Induced Smectic Phases
II. Influence of the Amino Substituent on the Induction of Smectic Phases *

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The diagrams of state have been studied for some liquid crystal mixtures which show the induction of smectic phases. Each of the systems studied contains one component with an amino group which influences the polarity and the electron donor property of the molecules. The discussion of the diagrams of state, of the thickness of the smectic layers and of the colours of the mixtures, which indicate the formation of CT complexes, shows that existing models can not explain the induction of smectic phases.

Introduction

The formation of induced smectic phases in mixtures of nematic liquid crystals is a well known phenomenon. Many models have been proposed in order to explain this phenomenon. However, a complete explanation of the induction of smectic phases is still missing. Even no definite criterion for the appearance of this effect has been presented up to now. At present, the best criterion is the classification scheme proposed by Engelen et al. [1]. According to this classification scheme liquid crystals are divided into terminal polar (P) and terminal non-polar (N) compounds. Mixtures of the type PN are supposed to form induced smectic phases, whereas mixtures of the types PP and NN should show no enhancement of the thermal stability of smectic phases. This rule is obeyed by a large number of systems but some exceptions are known [2].

According to the CT interaction model of Park et al. [3], the formation of induced smectic phases is caused by a CT interaction between electron donor and acceptor molecules. This model is supported by the recent observation of CT bands in the absorption spectra of induced smectic phases. Thus, mixtures of dimethylamino and nitro substituted benzylidene-anilines [4, 5], as well as 4,4′-bis-[alkylamino]-biphenyls in mixtures with liquid crystals containing NO_2 and CN substituents [6, 7] form coloured CT complexes and show the induction of smectic or nematic phases.

For all of the mixtures investigated up to now, e. g. the system 4-n-pentyl-4′-cyanobiphenyl/4-methoxybenzylidene-4′-n-butylaniline [3, 8], the PN rule as well as the donator acceptor (DA) model predict the same behaviour since the polar terminal groups used (CN and NO_2) lead to electron acceptor molecules. Therefore, the investigation of mixtures, for which the two rules predict a different behaviour with respect to the induction of smectic phases, is important. For this purpose liquid crystals containing an amino group are interesting, because the unsubstituted amino group is a polar terminal group, which favours the electron donor behaviour of a molecule. The induction of smectic phases in systems containing alkylamino substituted compounds can be compared with the induction of the analogous alkyloxy compounds which show weaker electron donor behaviour.

This paper reports on the diagrams of state of mixtures of 4,4′-bis-[n-hexylamino]-biphenyl, 4-n-octylamino-4′-cyanobiphenyl and 4-n-octyl-4′-aminobiphenyl with other liquid crystals. X-ray studies give information on the thickness of the smectic layers. Colour changes, which may be attributed to CT complex formation, are reported.

Experimental

Details of the experimental method for the determination of the diagrams of state and the X-ray

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patterns are described in an earlier paper [9]. The colours of the mixtures were determined with the unaided eye. Measurements with an UV spectrophotometer showed that a precise determination of the absorption maxima is not possible, as the extinction coefficients are very small and the absorption is superimposed by the absorption edges of the pure components, especially for 8ACBP and 11ONPB.

The following liquid crystals were used in this investigation:

4-n-octylamino-4'-cyanobiphenyl	8ACBP
4-n-octyloxy-4'-cyanobiphenyl	8OCBP
4-n-octyl-4'-cyanobiphenyl	8CBP
4-n-octyl-4'-aminobiphenyl	8ABP
4,4'-bis-[n-hexylamino]-biphenyl	6A6ABP
4-n-undecyloxy-[4-nitrophenyl]-benzoate	11ONPB
4-n-decyloxy-[4-n-hexyloxyphenyl]-benzoate	10O6OPB

8ACBP and 9ACBP were generously provided by Dr. M. Osman (Brown Boveri & Co, Switzerland). The other liquid crystals were either purchased from BDH (8CBP and 8OCBP) or synthesized in our laboratory (6A6ABP, 11ONBP and 10O6OPB). 8ABP was synthesized from 8CBP by a procedure reported by MacMillan and Labes [10] for the corresponding compound 5ABP. Properties of 8ABP: Melting point 76 °C; ^{1}H NMR in CDCl$_3$ (ppm from TMS) 0.9 (3H, triplet), 1.4 (12H, multiplet), 2.6 (2H, triplet), 3.6 (2H, singlet), 6.7 – 7.6 (8H, multiplet); MS m/e 281 (80), 182 (100). 8ABP exhibits mesomorphic behaviour only in mixtures with other liquid crystals.

