# Liquid Crystal Formation in Binary Systems. V.[1] Liquid Crystals Induced in *N*-[4-(Dimethylamino)benzylidene]-4-ethoxyaniline–*N*-(4-Nitrobenzylidene)-4-nitroaniline and Related Mixtures

Kotaro Araya and Yoshio Matsunaga*
*Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060*
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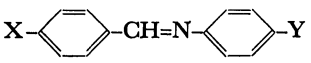
The induction of liquid crystals was demonstrated with binary mixtures comprising *N*-(4-nitrobenzylidene)-4-nitroaniline and *N*-[4-(dimethylamino)benzylidene]-4-alkoxyaniline or *N*-(4-alkoxybenzylidene)-4-(dimethylamino)aniline. Both nematic and smectic phases were observed with the ethoxy derivatives, but only a smectic A phase with the propoxy derivatives. The mesophases appear in the region centered around 30 mol% of the dinitro compound. Similarly, liquid crystals could be induced in several mixtures of *N*-[4-(dialkylamino)benzylidene]-4-(dialkylamino)aniline with *N*-(4-nitrobenzylidene)-4-alkoxyaniline or *N*-(4-alkoxybenzylidene)-4-nitroaniline. The bis(dialkylamino) and dinitro derivatives of azoxybenzene were also shown to be efficient as one of the component compounds in producing binary liquid crystals.

As we reported earlier, nematic and smectic liquid crystals can be induced by mixing a nonmesogenic electron donor and a nonmesogenic electron acceptor of the type 4-X-$C_6H_4$-Z-$C_6H_4$-Y-4.[2,3] Donor molecules having a dimethylamino group on one end and acceptor molecules having a nitro group on one end were employed in those works. The donor and acceptor molecules each had a short alkoxyl group of the same kind on the other end. The central double bond linkages were chosen from –CH=CH–, –CH=N–, and –N=N– groups. Although the component compounds themselves form no mesophase, they may be considered potentially mesogenic, because the molecules are elongated and lath-liked in shape. The induction or the enhancement of the thermal stability of liquid crystals in the above-mentioned mixtures is maximized when the mole ratio is near 1 : 1. The orientational cohesive force arising from the interaction of the electron donor-acceptor type may be responsible for the ordered arrangement of the molecules in liquid crystals. In ordinary crystals, this sort of intermolecular interaction is known to result in the parallel alignment of the planar component molecules.

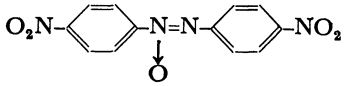
As the molecules of *N*-benzylideneanilines are generally nonplanar, the intermolecular interaction in the induced liquid crystals may be more or less localized between the benzene ring with a dimethylamino group in the donor molecule and that with a nitro group in the acceptor molecule. If so, each benzene ring in the dinitro derivative may be able to interact with a molecule of the dimethylamino derivative. Similarly, a molecule of the bis(dimethylamino) derivative may associate with two molecules of the mononitro derivative. In this paper, we wish to report that liquid crystalline phases are really induced with such combinations.

## Experimental

*Materials.* The *N*-benzylideneanilines were prepared



by a condensation reaction between a *p*-Y derivative of benzaldehyde and a *p*-X derivative of aniline, and were purified by repeated recrystallizations from a suitable solvent. Hereafter, they are represented by the terminal groups in parentheses, (X, Y). 4,4′-Dinitroazoxybenzene (DNAO)



was obtained by the oxidation of *p*-nitroaniline with ammonium peroxodisulfate, as described by Witt and Kopetschni.[4] The crude product was treated with fuming nitric acid and then recrystallized from benzene.[5] 4,4′-Bis(dimethylamino)azoxybenzene (BDMAAO) was synthesized by the catalytic reduction of *p*-nitroso-*N*,*N*′-dimethylaniline with hydrazine hydrate, following the method reported by Busch and Schulz.[6] 4,4′-Bis(diethylamino)azoxybenzene (BDEAAO) was analogously prepared. The procedure of preparing binary mixtures was given in our previous paper.[2]

