Induced Smectic Phases

I. Polymorphism in Binary Mixtures of Alkyloxybenzylidene-alkylanilines with Alkyl- and Alkyloxy- cyanobiphenyls

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The diagrams of state of mixtures of 4-*n*-alkyloxybenzylidene-4′-*n*-butylanilines with 4-*n*-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls are studied. The mixtures form induced smectic phases of type S_A, S_B and S_E. In all three smectic phases the thickness of the smectic layers agrees with the mean values of the molecular lengths. In most cases the induced S_A phases do not show uninterrupted miscibility with the S_A phases of the pure components. For instance, the system 4O · 4/8CBP exhibits three separate S_A phase areas. The maximum transition temperatures of the induced smectic phases increase with increasing chain length of the azomethines, but remain constant in case of the S_A and S_B phases or even decrease in case of the S_E phases with increasing chain length of the cyanobiphenyls.

1. Introduction

Mixtures of liquid crystals with similar chemical structures exhibit in general diagrams of state with nearly linear phase boundaries. In contrast, very complicated phase boundaries can be obtained, if the intermolecular interaction in the mixture differs from the interactions in the pure compounds. Thus, mixtures of liquid crystals that are different with respect to their molecular properties show in some cases a minimum or a maximum in the transition temperatures [1]. A strong enhancement in the stability of smectic phases or even the formation of smectic phases from non-smectic liquid crystals is observed in mixtures of cyano- or nitro-substituted liquid crystals with liquid crystals which do not possess such substituents. For the first time Dave, Patel and Vasanth [2] observed such a very stable smectic phase, which will be called induced smectic phase, in a mixture of diethyl-4,4′-azoxydibenzoate with 4-nitrobenzylidene-4′-ethoxyaniline.

In general these induced smectic phases form smectic A phases. An exception to this rule are the mixtures 4-methoxybenzylidene-4′-*n*-butylaniline/4-*n*-pentyl-4′-cyanobiphenyl, 4,4′-di-*n*-pentylbiphenyl/4-*n*-heptyloxy-4′-cyanobiphenyl [3], 4,4′-bis-[*n*-hexylamino]-biphenyl/4-[4-*n*-heptyloxybenzoyloxy]-benzylidene-4′-cyanoaniline [4]. They exhibit S_B or S_E phases or both. In most cases the classification of the induced phases as solid phases [5, 6] seems to be incorrect.

This paper presents a detailed investigation of the polymorphism of induced smectic phases in mixtures of 4-*n*-alkyloxybenzylidene-4′-*n*-butylanilines with 4-*n*-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls. Especially, we are interested in the appearance of the different smectic phase types and in the dependence of the transition temperatures on the alkyl chain length of the components.

2. Experimental

The diagrams of state were investigated by means of microscopical observations of the samples on a heating stage. Some diagrams were investigated by observation of mixtures with known concentrations, whereas in most cases the contact method was used.

X-ray diffraction patterns were recorded with nickel-filtered CuKα radiation on a flat film. The samples were contained in thin walled glass tubes of 0.5 mm diameter and were heated with an air stream.

The 4-*n*-alkyl-4′-cyanobiphenyls (*n*CBP) and the 4-*n*-alkyloxy-4′-cyanobiphenyls (*n*OCBP) were obtained from BDH. Two of the 4-*n*-alkyloxybenzylidene-4′-*n*-butylanilines (*n*O·4) were obtained from Riedel-de Haën AG (1O·4 and 2O·4); 3O·4

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and 4O·4 were available from earlier investigations [7].

