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W. Weissflog [a], G. Pelzl [b], A. Wiegeleben [b] & D. Dews [b]

[a] VEB Spezialchemie Leipzig, Abt. FE, GDR, Elsteraue 9, DDR-7143, Leipzig-Lützschena

[b] Sektion Chemie, Martin-Luther-Universität Halle, GDR, Mühlpforte 1, DDR-402, Halle

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A NEW POLYMORPHISM VARIANT: NEMATIC - SMECTIC C - SMECTIC A - NEMATIC

W.WEISSFLOG [+], G.PELZL, A.WIEGELEBEN and D.DEMUS

[+]VEB Spezialchemie Leipzig, Abt. FE, GDR, Elsteraue 9, DDR-7143 Leipzig-Lützschena,

Sektion Chemie, Martin-Luther-Universität Halle, GDR, Mühlpforte 1, DDR-402 Halle

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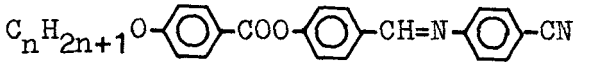
Abstract: Some homologous 4[4-n-Alkyloxy-benzoyloxy]-benzylidene-4'-cyanoanilines are presented. Three of them exhibit a reentrant nematic phase. For the decyloxy compound the variant of polymorphism N_{re} S_C S_A N is. was found.

As recently reported[1] 4[4-n-octyloxybenzoyloxy]-benzylidene-4'-cyanoaniline exhibits a reentrant nematic phase similar to the analogous stilbene [2,3]. Now we present some additional members of this homologous series. The substances were synthesized by condensation of 4-formyl-phenyl 4'-alkyloxy-benzoates[4] and 4-cyanoaniline in ethanolic solution. The substances were purified by recrystallization from ethanol or amylalcohol.

The transition temperatures observed with a polarizing microscope are given in table 1.

TABLE 1



n	cr	N_{re}	S_C	S_A	N	is.
4	.	137.5 -	-	.	(101) .	299 .
5	.	122 -	-	.	(102) .	280 .
6	.	115 -	-	.	(84) .	272 .
7	.	115 -	-	.	(68) .	265 .
8	.	108 .	152 -	.	198 .	255 .
9	.	97 (.	94) -	.	224 .	247 .
10	.	100 (.	66 .	79) .	232 .	242 .

cr : solid crystal
S_A, S_C: smectic A, C
N : nematic
is. : isotropic

The numbers are the transition temperatures (°C). Brackets denote monotropic phases.

As seen from the table, the first four homologues show nematic phases with a large temperature range and also metastable S_A phases. In the octyloxy compound additionally a stable reentrant nematic phase (N_{re}) occurs. In the following members of the homologous series [9,10] metastable reentrant nematic phases exist. Surprisingly, in the decyloxy derivative, between the reentrant nematic phase and the S_A phase a smectic C phase appears. To our knowledge this is the first case that a smectic C liquid crystal compound possesses a strong longitudinal dipole moment.

The identification of the S_A and the reentrant nematic phase has been made by texture observation and by the study of miscibility with suitable reference substances [1].

Unfortunately, the S_C phase and also the reentrant nematic phase of the decyloxy compound could not be identified by miscibility studies, because in the phase diagrams they always were separated by other phases (S_A) from the corresponding phase regions of a reference substance.

The occurrence of the S_C phase is indicated by texture observation: This phase appears either as a schlieren texture exhibiting only points with four dark brushes or as a broken fan-shaped texture. On cooling the S_C schlieren texture, the reentrant nematic phase shows also a schlieren texture. On cooling the broken fan-shaped texture of S_C, the nematic phase forms a **paramorphic** fan-shaped texture. The same texture was also observed in the nematic phase of the nonyloxy derivative.

The transition $S_C \longrightarrow$ reentrant nematic could be detected by differential scanning calorimetry (see table 2).

As can be seen further from the table 2, the transition enthalpies N_{re}/S_A and S_A/N distinctly increase from the C_8 to the C_{10} homologues.