*Measurements.* The calorimetric and spectroscopic measurements were carried out as described in Part II of this series.[2]

## Results and Discussion

*N-(4-Nitrobenzylidene)-4-nitroaniline ($NO_2$, $NO_2$) as an Electron Acceptor.* The following four donor Schiff bases were found to form liquid crystals when mixed with this acceptor: ($NMe_2$, EtO), (EtO, $NMe_2$), ($NMe_2$, PrO), and (PrO, $NMe_2$). As the acceptor has a melting point of 200 °C, which is higher by 53 to 85 °C than those of the donors, and the observation of liquid crystals is limited to the composition range from 15 to 40 mol% of ($NO_2$, $NO_2$), we studied the phase diagrams only up to 50 mol%.

In the ($NMe_2$, EtO)–($NO_2$, $NO_2$) system, the nematic and smectic liquid crystals appear from the supercooled isotropic melt (see Fig. 1a). The former phase exists as a single phase only below 20 mol%. When the temperature drops, two transitions associated with liquid crystals were detected at the composition of 25 mol%. The first transition is found at 127 °C and is ascribed to the appearance of a metastable smectic phase accompanied by the isotropic melt; the second one, at 120 °C, is ascribed to the transformation into a metastable nematic phase in equilibrium with the smectic phase. The latter temperature is that of the intersection between the isotropic liquid-smectic liquid crystal (I-S) transition curve and the isotropic liquid-

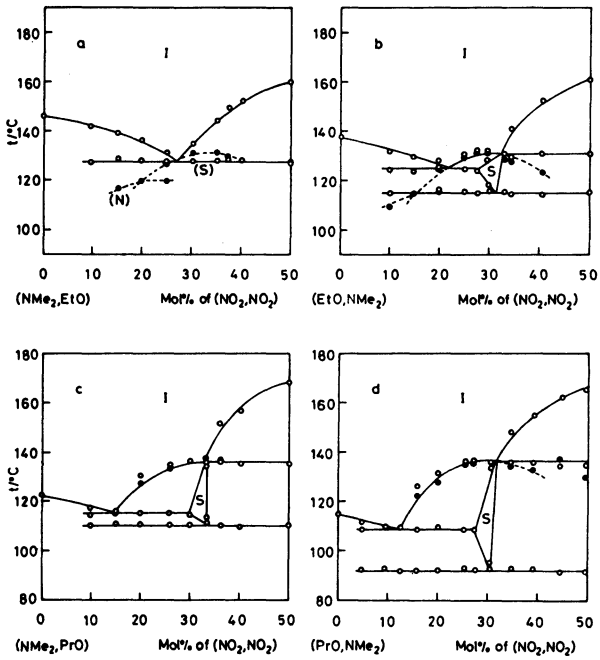



Fig. 1. Phase diagrams of the systems of ($NO_2$, $NO_2$) with (a) ($NMe_2$, EtO), (b) (EtO, $NMe_2$), (c) ($NMe_2$. PrO), and (d) (PrO, $NMe_2$). The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

