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Classification

Physics Abstracts

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New phase transitions S_C - S_{C_2} and S_{A_d} - S_{C_2} in pure mesogens

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Résumé. — Quatre homologues d'une série nouvelle 4-alkoxybenzylidène-4'-(4''-cyanobenzoyloxy) aniline sont présentés. Le dérivé decyloxy présente, pour la première fois, une transition S_C - S_{C_2} dans une séquence $N S_A S_C S_{C_2}$. L'identification de toutes ces phases a été effectuée conjointement par observation des textures au microscope et par l'étude des diagrammes de phase binaire. De plus, des mesures RX révèlent l'existence d'une nouvelle transition de phase S_{A_d} - S_{C_2} dans le dérivé tridecyloxy.

Abstract. — Four homologues of the new series 4-alkoxybenzylidene-4'-(4''-cyanobenzoyloxy) aniline are presented. The decyloxy compound exhibits for the first time a S_C - S_{C_2} transition with the $N S_A S_C S_{C_2}$ sequence. Microscopic observations and binary diagram studies give this result. Furthermore a new S_{A_d} - S_{C_2} sequence is revealed by X-ray measurements.

1. Introduction. — Sigaud *et al.* [1] reported in 1978 the first example of a transition S_A - S_A in a mixture between a polar compound 4-pentylphenyl 4'-(4''-cyanobenzoyloxy) benzoate (DB_5CN) and a non polar compound terephthal-bis butyl-aniline (TBBA). This transition S_A - S_A was discovered by D.S.C. measurements and confirmed as S_{A_1} - S_{A_2} (S_{A_1} : monolayered smectic A phase, S_{A_2} : bilayered one) by X-ray analysis [2]. Then, in 1980 there was revealed a transition S_{A_d} - S_{A_2} (S_{A_d} : partially bilayered smectic A phase) in a pure compound [3] : 4-heptylphenyl 4'-(4''-cyanobenzoyloxy) benzoate (DB_7CN) and finally in a mixture, a sequence of transitions S_{A_d} - S_{A_1} - S_{A_2} [4]. These results showed that there are probably three different smectic A phases and suggested by analogy that it should be possible to obtain different transitions between smectic C phases (it is evident to imagine that these phases are the tilted homologues of the various S_A phases).

Now we present four homologues of the new series 4-alkoxybenzylidene-4'-(4''-cyanobenzoyloxy) aniline in which the decyloxy derivative exhibits a novel transition S_C - S_{C_2} .

2. Results and discussion. — The substances were synthesized either by the condensation of the 4-alkoxybenzaldehydes and 4-(4''-cyanobenzoyloxy) aniline in ethanolic solution or by the esterification of 4-cyanobenzoyl chloride with the phenate of the 4-alkoxybenzylidene-4'-hydroxyaniline in benzene. They were purified by recrystallization from ethanol. Phase transitions were studied both by polarizing microscopy (equipped with a Mettler FP₅) 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 1.*

<i>n</i>	K	S_{C_2}	S_C	S_{A_d}	N	I
10	.	120	(106)	(112)	.	241 . 249 .
11	.	112	(102)	—	.	241 . 244 .
12	.	117	(113)	—	.	242 — .
13	.	112	(110)	—	.	234 — .

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

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

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

The compound $n = 10$ exhibits the tetramorphism : a nematic, a smectic S_{A_d} and two smectic C phases. On cooling the isotropic liquid of this compound one can observe the nematic phase with a schlieren texture (Fig. 1a). Below this nematic phase the smectic A phase with focal conics and homeotropic textures appears (Fig. 1b). 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 (Fig. 1c). On cooling this S_C phase another smectic phase makes its appearance as strongly birefringent droplets (Fig. 1d). On further cooling the droplets coalesce to give a schlieren texture typical of a S_C phase (Fig. 1e). Let us point out that, with longer chains, the germination of this S_{C_2} phase in the S_A phase is in every respect similar (Fig. 2). The undecyloxy derivative exhibits the trimorphism N S_{A_d} S_{C_2} and the nematic phase disappears in the two derivatives $n = 12$ and 13.

The smectic S_{C_2} phases of these four compounds appear entirely miscible among themselves (Fig. 3) but not miscible with the high temperature S_C phase of the decyloxy derivative. The bilayer S_{C_2} nature (by analogy with bilayer S_{A_2}) is suggested by the phase diagram (contact method) between $n = 13$ (or $n = 10$) and a standard compound 4-nonyloxy or decyloxyphenyl 4'-(4"-nitrobenzoyloxy) benzoate (DB_9ONO_2 or $DB_{10}ONO_2$ [5]) (Fig. 4). In addition three layering reflection orders are visible in the X-ray patterns of this phase with $d \simeq 51 \text{ \AA}$ and the experimental tilt angle is large ($\theta > 30^\circ$) in agreement with the calculation of θ considering the expected bilayer S_{C_2} arrangement with $d \simeq 2 / \cos \theta$ (l obtained from SASM stereomodel with the completely stretched conformation; $n = 13$, $l \simeq 35 \text{ \AA}$). The higher temperature S_A phase is not a bilayer but a partially bilayer S_{A_d} phase with $d \simeq 53 \text{ \AA}$ and with only one visible reflection order from the layers. Thus we think we have a new polymorphism S_{A_d} - S_{C_2} . Unfortunately we cannot confirm the S_C - S_{C_2} sequence by X-ray experiments because in the $n = 10$ compound both mesophases are too metastable and the crystallization first occurs in the supercooled region. Nevertheless we are able to confirm in the last compound that the S_A phase is a partially bilayer S_{A_d} ($d/l \simeq 1.3$) with an additional diffuse spot corresponding to the molecular length.

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a)

b)

c)

Fig. 1. — Mesophases textures of the decyloxy derivative of 1 : *a*) Nematic phase at 245 °C; *b*) Smectic A phase (S_{A_d}) at 150 °C; *c*) Smectic C phase at 110 °C; *d*) Appearance of S_{C_2} phase in S_C phase at 106 °C; *e*) S_{C_2} phase at 104 °C.

Fig. 2. — Appearance of S_{C_2} phase in S_{Ad} phase at 110 °C of $1_{\sim}(n = 13)$.

Fig. 3. — Phase diagram of mixtures of the compounds $1_{\sim} n = 13$ (on the left) and $1_{\sim} n = 10$ (on the right).

Fig. 4. — Phase diagram of mixtures of the compounds $1, n = 10$ (on the left) and $\text{DB}_{10}\text{ONO}_2$ (on the right).

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