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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] benzylidène-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] benzylidene-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] :

$$
\text{R} - \text{COO} - \text{X} - \text{CN}
$$

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] benzylidene-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 :

$$
\text{C}_n\text{H}_{2n+1}\text{O} - \text{CH} = \text{CH} - \text{COO} - \text{CH} = \text{N} - \text{CN}
$$

2. Results and discussion. — The substances were synthesized by the condensation of 4-formylphenyl 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

<table>
<thead>
<tr>
<th>n</th>
<th>K</th>
<th>N</th>
<th>S_C</th>
<th>S_A</th>
<th>N</th>
<th>I</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>●</td>
<td>120</td>
<td>—</td>
<td>—</td>
<td>●</td>
<td>(92)</td>
</tr>
<tr>
<td>7</td>
<td>●</td>
<td>92</td>
<td>—</td>
<td>—</td>
<td>●</td>
<td>124</td>
</tr>
<tr>
<td>8</td>
<td>●</td>
<td>99</td>
<td>152.5</td>
<td>—</td>
<td>●</td>
<td>223</td>
</tr>
<tr>
<td>9</td>
<td>●</td>
<td>93</td>
<td>(74)</td>
<td>—</td>
<td>●</td>
<td>244</td>
</tr>
<tr>
<td>10</td>
<td>●</td>
<td>100</td>
<td>(70)</td>
<td>●</td>
<td>(87)</td>
<td>257</td>
</tr>
<tr>
<td>11</td>
<td>●</td>
<td>95</td>
<td>—</td>
<td>—</td>
<td>●</td>
<td>(66)</td>
</tr>
</tbody>
</table>

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 \( X = \text{CH}==\text{CH} \ldots \text{Q} \). Concerning the octyloxy derivative of 2 a stable re-entrant nematic phase with the N S_A N sequence is ob-

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Fig. 1. — Diagram of the isobaric state for the mixture of 2 \( (n = 8) \) (on left) with 1 \( (R = \text{C}_8\text{H}_17\text{O}, X = \text{CH}==\text{N}) \) (on right).
A RE-ENTRANT POLYMORPHISM N S_A S_C N_re

served. In contrast with the low homologues $T_{NA}^{T8}$ is hence larger than 0.87, and this thermo-
dynamical 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
$X = -CH=NH$—. 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 deri-

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-S_C sequence of the octyloxy
derivative of 1 ($X = -CH=NH$) [7, 8, 13] (Fig. 1). In comparing the decyloxy compound of 2
with equal alkoxy chain derivative of 1 ($X = -CH=NH$) we give evidence for the perfect mis-
cibility 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 CuKα 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 ($R = C_{10}H_{21}$O,
$X = -CH=NH$) (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: $d_{SC} \rightarrow d_{SA}$. 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 $\alpha$ tends to zero and the layer spacing $d_{SC}$ is hence much larger than the average molecular length ($d_{SC} \rightarrow d_{SA} \simeq 1.2 L_M$) (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 ($\Delta H_{S_A-S_C} < 5 \text{ cal. mole}^{-1}$).

![Image of a graph showing the layer spacing $d$ and tilt angle $\alpha$ versus temperature for an equimolar mixture of decyloxy compound of 2 with decyloxy derivative of 1 ($X = \text{CH} = \text{N}$.)](image)

Fig. 3. — Layer spacing $d$ and tilt angle $\alpha$ versus temperature for an equimolar mixture of decyloxy compound of 2 with decyloxy derivative of 1 ($X = \text{CH} = \text{N}$). 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.

References