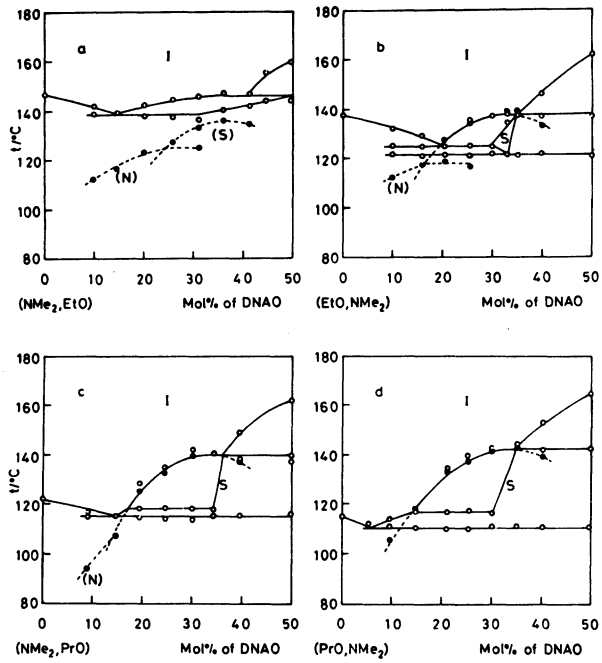



Fig. 2. Phase diagrams of the systems of DNAO with (a) ($NMe_2$, EtO), (b) (EtO, $NMe_2$), (c) ($NMe_2$, PrO), and (d) (PrO, $NMe_2$). As to the open and shaded circles, see the caption of Fig. 1.

nematic liquid crystal (I-N) transition curve. The maximum of the I-S transition occurs at 131.5 °C and 33 mol%.

The phase diagram of the (EtO, $NMe_2$)–($NO_2$, $NO_2$) system shown in Fig. 1b is more complicated than that described above. Enhancement of the smectic phase is so pronounced that the I-S transition curve encounters the freezing point curve of the donor compound at 125 °C and 22 mol% and also another freezing point curve at 131 °C and 32.5 mol% of ($NO_2$, $NO_2$). The horizontal line at 125 °C terminates at 27.5 mol%, indicating that the isotropic melt and a smectic liquid crystal are in equilibrium with each other in the temperature range specified by the I-S transition curve and this line. This smectic phase is stable above 115 °C with the coexisting solid. The region of existence of this mesophase as a single phase is represented by a triangle in the diagram and lies in the composition range between 27.5 and 32.5 mol%. The intersection between the I-S and I-N transition curves is at 115 °C and 14.7 mol%. Below this composition, the metastable nematic liquid crystal may be observed without any coexisting phase.

Figure 1c presents the diagram of the ($NMe_2$, PrO)–($NO_2$, $NO_2$) system. The area bounded by the following points represents the condition for the stable existence of the induced liquid crystal as a single phase: 115 °C and 30 mol%, 136 °C and 33.3 mol%, and 110 °C and 33.3 mol% of ($NO_2$, $NO_2$). The mesophase appearing at 33 mol% was identified as a smectic A phase by the miscibility test with *N*-(4-phenylbenzylidene)-4-(ethoxycarbonyl)aniline, which exhibits a smectic A phase stable between 121.6 and 131 °C.[7]

The diagram of the (PrO, $NMe_2$)–($NO_2$, $NO_2$) system shown in Fig. 1d is also of the same type. The corners of the region for a stable smectic phase existing without any other phase are located at 108.5 °C and 27.5 mol%, 136.5 °C and 31.8 mol%, and 92 °C and 30.5 mol% of ($NO_2$, $NO_2$).

*4,4'-Dinitroazoxybenzene (DNAO) as an Electron Acceptor.* This compound has a melting point of 192 °C. All the four donors employed for the systems shown in Fig. 1 can produce mesophases by mixing with DNAO. Their phase diagrams are given in Fig. 2. Again, the induction of the smectic liquid crystal in the combination with ($NMe_2$, EtO) is not sufficient to make the phase enantiotropic (see Fig. 2a). The maximum temperature of the induced smectic phase is 136 °C. The I-S and I-N transition curves meet each other at 125 °C and 24 mol%. The presence of a horizontal line extending from this intersection to 31 mol% is indicative of the coexistence of the smectic phase and the isotropic melt above this line and that of the smectic phase and the nematic phase below this line.

