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A fluid smectic A antiphase in a pure nitro rod-like compound

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Résumé. — Une transition entre une phase smectique A et une antiphase smectique A ($S_{\tilde{A}}$) est découverte pour la première fois dans un composé pur : le nitrobenzoyloxybenzoate d'heptylphényl. Jusqu'à présent les anomalies de périodicité liées à l'existence de telles transitions ne s'observaient que dans des systèmes cyanés. De plus, la phase solide de l'homologue inférieur de cette série nitrée est étrangement influencée par ces mêmes anomalies de périodicité.

Abstract. — A transition between a smectic A phase and a smectic A antiphase ($S_{\tilde{A}}$) is observed for the first time in a pure compound : the nitrobenzoyloxybenzoate of heptylphenyl. So far, the anomalies of periodicities which are connected to this type of transition were only detected in cyano systems. Moreover, the solid phase of the inferior homologue of this nitro series is surprisingly influenced by similar anomalies of periodicities.

1. **Introduction.** — Our earlier works about long aromatic cyano-derivatives gave evidence for several new transitions between disordered mesophases (nematic and smectic A) [1-3]. In particular the series of cyanobenzoyloxybenzoates of alkylphenyl (DB_nCN for short, n being the number of carbon of the alkyl chain) has provided some unexpected phenomena connected to anomalies of periodicities.

Let us recall briefly some peculiar recent results published elsewhere [4, 5] which can help the understanding of next section :

(i) A S_{A_1} - S_{A_2} transition is evidenced in the pure DB_7CN [4].

In the high temperature S_A phase two collinear wavelengths coexist such that $q_2 \neq 2 q_1$ ($q_2/q_1 \simeq 1.8$). The layer spacing

$$d = \frac{2\pi}{q_1} \simeq 1.6 l$$

(l being the molecular length). The other wavelength corresponds to a highly damped modulation. At the transition we observe the commensurate locking of these two wavelengths with $q_2 = 2 q_1$ keeping only one modulation such that $d \simeq 2 l$, characteristic of what we named a *bimolecular* smectic A (S_{A_2}) (previously revealed in pure DB_5CN and DB_6CN).

(ii) There exists a smectic A antiphase ($S_{\tilde{A}}$) obtained from a binary mixture of DB_6CN (or DB_5CN) with another cyano compound [5] : this phase is

intermediate between a *monomolecular* S_{A_1} phase and a *bimolecular* S_{A_2} phase. In the high temperature S_{A_1} phase, two wavelengths coexist such that $q_2/q_1 \simeq 1.8$ but, in this case, with $d = 2\pi/q_2 \simeq l$ and with q_1 characteristic of a damped modulation.

Then, with decreasing temperature, q_1 loses its unidimensional form. At the change into $S_{\tilde{A}}$ antiphase, long range lateral fluctuations take place in the layers and q_1 and q_2 seem now commensurate along the z axis ($\langle 00l \rangle$ row, normal to the layers) : $q_2/q_{1z} = 2$.

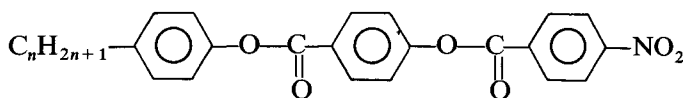
At last, this lateral modulation mode collapses and gives rise to the S_{A_2} phase : $q_2/q_1 = 2$.

Thus, the main cause of such behaviours ⁽¹⁾ appears to be the coexistence along z of two periodicities either commensurate or incommensurate [6, 7] : one corresponds to the molecular length (experimentally characterized by q_2 which is constant for a given system) and the other comes from the arrangement of the dipoles. Therefore, we have not varied the values of these parameters but only replaced the cyano head by a more hindering one.