The new polymorphism variant was confirmed by electrooptical investigations. The nematic high-temperature phase was oriented in a planar texture, in which the molecule director is aligned parallel to the substrate surfaces. On slowly cooling down, this director

TABLE 2

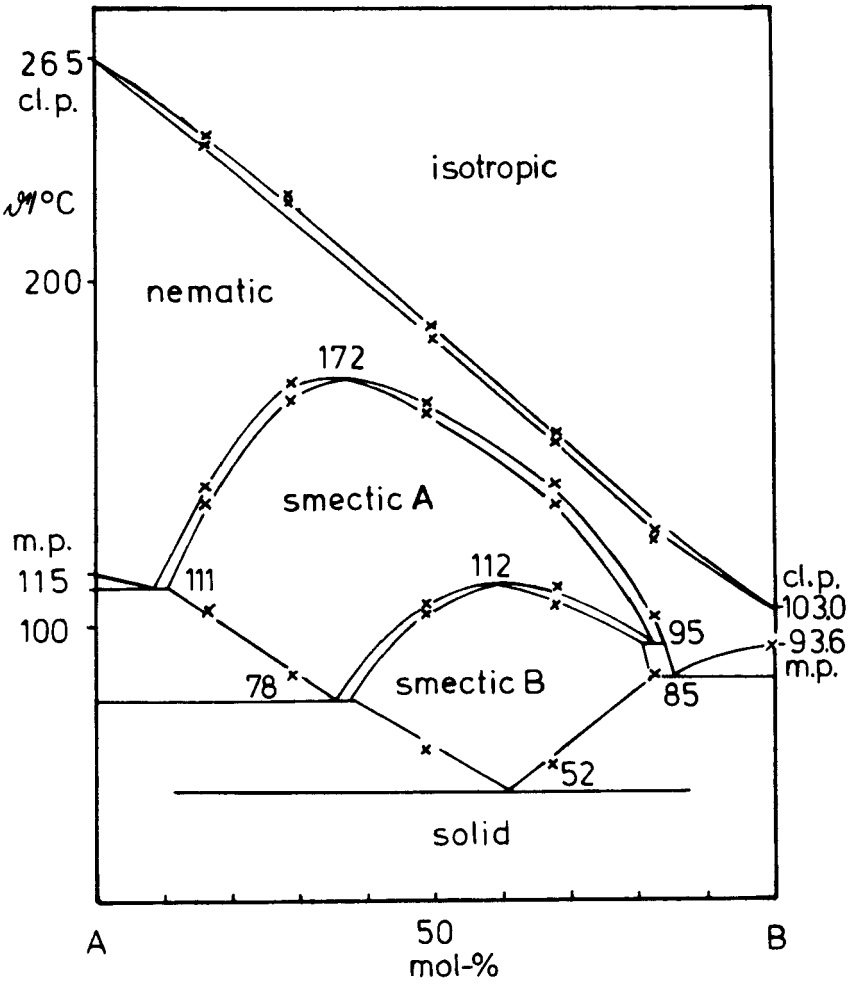
Transition Enthalpies (J mol^{-1}) for the C_8, C_9 and C_{10} Homologues

n	melt.	N_{re}/S_C	S_C/S_A	N_{re}/S_A	S_A/N	N/is.
8	39660	-	-	17.5	15	1396
9	8350	-	-	130	380	1600
10	43000	47	50×	-	800×	1600×

×The transition peaks are not sharp and therefore the analysis is more difficult

orientation remains in the S_A, S_C and N_{re} phase. When an electric field is applied perpendicularly to the director of the N or S_C phase, a dielectric reorientation (Fréedericksz transition) occurs. It was found that the threshold voltage of the reorientation in the reentrant nematic phase was a little higher (2.5 Volts) than that observed in the high-temperature nematic phase (2 Volts). The threshold voltage of the Fréedericksz effect in S_C was found to be about 4 Volts. This threshold voltage is unusually low compared with other S_C substances [5,6,7]. Obviously this is the result of the high positive dielectric anisotropy. Furthermore we could observe the typical optical pattern of S_C during the dielectric reorientation characterized by the occurrence of large homogenous regions with uniform interference colours [5].

The new compounds presented here act as good electron acceptors and form with suitable liquid crystalline



A: $C_7H_{15}O$-Ph-COO-Ph-CH=N-Ph-CN

B: $C_6H_{13}NH$-Ph-Ph-NHC_6H_{13}

FIGURE 1

electron donators, e.g. 4,4'-bis-[n-alkylamino]-biphenyls,[8] stable electron-donator-acceptor-(EDA) complexes. Whereas the 4-[4-n-alkyloxy-benzoyloxy]-benzylidene-4'-cyanoanilines are slightly yellow and the 4,4'-bis-[n-alkylamino]-biphenyls are colourless, the mixtures of these compounds become strongly yellow due to the charge transfer band in the visible region. This effect is clearly seen in the boundary line of a contact preparation. Fig. 1 shows the isobaric diagram of state of the C_7 - compound and the 4,4'-bis-[n-hexylamino]-biphenyl [9] containing induced S_B and S_A phases with maxima in the transition curves. The different concentration positions of the two maxima indicate that the concentrations at the maxima must not always be identical with the composition of the complexes. Obviously by the EDA interaction, the longitudinal shifting of molecules is restricted and therefore the formation of smectic layers is favoured.

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