The diagram for the (EtO, $NMe_2$)–DNAO system bears some similarity to that for the (EtO, $NMe_2$)–($NO_2$, $NO_2$) system (compare Figs. 1b and 2b). The I-S transition curve intersects the freezing point curve of the donor compound at 125 °C and 20 mol% of DNAO and the other freezing point curve at 138 °C and 35 mol%. The triangle for the stable single smectic phase is specified by the latter intersection and the following two: 125 °C and 30 mol% and 121.5 °C and 32 mol%. The intersection between the I-S and I-N transition curves occurs at 118 °C and 16 mol%.

The ($NMe_2$, PrO)–DNAO and (PrO, $NMe_2$)–DNAO systems yield diagrams greatly different from the preceding cases. The S-I transition curve encounters

Table 1. The maximum temperature of the smectic liquid crystal-isotropic liquid transition/°C

| Acceptor | Donor | | | |
|---|---|---|---|---|
| | ($NMe_2$, EtO) | (EtO, $NMe_2$) | ($NMe_2$, PrO) | (PrO, $NMe_2$) |
| ($NO_2$, $NO_2$) | 131.5 | 131 | 136 | 136.5 |
| DNAO | 136 | 139 | 140 | 143 |

the freezing point curve twice on the acceptor-rich side. The points of intersection are found at 118 °C and 17 mol% and at 140 °C and 36 mol% in the former system. As is evident from the presence of a horizontal line at 118 °C, the induced smectic phase and the isotropic melt are involved in the composition range from 17 to 34 mol%.

Similarly, the diagram of the (PrO, $NMe_2$)–DNAO system has two intersections between the S-I transition curve and the freezing point curve. They are located at 117 °C and 15 mol% and at 143 °C and 35 mol%. At the latter composition, the solid is wholly transformed into the mesophase at 110.5 °C and then into the isotropic melt at 143 °C. The horizontal line separating the solid and the smectic liquid crystal, both of which coexist with the isotropic melt, appears at 117 °C and below 30 mol%.

The maximum temperatures of the S-I transition in the eight systems described above are summarized in Table 1. For a given electron donor, DNAO gives consistently higher transition temperatures, but only by several degrees, than ($NO_2$, $NO_2$) does. It is not clear whether the differences are attributable to the effect of the central double bond linkage on the induction of mesophase or on the latent transition temperature of the acceptor compound. Nevertheless, it may be added that the same sequence has been found for the N-I transition temperatures.[8] As to the donor compounds, the smectic phases induced by the propoxy derivatives are more thermally stabilized than those induced by the ethoxy derivatives. This effect of terminal substituents is in agreement with our observation made in an earlier work.[2]

The donor and acceptor compounds employed in the present work are yellow, while their combinations are reddish brown or dark red, suggesting the formation of solid molecular complexes of the electron donor-acceptor type. The phase diagrams suggest that the solid complex is formed at the composition of 50 mol% or higher of the dinitro compound. The electronic spectrum of ($NMe_2$, PrO)–($NO_2$, $NO_2$) at 50 mol% is shown in Fig. 3, along with those of the solid component compounds. New absorption bands undoubtedly appear and are located at about 18 and $22\times10^3$ $cm^{-1}$. They may be assigned to the charge-transfer transitions from ($NMe_2$, PrO) to ($NO_2$, $NO_2$). The spectrum of ($NMe_2$, PrO)–DNAO at 50 mol% is very much like the aforementioned, but the first band is shifted further to the low-energy side, by $(1.5—2)\times10^3$ $cm^{-1}$. This shift may imply that the electron affinity of DNAO is larger by about this extent than that of ($NO_2$, $NO_2$). This postulate is not unreasonable if one compares the electronegativities of the atoms in the central linkages. As the color of the mesophases is similar to that of the corresponding solid complex, it is very likely that the unusually pronounced nonlinear behavior of smectic liquid crystals is caused by the complexation between the donor and acceptor molecules in appropriate mole ratios.

*N-[4-(Dimethylamino)benzylidene]-4-(dimethylamino) aniline ($NMe_2$, $NMe_2$) as an Electron Donor.* Smectic phase is produced when ($NO_2$, PrO) is combined with this donor compound. As is shown in Fig. 4a, the induced mesophase is entirely metastable. The maximum of the I-S transition curve is located at 121 °C near 30 mol% of ($NMe_2$, $NMe_2$).