2. **Experimental.** — We report some new observations obtained from nitro-compounds directly derived from the cyanodibenzoate series. Thus, the formula

⁽¹⁾ Presented at the 8th International Liquid Crystal Conference, Kyoto, June 1980.

of the substances, synthesized in our laboratory, is the following :



DB_nNO_2 for short by similarity with the indexing of the cyano-derivatives. We note that the value of the nitro dipole is quasi-similar to the cyano one : ~ 4 D. The D.S.C. investigations of the DB_7NO_2 show three mesomorphic states (Fig. 1) whereas the classical

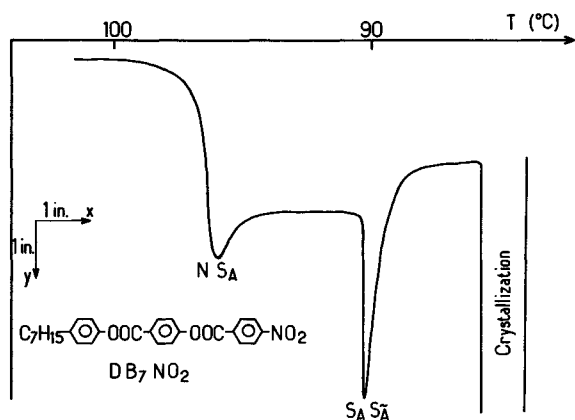


Fig. 1. — D.S.C. recording of pure DB_7NO_2 (decreasing temperature).

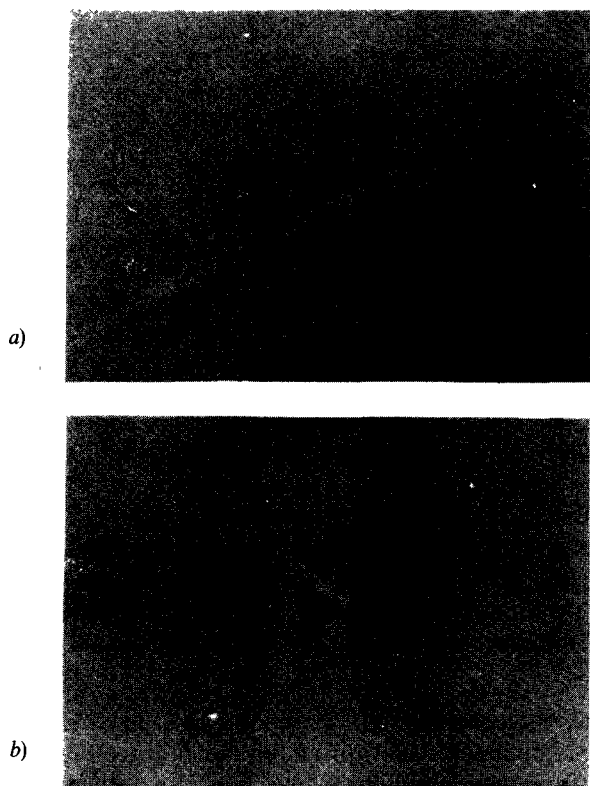


Fig. 2. — a) X-ray pattern of the high temperature phase of DB_7NO_2 . Orientated sample : the magnetic field direction is parallel to the $\langle 00l \rangle$ row (z axis). b) X-ray pattern of the $S_{\bar{X}}$ antiphase of DB_7NO_2 .

microscopic observations between glass slide and cover slip reveal only two mesophases : a nematic and only one smectic A phase. This apparent discrepancy already discussed in our previous papers [3, 5] is solved by the way of X-ray technique as demonstrated by the bright patterns of figure 2 : the first one, taken at $94^\circ C$ presents (i) one Bragg spot corresponding to a mass density periodicity characterized by a wavelength $d \simeq$ one molecular length l and (ii) a strong diffuse scattering corresponding to fluctuations the periodicity of which along the $\langle 00l \rangle$ row (z axis) appears incommensurate with d ($q_1/q_2 \neq 2$). Moreover one can remark the tendency for this diffuse spot to split off the z axis. This phase is a S_A phase with $d \simeq l$ and anomalies of periodicities similar to those described elsewhere [3, 5]. Then at $T = 87^\circ C$ (below the second enthalpic peak) the X-ray pattern is modified in that manner : the diffuse scattering seems now condensed in the form of two acute Bragg spots located out the z axis (clearly visible on the left part of the plate b) ⁽²⁾). In addition these spots have moved such that q_{1z} seems now commensurate with q_2 (which is for its part not modified) : $q_{1z}/q_2 = 2$. This pattern is characteristic of the fluid $S_{\bar{X}}$ antiphase that we have previously discovered in a cyano binary mixture [5]. This result is confirmed by the microscopic observation of the free surface of a droplet which shows a texture change at the temperature of transition determined by D.S.C. ($90^\circ C$). Note that this textural change is different from the one observed in the first example of $S_{\bar{X}}$ antiphase [5].

