# Liquid Crystal Formation in Binary Systems. VI.[1] Smectic Liquid Crystals Induced in N-[4-(Diethylamino)benzylidene]-4-ethoxyaniline–N-(4-Nitrobenzylidene)-4-ethoxyaniline and Related Systems

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**Synopsis.** The replacement of the dimethylamino group in the combinations of the 4-dimethylamino-4-alkoxy and 4-nitro-4-alkoxy derivatives of N-benzylideneaniline by a diethylamino group favors the induction of smectic phases in their mixtures.

In Part II of this series, we described the induction of nematic and smectic liquid crystals by mixing electron donors and acceptors of the type 4-X–$C_6H_4$–CH=N–$C_6H_4$–Y-4.[2] The donor molecules had a dimethylamino group as X or Y, while the acceptor molecules had a nitro group as X or Y. The substituents on the remaining ends were methoxyl, ethoxyl, or propoxyl groups. The stabilization of mesophases in these binary mixtures was ascribed to the parallel molecular arrangement achieved by an electron donor-acceptor interaction.

In order to obtain a better understanding of the relations between the induction of liquid crystals and molecular structure, systematic studies of the effects of substituents are obviously important. As the first step along this line, we wish to report on the liquid crystals induced by mixing the diethylamino and nitro derivatives of N-benzylideneaniline.

N-[4-(Diethylamino)benzylidene]-4-alkoxyanilines, hereafter abbreviated ($Et_2N$, RO), and N-(4-alkoxybenzylidene)-4-(diethylamino)anilines, (RO, $Et_2N$) were prepared by the condensation reaction between appropriate benzaldehyde and aniline, and had the following melting points: ($Et_2N$, MeO) 100 °C, (MeO, $Et_2N$) 89.5 °C, ($Et_2N$, EtO) 106 °C, (EtO, $Et_2N$) 107 °C, ($Et_2N$, PrO) 110 °C, and (PrO, $Et_2N$) 98.5 °C. The nitro derivatives were similarly prepared. The measurements were carried out as described in our earlier works.[1,2]