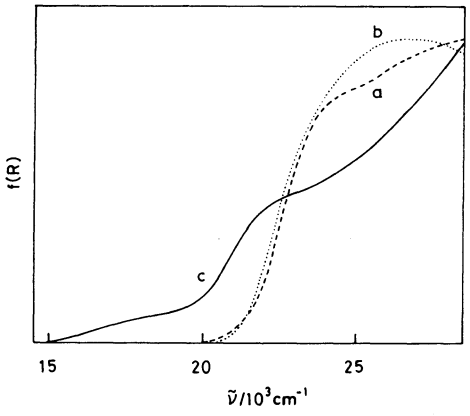



Fig. 3. Diffuse reflection spectra of (a) ($NMe_2$, PrO), (b) ($NO_2$, $NO_2$), and (c) the binary system at 50 mol%.

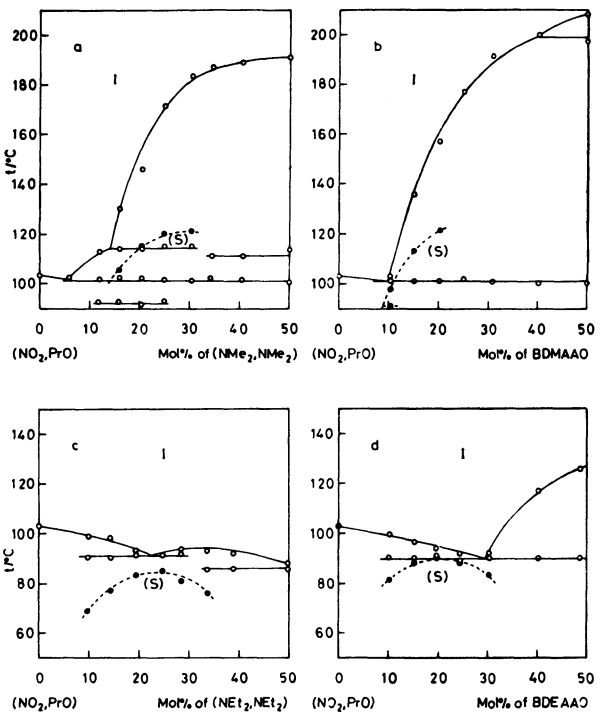



Fig. 4. Phase diagrams of the (a) ($NMe_2$, $NMe_2$)–($NO_2$, PrO), (b) BDMAAO–($NO_2$, PrO), (c) ($NEt_2$, $NEt_2$)–($NO_2$, PrO), and (d) BDEAAO–($NO_2$, PrO) systems. As to the open and shaded circles, see the caption of Fig. 1.

Metastable nematic liquid crystals appear when the donor compound is mixed with ($NO_2$, EtO) and also with (PrO, $NO_2$). In the former combination, the mesophase is observable in the composition range from 10 to 20 mol% of ($NMe_2$, $NMe_2$) and at temperatures between 105 and 113 °C. The mesophase relatively rich in the donor compound can persist only within a few degrees below the transition curve. The nematic liquid crystal in the latter system can be found below 25 mol%. The curve extends from the I-N transition point of (PrO, $NO_2$) and reaches 112 °C by the said composition.

*4,4'-Bis(dimethylamino)azoxybenzene (BDMAAO) as an Electron Donor.* According to our survey, made by the contact method,[9] the induction of mesophase occurs only in the system with ($NO_2$, PrO). The metastable smectic phase is observed in the range from 10 to 20 mol% of BDMAAO (see Fig. 4b). The transition temperature at the former composition is 98 °C, while that at the latter is 122 °C. The coexistence of smectic and nematic liquid crystals is found at 10 mol% and below 91 °C.