3. Results and Discussion

In order to study the phase sequences and the transition temperatures systematically, four series of binary mixtures were investigated. In each series one component was kept constant, whereas the alkyl chain length of the other component was varied as follows:

I 2O·4/*n*CBP $n = 5$ to 8,
II 2O·4/*n*OCBP $n = 5$ to 8,
III *n*O·4/7CBP $n = 1$ to 4,
IV *n*O·4/7OCBP $n = 1$ to 4.

a) Observed Types of Diagrams of State

Figure 1 shows the diagram of state of the system 2O·4/8OCBP. At medium concentrations, i.e. in the region of the induced smectic phases, the phase sequence N, S_A, S_B, S_E is observed. The induced nematic phase exhibits an uninterrupted miscibility with the nematic phases of 2O·4 and 8OCBP, whereas in case of the induced smectic phases no uninterrupted miscibility with one of the phases of the pure components is observed.

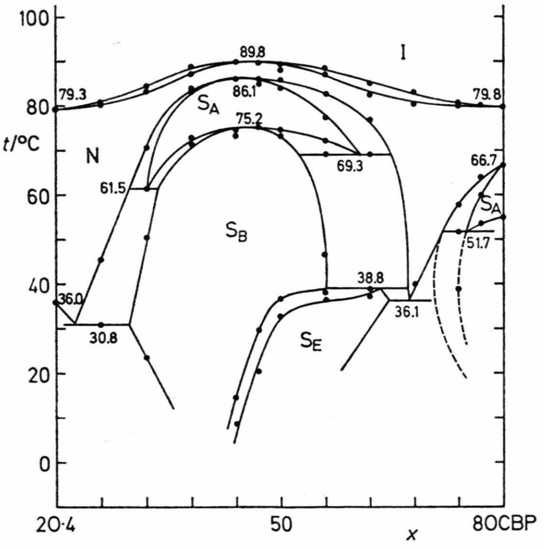

Fig. 1. Diagram of state of the system 2O · 4/8OCBP. The phases are characterized as follows: *I*: isotropic; *N*: nematic; S_A, S_B, S_E and S_G: smectic phases of type A, B, E and G, resp. *x* is the composition in mole %.

The observed textures suggest the assignment S_A, S_B and S_E for the smectic phases. The smectic A phases exhibit fan shaped textures in most cases. Transition bars appear at the transition to the smectic B phases. These fan shaped textures change on standing for some time into the stable mosaic textures. The transition S_B to S_E is accompanied by a colour change in the single domains of the mosaic textures, which is caused by new orientations of the single domains. In case of fan shaped textures of the smectic B phase concentric arcs appear at the transition to the S_E phase.

The assignment of the smectic phases on the basis of textures was further confirmed by an X-ray investigation of a 50 mole% sample at 80, 60 and 22 °C, which yielded the typical X-ray patterns of S_A, S_B and S_E phases. The layer thickness, which is determined from the diameter of the inner ring, is constant for the three smectic phases within the uncertainty of the measurement and amounts to 2.22 nm. The mean value of the molecular lengths of 2O·4 (2.1 nm) and of the 8OCBP monomer (2.4 nm), which were measured on Dreiding models, is 2.25 nm. Hence it follows in agreement with an earlier statement [3] that in the induced smectic phases no bilayer is formed.

The nematic, S_A and S_B phase exhibit a pronounced maximum in the transition temperatures at medium concentrations. The S_E phase shows no maximum but disappears in a three phase transition. Besides the S_A phase at medium concentrations a second S_A phase, which is separated by a nematic miscibility gap, appears at high 8OCBP concentrations in this system. Furthermore, a reentrant nematic behaviour is observed at high concentrations of 8OCBP in accordance with earlier results [8].

Some further diagrams of different type, which will be discussed only with regard to their special features, are shown in Fig. 2 to 7. The uninterrupted miscibility of the induced S_B phases with the monotropic S_B phase of 3O·4 (Fig. 2 and 6) and with the enantiotropic S_B phase of 4O·4 (Fig. 4) provides a further confirmation of the classification of this smectic phase. In all systems S_B phases appear covering the largest part of the induced smectic phase area. Thus, the usual phase sequence of induced phases N, S_A, solid is not observed in any case. As the cyanobiphenyls and the azomethines exhibit the usual phase sequence in mixtures with