Results and Discussion

At first the diagrams of state of 8ABP with other liquid crystals will be discussed. The induction of smectic phases by this component is of special interest, as it possesses a polar terminal group and exhibits electron donor properties. According to the PN classification, the system 8ABP/10O6OPB should exhibit an induced smectic phase. However, Fig. 1 shows that the transition temperatures of the S$_\mathrm{A}$ and S$_\mathrm{C}$ phase of 10O6OPB are strongly depressed by the addition of 8ABP. One might assume that this depression is due to the low lying transition temperatures in the pure 8ABP and that the phase boundaries are therefore strongly inclined. But the appearance of a second S$_\mathrm{A}$ phase, which is separated from the S$_\mathrm{A}$ phase of 10O6OPB by a solid phase, shows that this argument is not valid. Furthermore, 8ABP does induce a smectic phase in mixtures with 8OCBP as shown in Figure 2. According to the DA model, both the components of the system 8ABP/10O6OPB are donors and therefore no induction of a smectic phase is expected.

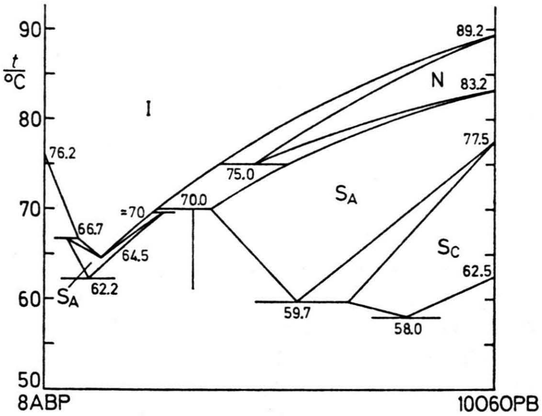

Fig. 1. Diagram of state of the system 8ABP/10O6OPB. The phases are designated as follows: isotropic: I; nematic: N; smectic phases of type A, C, B and E: S$_\mathrm{A}$, S$_\mathrm{C}$, S$_\mathrm{B}$ and S$_\mathrm{E}$, resp. The low temperature phase is always the crystalline solid phase.

The system 8ABP/8OCBP (Fig. 2) exhibits the formation of a solid phase, which may be attributed to a donor acceptor interaction. The S$_\mathrm{A}$ phase range of 8OCBP is also increased in the medium concentration range. This example, too, agrees with the DA model and disagrees with the PN rule. A similar behaviour is observed, if 8OCBP is exchanged by 8CBP (see Table 1). On mixing

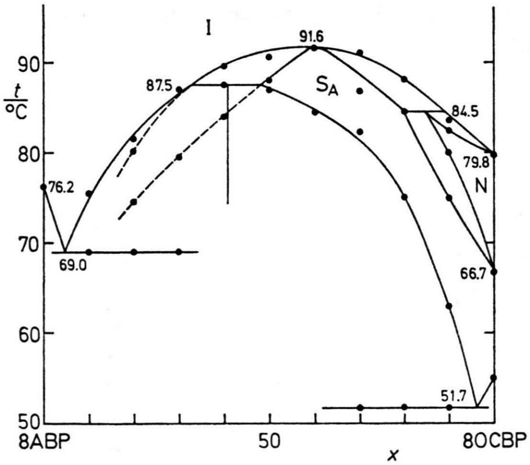

Fig. 2. Diagram of state of the system 8ABP/8OCBP. x is the composition in mole %.

8ABP with 10O10PB, 8ABP with 8OCBP or 8ABP with 8CBP no colour changes could be detected.