In contrast to the mesophases obtained with the dinitro compounds shown in Figs. 1 and 2, the liquid crystals induced with the bis(dimethylamino) compounds are not very stable. The melting point of ($NMe_2$, $NMe_2$) is as high as 234.5 °C and that of BDMAAO is even higher: *i.e.*, 244 °C. Because of the large differences in melting point between the donor and acceptor compounds, the major part of the induced mesophases is far below the freezing point curve on the donor-rich side. In such a situation, it is hard to suspend the solidification down to the I-S transition temperature. Consequently, we tried the bis(diethylamino) compounds, the melting points of which are expected to be appreciably lower, as electron donors.

*N-[4-(Diethylamino)benzylidene]-4-(diethylamino)aniline ($NEt_2$, $NEt_2$) as an Electron Donor.* This compound melts at 118 °C. Nevertheless, liquid crystal can be produced only when the compound is mixed with ($NO_2$, PrO) and exists as a metastable phase (see Fig. 4c). The smectic phase is induced in the range from 10 mol% of ($NEt_2$, $NEt_2$) to the composition of the solid complex. The maximum of the I-S transition curve lies at 85 °C and about 25 mol%. This temperature is markedly lower than that found in the ($NMe_2$, $NMe_2$)–($NO_2$, PrO) system.

*4,4'-Bis(diethylamino)azoxybenzene(BDEAAO) as an Electron Donor.* The melting point of this compound is 158 °C, which is lower by 86 °C than that of BDMAAO. Smectic liquid crystals could be observed in the mixtures not only with ($NO_2$, PrO) but also with (PrO, $NO_2$). The diagram of the former system is presented in Fig. 4d. The mesophase is seen in the range from 10 to 30 mol% of BDEAAO. The maximum transition temperature is almost in coincidence with the eutectic temperature and is found at about 20 mol%. The smectic phase induced by mixing with (PrO, $NO_2$) is less stable; the maximum lies at 71 °C and about 20 mol%.

Thus, the lowering of the melting point by the replacement of dimethylamino groups with diethylamino groups is appreciable; however, the observation of induced mesophases is not made much easier. It seems highly likely that the latent I-S transition temperature is also lowered by this replacement, as we suggested in our earlier work on the *N*-benzylidene-4-aminoazobenzenes.[1] The latter effect may be, at least partly, lifted if the *N*-benzylideneanilines carrying a dimethylamino group on one end and a diethylamino group on the other end are employed. Indeed, ($NEt_2$, $NMe_2$) is known to melt at 140—141 °C.[10] This temperature is only 22 °C higher than the melting point of ($NEt_2$, $NEt_2$).