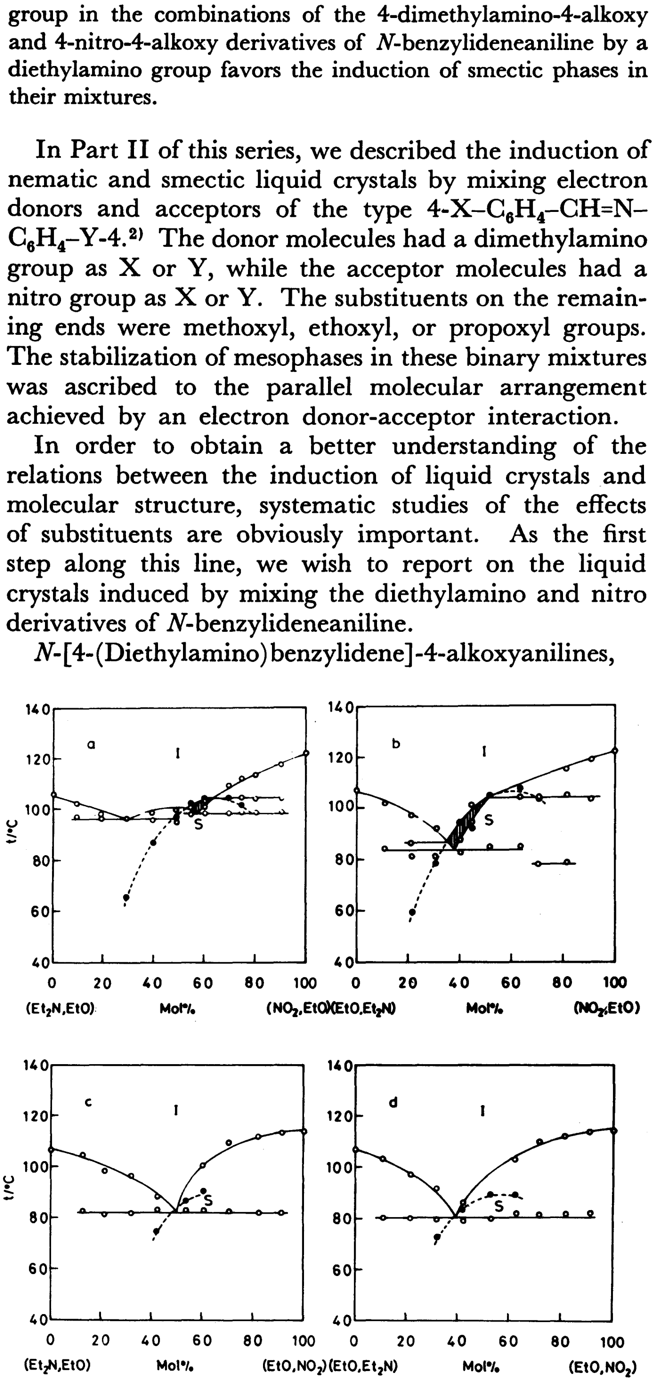


Fig. 1. Phase diagrams of (a) ($Et_2N$, EtO)–($NO_2$, EtO), (b) (EtO, $Et_2N$)–($NO_2$, EtO), (c) ($Et_2N$, EtO)–(EtO, $NO_2$), and (d) (EtO, $Et_2N$)–(EtO, $NO_2$) systems. The open and shaded circles are transitions recorded in the processes of heating and cooling respectively.

No liquid crystal could be found in the systems consisting of the methoxy derivatives. The results are in sharp contrast to the observation that the induction of nematic liquid crystals occurs with the corresponding dimethylamino compounds. As the diethylamino group is known to be less efficient in promoting nematic liquid crystals than the dimethylamino group,[3] the absence of nematic liquid crystals in the present systems may not be unexpected.

Figure 1 indicates that all the four combination of the ethoxy derivatives can induce smectic liquid crystals. The ($Et_2N$, EtO)–($NO_2$, EtO) system produces a 1 : 1 solid complex which melts congruently at 100.5 °C. The induced mesophase is stable between 53 and 64 mol% of ($NO_2$, EtO) but it is observable as a metastable phase in a much wider range: from 20 to 75 mol%. The isotropic liquid-smectic liquid crystal (I-S) transition temperature at the former composition is as low as 65 °C. An incongruently melting complex, possibly of the 1 : 2 mole ratio, is found in the phase diagram of the (EtO, $Et_2N$)–($NO_2$, EtO) system. The I-S transition curve meets the freezing point curve of the donor compound at 86.5 °C and 35 mol% of ($NO_2$, EtO) and that of the acceptor compound at a point which is not distinguishable from the peritectic point located at 104 °C and 51 mol%. The maximum lies at 106 °C and near 60 mol%.

The combination of ($Et_2N$, EtO) and (EtO, $NO_2$) gives a diagram of the eutectic type. The mesophase is observed in the range from 40 to 60 mol% and is metastable with the possible exception of a very small area near the eutectic point: 82 °C and 50 mol%. No solid complex is formed in the (EtO, $Et_2N$)–(EtO, $NO_2$) system. The induced smectic phase seems to be wholly metastable but covers a range wider than that in the ($Et_2N$, EtO)–(EtO, $NO_2$) system. The I-S transition curve passes through the eutectic point located at 81.5 °C and 39 mol% of (EtO, $NO_2$) and reaches the maximum at 89 °C and about 57 mol%.