The second liquid crystal investigated by us is 8ACBP, which contains a terminal CN group (acceptor group) and an alkyl substituted amino group (donor group). The diagram of state of the system 8ACBP/10O6OPB (Fig. 3) shows in the region of medium concentrations the induction of a smectic phase which can be classified as an S_A phase by its uninterrupted miscibility with the S_A phase of 10O6OPB. The PN classification predicts the formation of an induced smectic phase. However, there are difficulties to classify 8ACBP as donor or acceptor. If the DA model is valid, 8ACBP should behave as acceptor. The thermal stability of the induced smectic phase should therefore be much smaller than in a system in which the amino group is exchanged against an oxygen atom, for example. The corresponding system 8OCBP/10O6OPB [8] shows an S_A phase with a maximum transition temperature which is 19.7 °C higher than the arithmetical mean of the clearing point temperatures of the pure components. In the system 8ACBP/10O6OPB the corresponding difference of 13.2 °C is in fact smaller, but it has to be taken into account that, in contrast to 8OCBP, the pure 8ACBP as well as the eutectic mixture with 9ACBP do not exhibit an S_A phase, even not on undercooling. We therefore conclude that the insertion of an electron donor group into an acceptor molecule has only a small or no influence on the induction of smectic phases in mixtures with donor molecules in contrast to the prediction of the DA model.

Figures 4 and 5 show the diagrams of state of 8ACBP in mixtures with 8OCBP and 11ONPB, which exhibit no induction of smectic phases. As these mixtures are of PP type and AA type, resp., the absence of induced smectic phases in the two diagrams agrees with both rules. In the system 8ACBP/11ONPB the formation of a CT complex is indicated by the observation of a brown colour in a 50% mixture. This complex formation without any induction of a smectic phase disagrees with the DA model.

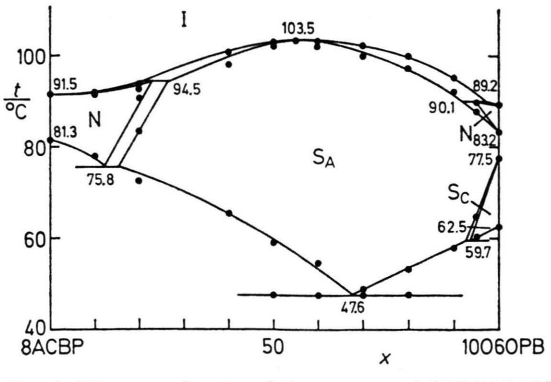

Fig. 3. Diagram of state of the system 8ACBP/10O6OPB.

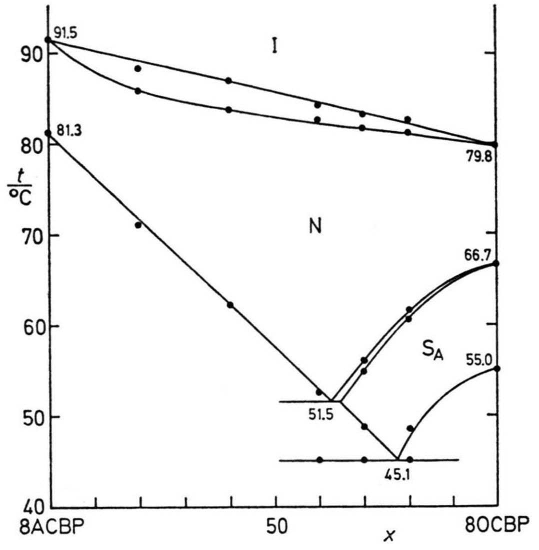

Fig. 4. Diagram of state of the system 8ACBP/8OCBP.

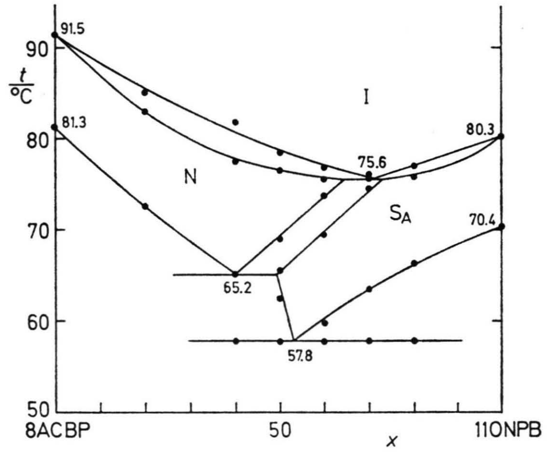

Fig. 5. Diagram of state of the system 8ACBP/11ONPB.