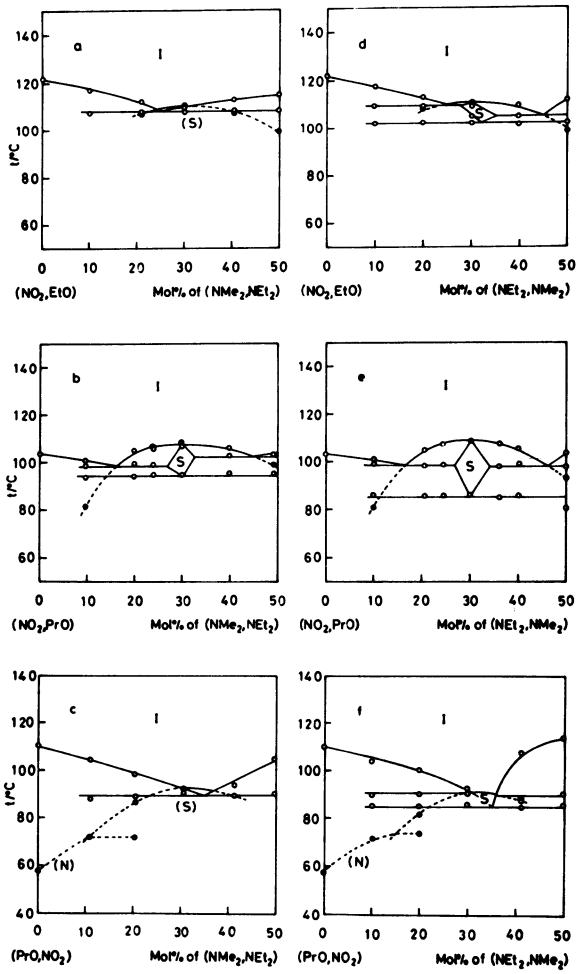



Fig. 5. Phase diagrams of the (a) ($NMe_2$, $NEt_2$)–($NO_2$, EtO), (b) ($NMe_2$, $NEt_2$)–($NO_2$, PrO), (c) ($NMe_2$, $NEt_2$)–(PrO, $NO_2$), (d) ($NEt_2$, $NMe_2$)–($NO_2$, EtO), (e) ($NEt_2$, $NMe_2$)–($NO_2$, PrO), and (f) ($NEt_2$, $NMe_2$)–(PrO, $NO_2$) systems. As to the open and shaded circles, see the caption of Fig. 1.

*N-[4-(Dimethylamino)benzylidene]-4-(diethylamino)aniline ($NMe_2$, $NEt_2$) as an Electron Donor.* The acceptors, ($NO_2$, EtO), ($NO_2$, PrO), and (PrO, $NO_2$) were found to produce smectic liquid crystals when combined with this donor, the melting point of which is 136 °C. Their phase diagrams are given in Figs. 5a, b, and c. In all the cases, the induced mesophase has an area where it can exist as a single stable phase. The system with ($NO_2$, EtO) produces a mesophase observable in the range from 20 to 50 mol% of ($NMe_2$,

$NEt_2$). The maximum of the transition curve lies at 111 °C and about 30 mol%.

The smectic phase is most stabilized in the system with ($NO_2$, PrO). The I-S transition curve is met by the freezing point curve of ($NO_2$, PrO) at 98 °C and 16 mol% and by that on the ($NMe_2$, $NEt_2$)-rich side at 102 °C and 44.5 mol%. The maximum of the transition curve is found at 107 °C. The composition is not distinguishable from that of the eutectic point, 94 °C and 30 mol%.

The mesophase induced in mixtures with (PrO, $NO_2$) is metastable except for the small area above the eutectic point. The enantiotropic I-S transition is seen only between 31 and 36.5 mol%. The maximum is located at 92 °C. Below 72 °C and 11 mol%, the nematic phase can exist as a single phase.

*N-[4-(Diethylamino)benzylidene]-4-(dimethylamino)aniline ($NEt_2$, $NMe_2$) as an Electron Donor.* Smectic liquid crystals are induced in the systems with ($NO_2$, EtO), ($NO_2$, PrO), and (PrO, $NO_2$) and are generally more stable than those induced with the isomeric donor compound, ($NMe_2$, $NEt_2$) (see Figs, 5d, e, and f).

The diagrams in Figs. 5d and e are similar to that given in Fig. 5b. With ($NO_2$, EtO), the I-S transition curve intersects the freezing point curve of ($NO_2$, EtO) at 109.5 °C and 25 mol% and that on the donor-rich side at 105 °C and 45 mol%. The maximum temperature of 111.5 °C is found around 30 mol%. The smectic phase and the isotropic melt coexist in most of the area below the I-S transition curve. The lower temperature limit as a single stable mesophase is 102 °C located at 32 mol%.

The enantiotropic I-S transition curve in the system with ($NO_2$, PrO) covers the composition range from 16.5 to 46 mol% of ($NEt_2$, $NMe_2$), passing through a maximum at 109 °C and about 30 mol%. The area in which the induced smectic phase appears as the sole stable phase covers the temperature range from 85 to 109 °C and the composition range from 27 to 34 mol%.

