden textural change makes the S_{C_2} → mesophase IV transition obvious for the microscopic observations and a clear heat peak is recorded by D.S.C. (Fig. 1). At lower temperatures, schlieren textures far different from these observed in the S_{C_2} phase are established and the fan shaped textures no longer appear broken (Fig. 2*c*).

In contrast, the differences between this phase and the S_{C_2} phase are much less evident from X-ray photographs : at wide angles the diffuse scattering always indicates a liquid-like order at very short-range (Fig. 5). At small angles for a given exposure time, only an enhancement of the intensities of the 001 and 002 Bragg reflections and the occurrence of higher orders are noticeable (Fig. 3*d*). Considering reticular measurements, at the S_{C_2}-$S_?$ transition a sharp drop of the layer thickness is observed which is consistent with the fact that this transition is first order. Then the tilt angle smoothly decreases in the low temperature $S_?$ phase (Fig. 4).

3. **Discussion.** — As expected the substitution of a chlorine on the rigid core of the DB_n series induces a biaxial-bilayer fluid phase of S_{C_2} type through the new N-S_{A_2}-S_{C_2} sequence. Note that the S_{A_2}-S_{C_2} change is characterized by a heat capacity discontinuity (much stronger than in the usual S_A-S_C transitions) without latent heat or critical heat capacity excess, strongly suggesting a mean-field behaviour of this second order transition.

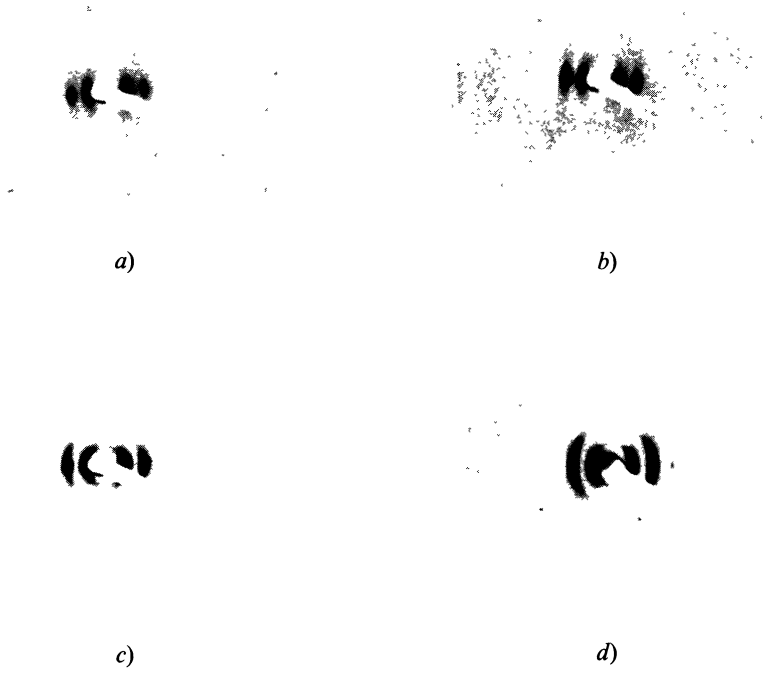


Fig. 3. — X-ray diffraction photographs of DB_8 Cl (CuK_α) 30′ exposure time : *a*) smectic A_2 $T = 152$ °C (X-ray beam parallel to the smectic layers); *b*) smectic A_2 $T = 122$ °C; *c*) smectic C_2; *d*) smectic$_?$.

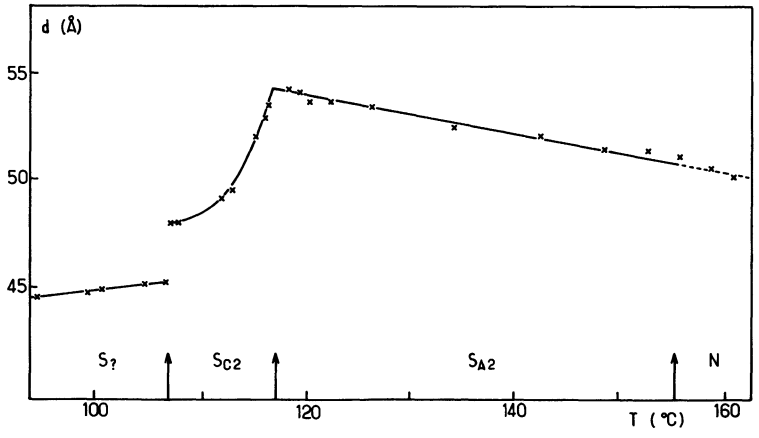


Fig. 4. — Smectic layer thickness *d* as function of temperature (Guinier camera on powder sample).