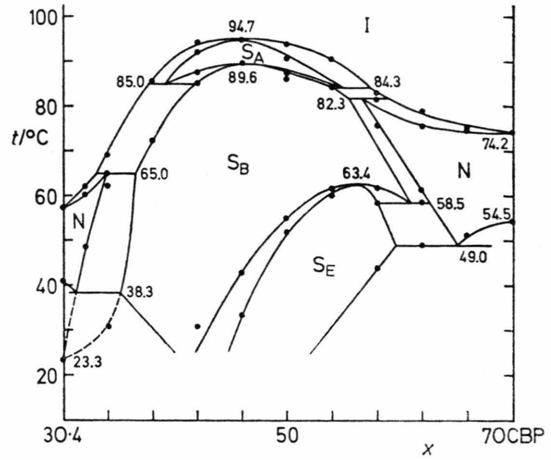

Fig. 2. Diagram of state of the system 3O · 4/7OCBP.

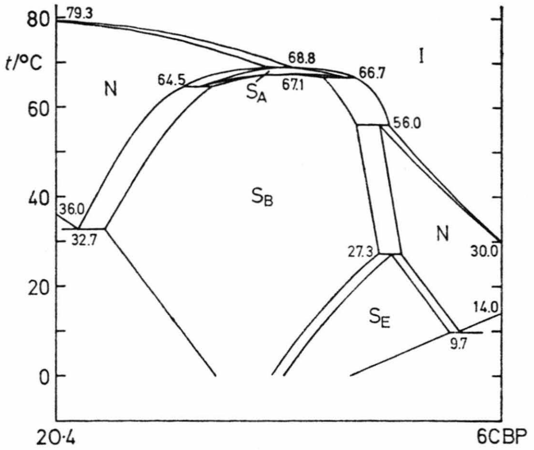

Fig. 5. Diagram of state of the system 2O · 4/6CBP.

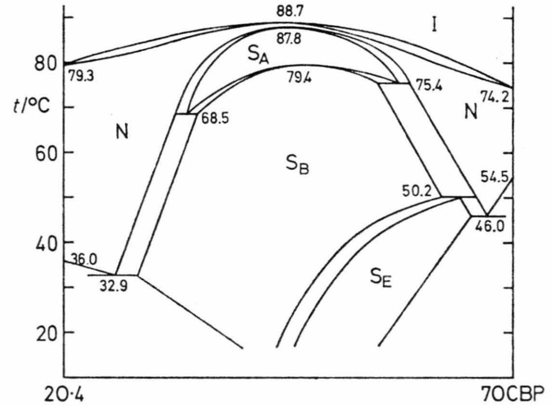

Fig. 3. Diagram of state of the system 2O · 4/7OCBP.

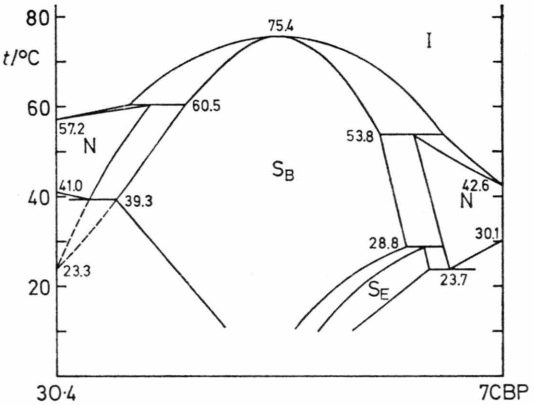

Fig. 6. Diagram of state of the system 3O · 4/7CBP.