When mixed with (PrO, $NO_2$), the mesophase is stable in the area specified by the intersections between the I-S transition curve with the freezing point curves at 91 °C and 31 mol% and at 90 °C and 36 mol% and by the eutectic point at 85 °C and 35 mol%. The metastable I-S transition curve encounters the metastable I-N transition curve at 74 °C and 15 mol%.

The upper temperature limits of the smectic phases induced with the six donor compounds are compared in Table 2. As to the donors, the temperature changes in this order:

Table 2. The maximum temperature of the smectic liquid crystal-isotropic liquid transition/°C

| Donor | Acceptor | | |
|---|---|---|---|
| | ($NO_2$, EtO) | ($NO_2$, PrO) | (PrO, $NO_2$) |
| ($NMe_2$, $NMe_2$) | — | 121 | — |
| BDMAAO | — | 122 | — |
| ($NMe_2$, $NEt_2$) | 111 | 107 | 92 |
| ($NEt_2$, $NMe_2$) | 111.5 | 109 | 92 |
| ($NEt_2$, $NEt_2$) | — | 84 | — |
| BDEAAO | — | 90 | 71 |

$$\text{BDMAAO} \simeq (NMe_2, NMe_2) > (NEt_2, NMe_2) \simeq (NMe_2, NEt_2) > \text{BDEAAO} > (NEt_2, NEt_2).$$

As the melting point follows the same order except for the last two, it is not possible to compare the stabilization of the induced phases based on this order.

The color developed with these bis(dialkylamino) compounds is not so deep as that developed with the dinitro compounds. For example, the 1:2 ($NMe_2$, $NMe_2$)-($NO_2$, PrO) complex is brown. Comparison of the diffuse reflectance spectrum of the complex with those of the components reveals the occurrence of a weak absorption around $19 \times 10^3$ $cm^{-1}$. This energy value is only a little bit lower than that found in the combination of ($NMe_2$, EtO) and ($NO_2$, EtO) reported earlier.[2] The shift arises from the rather small improvement of the donor strength by the replacement of an electron-donating alkoxyl group with another electron-donating dialkylamino group. In contrast, the shift found in Fig. 3 is large. The increase in the acceptor strength is due to the replacement of an alkoxyl group with an electron-withdrawing nitro group. The thermal stabilization of smectic liquid crystals induced by the dinitro compounds is more extensive than that induced by the mononitro compounds. This observation may be also attributed to the rather large difference in the acceptor strength.

The composition at the maximum of the I-S transition curve varies with the combination of electron donor and acceptor but, without exception, occurs near 30 mol% of the dinitro or bis(dialkylamino) compound. The exact composition is supposed to depend not only on the extent of the formation of 2 : 1 or 1 : 2 molecular complexes in the mesophases but also on the difference in the latent I-S transition temperature between the component compounds. The above-mentioned compositions suggest that the temperatures of the dinitro and bis(dialkylamino) compounds are considerably lower than those of the other component compounds employed in this work.

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**References**

1) Part IV: M. Fukui and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **54**, 3137 (1981).
2) K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **53**, 3079 (1980).
3) K. Araya and Y. Matsunaga, *Bull. Chem. Soc. Jpn.*, **54**, 2430 (1981).
4) O. N. Witt and E. Kopetschni, *Ber.*, **45**, 1134 (1912).
5) A. Werner, *Ber.*, **32**, 3256 (1899).
6) M. Busch and K. Schulz, *Ber.*, **62**, 1458 (1929).
7) D. Demus and H. Sackmann, *Z. Phys. Chem. (Leipzig)*, **222**, 127 (1963).
8) L. E. Knaak, H. M. Rosenberg, and M. P. Serve, *Mol. Cryst. Liq. Cryst.*, **17**, 171 (1972).
9) H. Sackmann and D. Demus, *Z. Phys. Chem. (Leipzig)*, **222**, 143 (1963).
10) R. Mohlau, *Ber.*, **31**, 2250 (1898).