The third liquid crystal investigated by us is 6A6ABP, which exhibits strong electron donor properties. This liquid crystal forms coloured CT complexes with a series of liquid crystals containing NO_2 and CN groups [6, 7]. Both rules lead to the same prediction for mixtures of 6A6ABP: no induction of smectic phases with 10O6OPB (Fig. 6) and an induction with 8OCBP (Fig. 7) and 8ACBP (Figure 8). In both cases smectic B and especially smectic E phases of high thermal stability are formed. A classification of the smectic phases by the uninterrupted miscibility with the pure components is not possible, as the pure liquid crystals do not exhibit smectic phases of these types. The observation of lancet textures indicates the formation of S_B and S_E phases, resp. A further confirmation was obtained by X-ray studies, which yielded the characteristic X-ray patterns of the S_E and S_B phase in these two systems. The thickness of the smectic layers of a 50 mole% mixture of 6A6ABP and 8ACBP amounts to 2.55 nm and corresponds to the thickness of a monolayer as calculated from the mean value of the molecular lengths (2.58 nm) measured on Dreiding models.

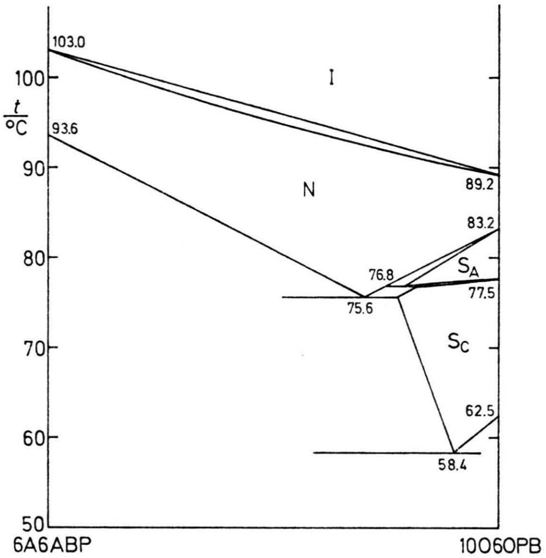

Fig. 6. Diagram of state of the system 6A6ABP/10O6OPB.

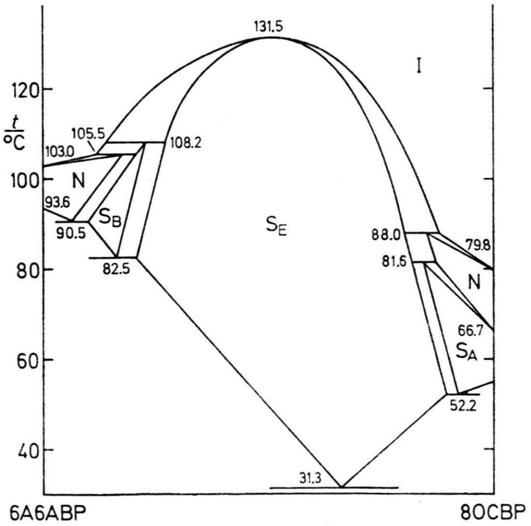

Fig. 7. Diagram of state of the system 6A6ABP/8OCBP.

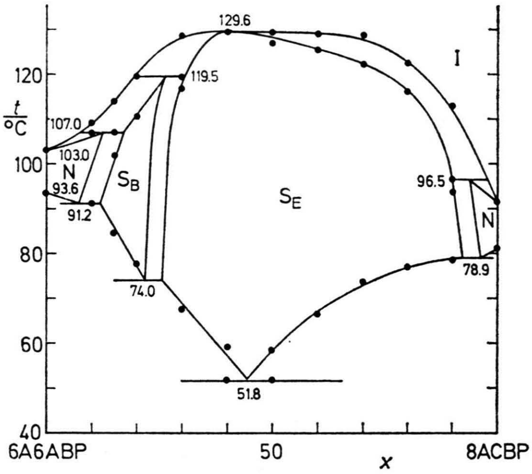

Fig. 8. Diagram of state of the system 6A6ABP/8ACBP.