Thus, these experiments give evidence for the first S_A to $S_{\bar{X}}$ transition in a pure compound, namely the nitrobenzoyloxybenzoate of heptylphenyl (DB_7NO_2).

Now, the homologue with $n = 6$ (DB_6NO_2) exhibits only one smectic phase characterized by optical microscopy as well as by D.S.C. measurements ($T_{N-S} = 91^\circ C$). The X-ray pattern indicates undoubtedly that it is a smectic A phase like the high temperature S_A phase of the DB_7NO_2 .

It is obvious that this phase differs from a S_{A_2} phase on the binary phase diagram of figure 3, in which DB_6NO_2 and DB_6CN are mixed. In fact three smectic A domains appear : the S_{A_2} phase on the DB_6CN side, the S_A phase of the pure DB_6NO_2 and, as could be expected from the polymorphism of the DB_7NO_2 , a $S_{\bar{X}}$ domain comprised between the S_A and the S_{A_2} phases. But in the case of the pure DB_6NO_2 the $S_{\bar{X}}$ phase is virtual since crystallization occurs first.

Nevertheless a striking fact must be pointed out from the diagram of figure 3 and the D.S.C. recording of pure DB_6NO_2 represented on figure 4.

⁽²⁾ We point out that the Bragg reflection corresponding to the monomolecular modulation is not split out the z axis in the figure 2b. Thus, this spot is not the second order of reflection of a smectic C tilted structure.

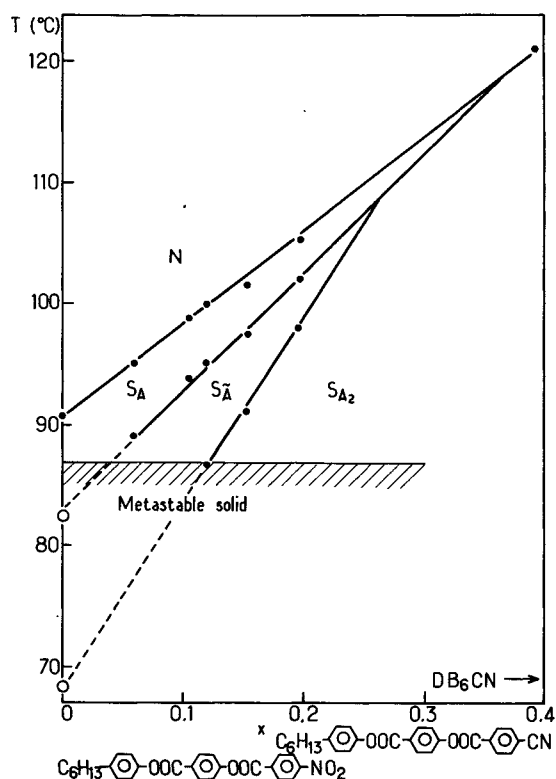


Fig. 3. — Binary isobaric diagram between DB_6NO_2 (left side) and DB_6CN (right side). The horizontal line represent the transition to a metastable crystalline form. (Diagram obtained from D.S.C. measurements.)

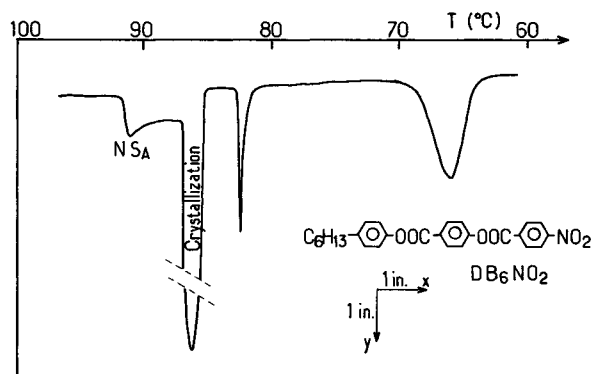


Fig. 4. — D.S.C. recording of pure DB_6NO_2 (decreasing temperature).

