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A re-entrant polymorphism $N S_A S_C N_{re}$

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Résumé. — Le polymorphisme d'une nouvelle série : 4-[-4"-alkoxy-cinnamoyloxy] benzyldène-4'-cyanoaniline a été étudié et la phase nématique rentrante a été observée pour les trois homologues $n = 8, 9, 10$. Le composé $n = 10$ présente la séquence $N S_A S_C N_{re}$. Cette séquence inhabituelle est pour la première fois confirmée par les diagrammes de phase et par l'analyse des clichés de diffraction des Rayons X. La notion de S_C *partiellement bimoléculaire* est introduite.

Abstract. — The polymorphism of a new series 4-[-4"-alkoxy-cinnamoyloxy] benzyldene-4'-cyanoaniline was studied and a re-entrant nematic phase was observed for the three homologues $n = 8, 9, 10$. The decyloxy compound exhibits the unusual $N S_A S_C N_{re}$ sequence. For the first time, phase diagrams connected with X-ray analysis confirm this result. The *partial bilayer* S_C notion is introduced.

1. Introduction. — After the first observations of an enantiotropic re-entrant nematic phase at atmospheric pressure in pure compounds of the series : 4-alkoxy-benzoyloxy-4'-cyanostilbenes [1, 2, 3], we have carried on the systematic study of series with three phenyl rings and a cyano end group. The general formula of these substances is the following [1-13] :

For $X = -\text{CH}=\text{N}-$, Weissflog *et al.* [7] reported the novel $N S_A S_C N_{re}$ sequence with the decyloxy compound. In this paper we present some homologues of a new series 4-[-4"-alkoxy-cinnamoyloxy] benzyldene-4'-cyanoaniline **2** which exhibit the same properties i.e. the occurrence of a S_C phase between the S_A phase and the re-entrant nematic phase :

2. Results and discussion. — The substances were synthesized by the condensation of 4-formyl-phenyl 4'-alkoxycinnamates and 4-cyanoaniline in ethanolic solution. They were purified by recrystallization from ethanol. Phase transitions were studied both by polarizing microscopy (equipped with a Mettler F.P. 5 heating stage) and Differential Scanning Calorimetry (Dupont 990). The transition temperatures and types of mesophases are given in table I.

Table I. — Transition temperatures (°C) of compounds of the series **2**

<i>n</i>		K	N	S _C	S _A	N	I
6	•	120	—	—	• (92)	• > 285	•
7	•	92	—	—	• 124	• > 285	•
8	•	99	• 152.5	—	• 223	• 281	•
9	•	93	• (74)	—	• 244	• 272	•
10	•	100	• (70)	• (87)	• 257	• 267	•
11	•	95	—	• (66)	• 260	• 264	•

K : solid crystal; S_A, S_C : smectic A, C;

N : nematic; I : isotropic; • : the phase exists;

— : the phase is not observed; () : monotropic transition.

As seen from table I, the *n* = 6,7 homologues of **2** only show nematic (N) and smectic A (S_A) phases. These S_A phases give a McMillan parameter $\frac{T_{NA}}{T_{NI}} \approx 0.87$ (*T*_{NA} and *T*_{NI} are respectively the temperatures (K) of the smectic A-nematic and the nematic-isotropic transitions) and they are probably similar to the low temperature S_A phases of **1** with X = —CH=CH— [3]. Concerning the octyloxy derivative of **2** a stable re-entrant nematic phase with the N S_A N sequence is ob-

Fig. 1. — Diagram of the isobaric state for the mixture of **2** (*n* = 8) (on left) with **1** (R = C₈H₁₇O, X = CH=N) (on right).

served. In contrast with the low homologues $\frac{T_{NA}}{T_{NI}}$ is hence larger than 0.87, and this thermodynamical behaviour recalls the high temperature S_A phase of the so-called « T₈ » [2-3] or similar compounds [4, 5, 9-12]. For the two following members of **2** a metastable re-entrant nematic phase exists. In addition, the decyloxy derivative exhibits an unexpected smectic C phase between the re-entrant nematic and the S_A, as reported by Weissflog *et al.* [7] in the series **1** with X = —CH=N—. In the undecyloxy derivative the re-entrant nematic phase disappears while the monotropic S_C phase is still revealed.