As in the systems 8ACBP/10O6OPB and 8OCBP/10O6OPB, a comparison of the thermal stability of the systems 6A6ABP/8ACBP and 6A6ABP/8OCBP, in which the clearing point temperatures are increased by 32.3 and 40.1 °C, resp., shows the small influence of a change in the acceptor strength. At least in the system 6A6ABP/8OCBP the formation of a CT complex could be established by the observation of a colour change to yellow when the two liquid crystals are mixed.

The properties of the systems investigated by us and their classification by the two models are summarized in Table 1. Furthermore, Table 1 contains a third classification with respect to the mono or bilayer formation in the pure liquid crystals. In order to determine the layer type of 8ACBP, an X-ray investigation of this component was undertaken. The pure 8ACBP, however, does not show X-ray reflections for the smectic short range order, because this liquid crystal shows only a very small nematic phase range. Therefore at 50 mole% 8ACBP/9ACBP mixture, which has a broader nematic phase range, was studied at 63 °C. This mixture shows a bilayer short range order, since the layer thickness of 3.28 nm is greater than

Table 1. Properties and classification of the investigated systems.

System	Fig.	Type of induced phase	Colour	PN classification	DA classification	MB classification *
8ABP/10O6OPB	1	–	–	PN	DD	?M
8ABP/8OCBP	2	S_A	–	PP	DA	?B
8ABP/8CBP	–	S_A	–	PP	DA	?B
8ACBP/10O6OPB	3	S_A	–	PN	?D	BM
8ACBP/8OCBP	4	–	–	PP	?A	BB
8ACBP/11ONPB	5	–	brown	PP	?A	BB
6A6ABP/10O6OPB	6	–	–	NN	DD	MM **
6A6ABP/8OCBP	7	S_B, S_E	yellow	NP	DA	MB
6A6ABP/8ACBP	8	S_B, S_E	?	NP	D?	MB
6A6ABP/11ONPB	–	S_A	brown	NP	DA	MB

* M and B stand for mono and bilayer, resp.

** The formation of monolayers in the higher homologues of 6A6ABP has been proved by Walther [11].

the mean molecular length of 2.45 nm which was determined with Dreiding models. The layer type of 8ABP could not be determined as the pure component does not show liquid crystalline properties.

The MB classification is very similar to the PN classification as only liquid crystals of P type exhibit bilayers. Table 1 shows that the rule – MB mixtures exhibit induced smectic phases and MM as well as BB mixtures do not – is valid if 8ABP is assumed to be of the monolayer type. This rule is obeyed by nearly all systems studied up to now. Only Domon and Billard [2] report on some systems which seem to violate this rule.

From the foregoing discussion the untouched question remains in which cases mono or bilayers are formed. In general, it is assumed that the bilayer formation is due to the strong dipole moments caused by the CN and NO_2 substituents of the corresponding liquid crystals. If this assumption is valid the sign of the dipole moment should have no influence on the formation of bilayers. Unfortunately, there are hardly good examples for liquid crystals with electron donating substituents (NH_2) in contrast to the large number with electron withdrawing substituents (CN and NO_2). For example, the dipole moment of 8ABP should be comparatively small (nitrobenzene 4.22 D, benzonitrile 4.18 D, and aniline 1.53 D) and does not lie parallel to the long molecular axis [12]. Therefore it may be that the P type properties of 8ABP are too small for a bilayer formation and for the induction of smectic phases in mixtures with monolayer liquid crystals.

A second problem is the prediction of the induction of smectic phases in mixtures of liquid crystals where one component contains a weak polar terminal substituents, as for instance the Cl substituent. In some cases induced smectic phases with a medium thermal stability are formed [13] but in other cases no induction or even the appearance of a minimum transition temperature nematic – smectic is observed [2]. We think that in these cases specific intermolecular interactions or volume effects [14] are important which can lead to small deviations from the linear course of the phase boundaries. Therefore, the designation induced smectic should only be used for mixtures in which the maximum transition temperature nematic – smectic is some ten degrees higher than the corresponding transition temperatures of the pure components.

Despite of this restriction there are still systems which do not obey the MB rule. Probably, none of these rules will explain all cases of induced smectic phases without additional assumptions. We think that all effects discussed have to be taken into account and the contributions of the dipole interaction, CT interaction, volume effects and other specific interactions will depend on the particular system.

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