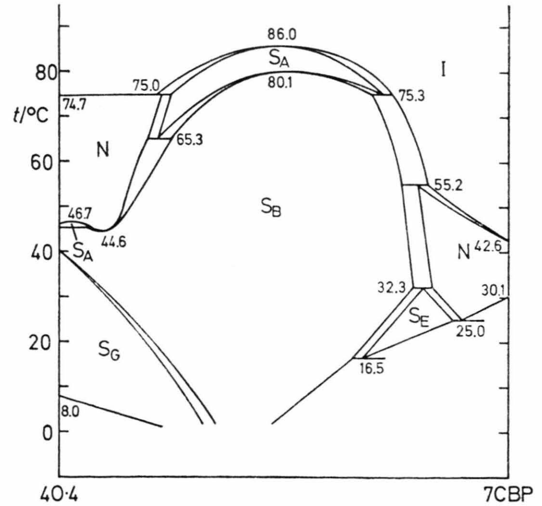

Fig. 4. Diagram of state of the system 4O · 4/7CBP.

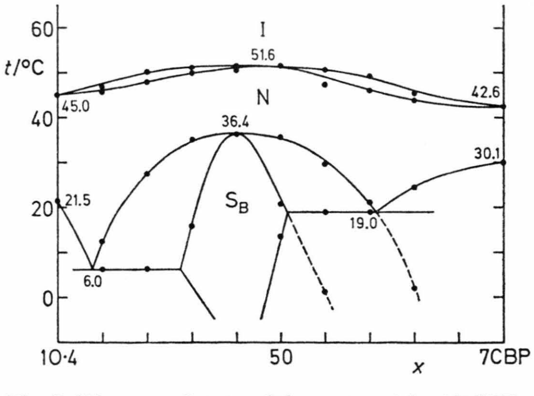

Fig. 7. Diagram of state of the system 1O · 4/7CBP.

other liquid crystals (e.g., the systems 4,4′-di-*n*-heptyloxy-azoxybenzene/7OCBP [9] and 2O·4/4-nitrophenyl-4′-*n*-octyloxybenzoate [10]) the observed phase sequence must be due to a special interaction of these liquid crystals.

The S_E phase is exhibited in most of these systems. Even in the systems 1O·4/7CBP (Fig. 7), 1O·4/7OCBP and 2O·4/8CBP, in which the S_E phases are missing, they may possibly be obtained by further undercooling of the samples below 0 °C. All systems except 3O·4/7OCBP (Fig. 2), which exhibits a maximum in the S_B-S_E transition temperature, show an increase in this temperature with increasing cyanobiphenyl concentration. It seems that the S_E phase in these systems is mainly caused by the cyanobiphenyl compounds. The ratio of the S_E phase area to the total smectic phase area is relatively small as compared with the system 4,4′-di-*n*-pentylbiphenyl/7OCBP [3], in which the S_E phase occupies by far the largest part of the induced phase area. Probably, this is due to the fact that, in contrast to the azomethines, the pure 4,4′-di-*n*-pentylbiphenyl already exhibits a very stable S_E phase. The S_G phase [11] of the component 4O·4 (Fig. 4) is not enhanced in the region of medium concentrations.

Further diagrams, which were investigated by us and which are of similar shape as those of Fig. 1 to 7, are not shown separately. Their shapes are described in Table 1.

As the system 4O·4/7CBP exhibits a second S_A phase on the left side of the diagram of state and the system 2O·4/8OCBP does the same on the right side, it is likely that a diagram of state with three separate S_A phase areas is obtainable. Actually, this is the case in the system 4O·4/8CBP (Fig. 8), whereas in the system 4O·4/8OCBP the induced S_A phase is miscible with the S_A phase of 8OCBP.

Table 1. Observed types of diagrams of state. The numbers refer to the Fig. 1 to 8. Boldfaced numbers indicate that the corresponding diagram of state is provided in this paper.

	1O·4	2O·4	3O·4	4O·4
5CBP	—	3	—	—
6CBP	—	**5**	—	—
7CBP	**7**	3	**6**	**4**
8CBP	—	1*	—	**8**
5OCBP	—	4	—	—
6OCBP	—	3	—	—
7OCBP	7	**3**	**2**	4
8OCBP	—	**1**	—	—

* The system 2O · 4/8CBP exhibits no S_E phase.