2.1 OPTICAL TEXTURE OBSERVATIONS. — On cooling the isotropic liquid of the decyloxy derivative, one can first observe the nematic phase with a classical thread-like texture. Below this nematic phase, the smectic A phase with a focal conic or homeotropic texture appears. On further cooling, the smectic C phase becomes visible through a schlieren texture in the previous homeotropic domains and through a broken fan shaped texture in the other ones. On cooling the S_C phase, the re-entrant nematic phase shows a schlieren texture or a paramorphic fan shaped texture.

2.2 ISOMORPHISM. — The identification of the polymorphism of the octyloxy derivative has been obtained by the miscibility method with the well known N-S_A-N sequence of the octyloxy derivative of **1** (X = —CH=N—) [7, 8, 13] (Fig. 1). In comparing the decyloxy compound of **2** with equal alkoxy chain derivative of **1** (X = —CH=N—) we give evidence for the perfect miscibility of the two smectic C phases (Fig. 2). In order to prove definitely these identifications X-ray investigations were performed using an equimolar mixture of the two decyloxy derivatives in which the S_C phase is stable and the re-entrant nematic phase could exist till 50 °C. With the purpose of observing the Bragg reflections on the layers we used a monochromatic CuK_α X-ray beam perpendicular to a magnetic field (0.3 T). On cooling from the nematic phase we obtain

Fig. 2. — Diagram of the isobaric state for the mixture of **2** ($n = 10$) (on left) with **1** ($R = \text{C}_{10}\text{H}_{21}\text{O}$, X = —CH=N—) (on right). The dashed lines correspond to monotropic transition temperatures S_A-S_C and S_C-N_{re}.

a S_A single domain with a weak thermal dependence of the layer spacing d . The d value is somewhat larger than the average molecular length L_M of the binary system : $d \sim 1.2 L_M$. Thus this S_A structure recalls the high temperature S_A phase of the double re-entrant N- S_A -N- S_A sequence [14, 15]. Then, in the S_C phase the smectic planes are rather disordered and the molecules are not quite aligned along the magnetic field direction. On the other hand, heating from the re-entrant nematic the molecules of the skewed cybotactic groups are of course parallel to the magnetic field and above the re-entrant nematic-smectic C transition (which is weakly first order $\Delta H_{N_{re}-S_C} < 7 \text{ cal. mole}^{-1}$).

This alignment remains in S_C with tilted layers : $d_{S_C} \rightarrow d_{S_A}$. Therefore we have been able to measure directly the tilt angle from the position of the small angles spots on diffraction patterns obtained by increasing temperature from the reentrant nematic phase. Close to the S_A phase, the tilt angle α tends to zero and the layer spacing d_{S_C} is hence much larger than the average molecular length ($d_{S_C} \rightarrow d_{S_A} \simeq 1.2 L_M$) (Fig. 3). This kind of S_C is a *partial bilayer* S_C similar to the S_C phase studied by G. Pelz *et al.* [14] in a binary mixture. Moreover the S_C - S_A transition appears like a continuous change of a *partial bilayer* biaxial medium in a uniaxial one ($\Delta H_{S_A-S_C} < 5 \text{ cal. mole}^{-1}$).

Fig. 3. — Layer spacing d and tilt angle α versus temperature for an equimolar mixture of decyloxy compound of 2 with decyloxy derivative of 1 ($X = -CH=N-$). In the re-entrant nematic phase these parameters are connected with the S_C fluctuations.

At last, decreasing temperature in the re-entrant nematic phase, a second diffuse scattering slightly appears with a smaller wavelength than the one of the high temperature S_C fluctuations (Fig. 4). This suggests a virtual low temperature smectic modulation (S_A or S_C ?) at lower temperature and confirms that the re-entrant nematic phase originates from the competition between two kinds of damped smectic fluctuations [15, 17].

Fig. 4. — X-ray pattern of the re-entrant nematic phase at low temperature with skewed cybotactic groups and additional diffuse spots at larger angles.

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