We reported earlier the formation of congruently melting solid complexes in both the ($Me_2N$, EtO)– and (EtO, $Me_2N$)–($NO_2$, EtO) systems and that of an

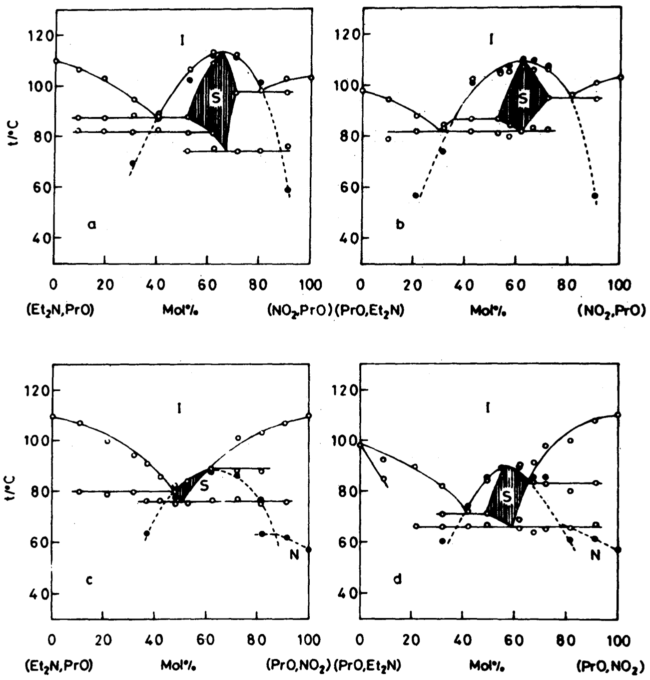


Fig. 2. Phase diagrams of (a) ($Et_2N$, PrO)–($NO_2$, PrO), (b) (PrO, $Et_2N$)–($NO_2$, PrO), (c) ($Et_2N$, PrO)–(PrO, $NO_2$), and (d) (PrO, $Et_2N$)–(PrO, $NO_2$) systems. As to the open and shaded circles, see the caption of Fig. 1.

incongruently melting one in the (EtO, $Me_2N$)–(EtO, $NO_2$) system and also the induction of nematic liquid crystals with all the combinations.[2] Thus, smectic mesophases appear to be markedly stabilized by the introduction of a diethylamino group instead of a dimethylamino group into the donor molecules, while nematic mesophases and solid complexes are destabilized.

As is shown in Fig. 2, the solid complex in the ($Et_2N$, PrO)–($NO_2$, PrO) system has the composition of a 1 : 1 mole ratio and ceases to exist at 81.5 °C, giving a peritectic point at 62 mol% of ($NO_2$, PrO). A stable smectic liquid crystal appears in the composition range from 40 to 81 mol% and the maximum temperature of 114 °C is found at 65 mol%. The mesophase coexists with the isotropic melt except for the hatched area. The eutectic point is at 74 °C and 67 mol%. The diagram of the (PrO, $Et_2N$)–($NO_2$, PrO) system is of the eutectic type. The I-S transition curve intersects the freezing point curve of ($NO_2$, PrO) at 86.5 °C and 36 mol% and at 95 °C and 81 mol%. The maximum is found at 109 °C and 62 mol%. The combination of ($Et_2N$, PrO) and (PrO, $NO_2$) also gives a diagram of the eutectic type. The maximum stabilization of the induced smectic phase is achieved at the intersection between the I-S transition curve and the freezing point curve of the acceptor compound: 89 °C and 62 mol% of (PrO, $NO_2$). As the melt of this acceptor compound can be supercooled to the latent I-N transition temperature (57.5 °C), the induction of the nematic liquid crystal is observable above 87 mol%. The (PrO, $Et_2N$)–(PrO, $NO_2$) system produces no solid complex. The I-S transition curve meets the freezing point curve of the donor compound at 71 °C and 41 mol% of (PrO, $NO_2$) and that of the acceptor compound at 83 °C and 66 mol%.

It must be emphasized that the tendencies noted with the ethoxy derivatives are more pronounced with the propoxy derivatives. First of all, the four systems of the corresponding dimethylamino compounds produce solid molecular complexes stable up to their own melting points, while only the ($Et_2N$, PrO)–($NO_2$, PrO) system can form a solid complex with a limited stability. On the other hand, the induced smectic phases are stable in all the systems of the present compounds, contrary to those induced with the dimethylamino compounds, which are entirely metastable.

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**References**

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