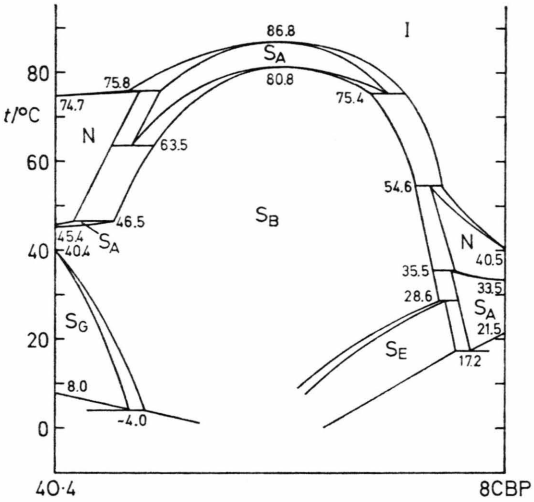

Fig. 8. Diagram of state of the system 4O · 4/8CBP.

Summarizing the observations on polymorphism of induced smectic phases, it follows that the induced smectic phases are S_A, S_B and S_E phases, whereas S_C [3, 9, 12], S_I [13] and S_G phases of the pure components are not enhanced in the area of the induced smectic phases [14]. This behaviour is an indication that only orthogonal smectic phases can form induced smectic phases, whereas tilted smectic phases do not show this property. The observed phase sequence *N*, S_A, S_B and S_E of the induced phases is in accordance with the phase sequence of pure components as stated by Sackmann and Demus [15].

b) Influence of the Alkyl Chain Length on the Polymorphism

In order to enable a comparison of the stability of the induced smectic phases as a function of the alkyl chain length, the maximum transition temperatures for the systems under investigation are given in Table 2.

The most striking effect is the strong increase in the maximum transition temperatures of all induced smectic phases with the alkyl chain length of the azomethines, whereas the transition temperatures of the S_A and S_B phases remain nearly constant or even decrease in case of the S_E phase with increasing chain length of the cyanobiphenyls. From this behaviour the disappearance of the S_E phase in the systems 1O·4/7CBP (Fig. 7) and 1O·4/7OCBP (Table 2), in which the azomethines have the

Table 2. Maximum transition temperatures t of the induced phases. The transition temperatures nematic — isotropic refer to the maximum transition temperature or in case of absence of a maximum they refer to the concentration of the temperature maximum of the induced smectic phase.

System	n	t_N/°C	$t_{\mathrm{S_A}}$/°C	$t_{\mathrm{S_B}}$/°C	$t_{\mathrm{S_E}}$/°C
I	5	67.8	66.7	64.2	28.0
2O·4/*n*CBP	6	—	68.8	67.1	27.3
	7	71.2	69.0	65.2	13.2
	8	69.0	68.3	63.8	—
II	5	—	88.0	83.5	68.5
2O·4/*n*OCBP	6	88.9	88.2	79.7	54.3
	7	88.7	87.8	79.4	50.2
	8	89.8	86.1	75.2	38.8
III	1	51.6	—	36.4	—
*n*O·4/7CBP	2	71.2	69.0	65.2	13.2
	3	—	—	75.4	28.8
	4	—	86.0	80.1	32.3
IV	1	58.7	—	55.3	—
*n*O·4/7OCBP	2	88.7	87.8	79.4	50.2
	3	—	94.7	89.6	63.4
	4	—	103.0	92.1	65.0

shortest alkyl chain, and the disappearance in the system 2O·4/8CBP (Table 2), which contains the cyanobiphenyl with the longest alkyl chain, can be understood.

The thermal stability of the induced smectic phases is not yet fully understood. In each case, the formation of these phases at medium concentrations shows that each molecule is favourably surrounded by molecules of the other kind. Furthermore, the formation of the smectic phases shows that there are intermolecular interactions which force the central parts of the molecules to lie side by side. An increase in chain length of the azomethines causes a strong increase of the potential barrier for parallel displacement, since the cyano group is very polar and interacts favourably with the central core part of the azomethines. An increase in chain length of the cyanobiphenyls influence the height of the potential barrier to a much smaller degree.