Cooling down from the S_{A_2}-S_{C_2} transition, the apparent magnetic anisotropy $\Delta\chi$ determined from measurements of the susceptibility parallel to the magnetic field [8, 9] (Fig. 6) indicates an increase of the biaxiality in the S_{C_2} phase in good agreement with the X-ray analysis and microscopic observations. Moreover we have to mention that in the case of « a more complex frustrated system » this S_{C_2} is likely to occur as the last fluid mesomorphic stage at low temperature [10].

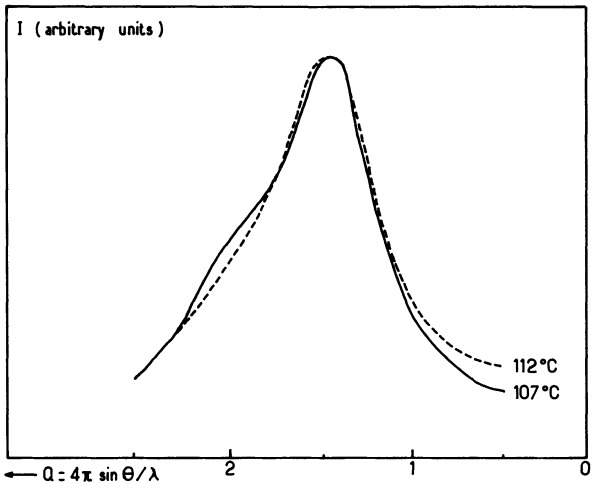


Fig. 5. — Comparison of the intensity profiles between the S_{C_2} phase and the $S_?$ phase (λ = CuK_α).

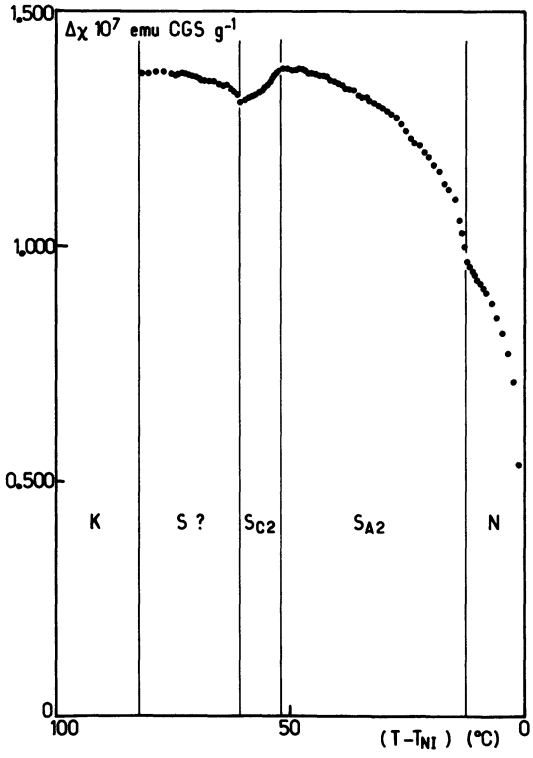


Fig. 6. — Thermal evolution of the apparent magnetic anisotropy for DB_8 Cl (determined from susceptibility measurements parallel to the magnetic field).

On the other hand, we can claim that in DB_8 Cl the mesophase IV is a new smectic modification with a well defined lamellar structure (no permeation ?) without any translational order. Moreover the occurrence of such an unexpected smectic structure induces an enhancement of the orienta-

tional order η, indeed $\Delta\chi$ which depends on η [9] increases at the $S_{C_2} \rightarrow$ mesophase IV transition (Fig. 6). Although not very pronounced, the asymmetric shape of the intensity profile of the diffuse ring at large angle on the powder diagrams in the $S_?$ phase (Fig. 5) might correspond to a molecular or bimolecular anisotropy change. Let us remark that a new mesophase having features similar to the mesophase IV has been seen in a chiral compound : the X-ray diffraction pattern is identical to that of S_C except for the number of observed Bragg reflections which is higher than usual, in this case the layer thickness corresponds to one molecular length with a 50° tilt angle. Moreover a transition between a smectic C and this mesophase has been observed in binary mixtures of chiral compounds [11].

Finally, in the DB_n series with $n \geqslant 7$ the two wave vectors appear incommensurated in the nematic phase. Consequently, only one-dimensional modulation is first condensed in these fluid systems giving a « partially bilayer » S_{A_d} with « monomolecular » fluctuations prior to the commensurate S_{A_2} lock-in at low temperature [3, 12]. The question raised in DB_8 Cl is : why the substitution of a chlorine on the rigid core with $n = 8$ favours a commensurate lock-in even in the nematic phase ?

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