Indeed, one can remark on this enthalpic spectrum that the crystallization to a metastable solid occurs a few degrees lower than the N-S_A transition : it corresponds to the large peak at 86°C . But with decreasing temperature two additional small peaks appear successively. Their shape is qualitatively the same as those corresponding respectively to $\text{S}_A\text{-S}_{\bar{A}}$ and $\text{S}_{\bar{A}}\text{-S}_{A_2}$ transitions. Now if we put the transition temperatures assigned to these peaks on the diagram of figure 3 (white circles) it is very surprising to find that these

points correspond to the extrapolations of the $\text{S}_A\text{-S}_{\bar{A}}$ and $\text{S}_{\bar{A}}\text{-S}_{A_2}$ lines (dotted lines). Consequently we can propose that the kind of transitions we have observed in the fluid S_A phases occurs as well in a solid matrix (we notice that this happens only in the case of a metastable crystalline form and that the two additional peaks do not appear when the stable solid is established).

More X-ray experiments are required but the metastability of the crystalline form makes them difficult.

Maybe the metastable solid exists in an incommensurate state in the temperature range defined by these two small peaks (like the one observed by Brownsey and Leadbetter [8] in S_E phase). This state, in terms of anomalies of periodicity, would be intermediate between a first commensurate one with one molecular length periodicity along z and a last one with a commensurate locking and a doubling of the periodicity along z . Up to now this assumed commensurate-incommensurate-commensurate sequence is not observed in smectic A matrices because the fluidity of this medium allows sort of an antiphase structure $\text{S}_{\bar{A}}$ (commensurate along z) while such a compromise would be prevented in a rigid solid matrix. However, the theoretical diagram of reference [9] predicts the possible existence of commensurate and incommensurate states as well as of an antiphase in smectic A systems of polar molecules. The stability of these phases depends not only on temperature, but also on the value of elasticity parameters which, of course, differ greatly in the case of solids.

3. Conclusion. — As the DB_nCN compounds, the nitro derivatives (DB_nNO_2) provide smectic A phases with anomalies of periodicities. Nevertheless, as so far as we have investigated this series, we do not find a S_{A_2} phase contrary to the DB_nCN ($n = 5, 6, 7$). On the other hand, the DB_7NO_2 is the first example of a pure compound exhibiting a $\text{S}_A\text{-S}_{\bar{A}}$ antiphase transition. This last phase seems stabilized by the higher hindrance of the NO_2 group. Since our studies of binary mixtures have shown that the $\text{S}_{\bar{A}}$ antiphase can be considered as a precursor of the S_{A_2} phase, may be we can expect the occurrence of this bimolecular smectic A_2 for the higher homologues of the series. In addition, the extrapolation of these unusual modulations in a solid matrix of DB_6NO_2 raises the question : is the intermediate phase in the metastable crystalline form a solid antiphase or a true incommensurate phase as above proposed ?

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References

- [1] HARDOUIN, F., LEVELUT, A. M., *J. Physique* **41** (1980) 41.
- [2] SIGAUD, G., NGUYEN HUU TINH, HARDOUIN, F., GASPAROUX, H., *Mol. Cryst. Liq. Cryst.*, to be published.
- [3] HARDOUIN, F., LEVELUT, A. M., BENATTAR, J. J., SIGAUD, S., *Solid State Commun.* **33** (1980) 337.
- [4] HARDOUIN, F., LEVELUT, A. M., SIGAUD, G., *J. Physique* **42** (1981) 71.
- [5] SIGAUD, G., HARDOUIN, F., ACHARD, M. F., LEVELUT, A. M., *J. Physique* **42** (1981) 107.
- [6] PROST, J., Proceedings of the liquid crystals of one- and two-dimensional order conference, Garmisch-Partenkirchen (1980), *Springer series in chemical physics* (Springer, Berlin, Heidelberg, New York) 1980.
- [7] PROST, J., Proceedings of Colloque Pierre-Curie (1980).
- [8] BROWNSEY, G. J., LEADBETTER, A. J., *Phys. Rev. Lett.* **44** (1980) 1608.
- [9] BAROIS, P., COULON, C., PROST, J., Colloque Pierre-Curie (1980), to be published.
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