The strong alternation of the clearing temperatures of the cyanobiphenyls is reduced to a very small effect in case of the induced phases. The disappearance of the nematic phase in the system 2O·4/5OCBP and 2O·4/6CBP, in which the cyanobiphenyls have about the same chain length and minimum clearing temperatures in the homologous series, is due to this small effect. The transition temperatures of the induced phases in the mixtures with the alkyloxy-cyanobiphenyls are about 20 K higher than the corresponding values for the alkylcyanobiphenyls. This effect seems to be caused by the properties of the pure cyanobiphenyls, for which a transition temperature difference of the order of 30 K in the same direction is observed. The disappearance of the nematic phase in the four systems with 3O·4 and 4O·4 is due to the appearance of monotropic or enantiotropic smectic phases, which are further enhanced in the region of medium concentrations.

4. Conclusion

Mixtures of 4-*n*-alkyloxybenzylidene-4′-*n*-butylanilines (*n*O·4) with 4-*n*-alkyl- and 4-*n*-alkyloxy-4′-cyanobiphenyls (*n*CBP and *n*OCBP, resp.) exhibit induced smectic phases of the type S_A, S_B and S_E. The largest part of the induced smectic phase areas in the diagrams of state is covered by S_B phases, whereas the S_A phases show only very small areas of stability or do not exist at all in some mixtures. In most cases the S_A phases of the pure components do not show an uninterrupted miscibility with the induced S_A phases. For example, the system 4O·4/8CBP exhibits three separate S_A phase areas. Furthermore, the transition temperature nematic-smectic A decreases on mixing 8CBP or 8OCBP with 2O·4. At the moment neither a reason nor a systematic scheme for the miscibility behaviour of the S_A phases of the cyanobiphenyls and the induced smectic phases can be presented. X-ray measurements [3] have shown that according to the layer thickness the induced phases contain the unassociated cyanobiphenyls, whereas the pure cyanobiphenyls are known to form bilayers owing to association. However, the expected difference in the dependence of the layer thickness on concentration for systems with interrupted and uninterrupted miscibility of the S_A phases could not be detected [8].

Comparing the magnitude of the areas of the different induced smectic phases in mixtures with cyanobiphenyls, it seems that this ratio is caused in many cases by the appearance of these smectic phases in the second component of the mixture or their higher homologues. Thus, 4,4′-di-*n*-pentylbiphenyl and its induced phase with 7OCBP exhibit a strong S_E phase [3]. 3O·4 as well as 4O·4 and their induced smectic phases exhibit mainly S_B phases.

If the S_A phase shows a greater temperature range of stability — as for instance 7O·4 in the *n*O·4 series —, the S_A phase is also stabilized for 20 K in the system 7O·4/7OCBP [10]. If the second component and their higher homologues exhibit neither S_B nor S_E phases, in most cases S_A phases are induced. This is the case in the systems 4,4′-di-*n*-alkyloxyazoxybenzenes/cyanobiphenyls [9] and aromatic esters/cyanobiphenyls [10]. At the moment a generalization of this rule to other liquid crystals, especially to reentrant nematic liquid crystals with three phenyl rings, is not possible, as only a very limited number of systems has been investigated [4]. Further investigations must show, how the replacement of the cyanobiphenyls by other liquid crystals exhibiting different smectic phases will influence the type of the induced smectic phase.

The transition temperatures of the induced smectic phases remain constant or even decrease, if the alkyl chain length of the cyanobiphenyls is increased, whereas a strong increase of the transition temperatures is observed with increasing chain length of the *n*O·4 compounds. This effect can be interpreted as a result of the strong interaction of the cyano substituents with the cores of the *n*O·4 compounds, as the potential barrier for a parallel displacement of different molecules increases with increasing chain length of the *n*O·4 compounds.

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