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Liquid Crystal Formation in Binary Systems. VII.[1] Liquid Crystals Induced in *N*-[4-(Dimethylamino)benzylidene]-4-alkoxyaniline-4,4′-Dinitrobiphenyl and Related Systems

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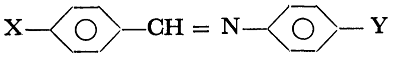
By the addition of 4,4′-dinitrobiphenyl to nonmesogenic 4-(dimethylamino)-4-alkoxy derivatives of *N*-benzylideneaniline, smectic liquid crystals could be induced. This dinitro compound induces liquid crystals more pronouncedly than *N*-(4-nitrobenzylidene)-4-nitroaniline and 4,4′-dinitroazoxybenzene do when the alkoxyl group in the donor molecule is methoxyl or ethoxyl, while it induces less pronouncedly when the alkoxyl group is propoxyl. 4,4′-Dicyanobiphenyl gives a metastable nematic liquid crystal when it is mixed with *N*-[4-(dimethylamino)-benzylidene]-4-propoxyaniline and a metastable smectic liquid crystal with *N*-(4-propoxybenzylidene)-4-(dimethylamino)aniline. Moreover, liquid crystals are formed in the binary systems of *N,N,N′,N′*-tetramethylbenzidine with 4-nitro-4-alkoxy derivatives of *N*-benzylideneaniline. They are metastable but cover rather wide composition ranges. The examination of the layer spacing of the smectic A phase revealed that the induced phase is a monolayer liquid crystal.

In one of our earlier papers,[2] the induction of liquid crystals in binary mixtures of *N*-(4-nitrobenzylidene)-4-nitroaniline or 4,4′-dinitroazoxybenzene with 4-(dimethylamino)-4-alkoxy derivatives of *N*-benzylideneaniline was reported. The interaction of the electron donor-acceptor type was supposed to contribute to the achievement of the ordered arrangement of the molecules required for the mesophases. The maximum temperatures of the smectic liquid crystal-isotropic liquid (S–I) transition in these systems vary over only eight degrees according to the dinitro compound employed. The absence of a large difference in the maximum temperature by the change in the central double bond linkage might be an indication that the central linkage does not play a dominant role in the induction of the mesophases. To develope this subject somewhat farther, the examination of the systems of 4,4′-dinitrobiphenyl with the same *N*-benzylideneanilines seemed to be worthwhile.

As liquid crystals could be observed in several mixtures of *N*-[4-(dialkylamino)benzylidene]-4-(dialkylamino)-aniline or 4,4′-bis(dialkylamino)azoxybenzene with 4-nitro-4-alkoxy derivatives of *N*-benzylideneaniline, the phase diagram approach was applied also to the systems consisting of *N,N,N′,N′*-tetramethylbenzidine and the same Schiff bases.

Experimental

Materials. The preparation of the Schiff bases was described in our previous papers,[3,4] In this text, *N*-(4-X-benzylidene)-4-Y-anilines (**1**) and 4-(4-X-benzylideneamino)-4′-Y-azobenzenes (**2**) are represented by the terminal substituents in parentheses or brackets, (X, Y) or [X, Y] respectively.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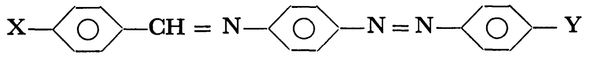
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The alkoxyl groups employed are methoxyl (MeO), ethoxyl (EtO), and propoxyl (PrO). 4,4′-Dinitrobiphenyl (DNBP) was prepared by nitration of biphenyl and recrystallized from acetone.[5] 4,4′-Dicyanobiphenyl (DCNBP) was synthesized starting from benzidine by the procedure reported by Ferriss and Turner.[6] *N,N,N′,N′*-Tetramethylbenzidine (TMB) Aldrich Chemical Co., was purified by recrystallization from a mixture of ethanol and toluene.

Measurements. The calorimetric and microscopic studies were carried out as described in Part IV of this series.[4] X-Ray diffraction by liquid crystalline phases was examined with the aid of a temperature-regulated sample holder described in a paper from this laboratory.[7]

Results and Discussion

4,4′-Dinitrobiphenyl (DNBP) as an Electron Acceptor. As is shown in Fig. 1a, the phase diagram of the binary system with (Me_2N, MeO) exhibits a metastable smectic phase of the A type in the composition range from 11 to 25 mol% of DNBP. The maximum lies a little bit below the eutectic temperature of 132 °C. By the exchange of the position of the terminal substituents on the donor compound (see Fig. 1b), the composition range becomes markedly narrower but the maximum temperature is shifted slightly above the eutectic temperature (135 °C).

When DNBP is added to (Me_2N, EtO), both smectic and nematic liquid crystals are observable (see Fig. 1c). The former phase appears in the range from 17 to 33 mol% of DNBP. The maximum temperature of the S–I transition curve coincides with the eutectic temperature of 138 °C. The stabilization of the smectic liquid crystal formed by mixing (EtO, Me_2N) and DNBP is more significant, the maximum being at about 164 °C and 37 mol%. Nevertheless, the induced mesophase is entirely below the freezing point curve on the DNBP-rich side. The N–I transition lines in these figures were drawn by connecting the observed point and the latent N–I transition temperature estimated in our earlier work.[3]

The smectic phase induced in mixtures with (Me_2N, PrO) is stable in a small area defined by the following points: the intersection between the horizontal S–I transition line in the coexistence of the solid donor compound and the freezing point curve of the donor compound located at 117 °C and 16 mol%, the eutectic point at 115 °C and 22 mol%, and the intersection between the other horizontal S–I transition line and the

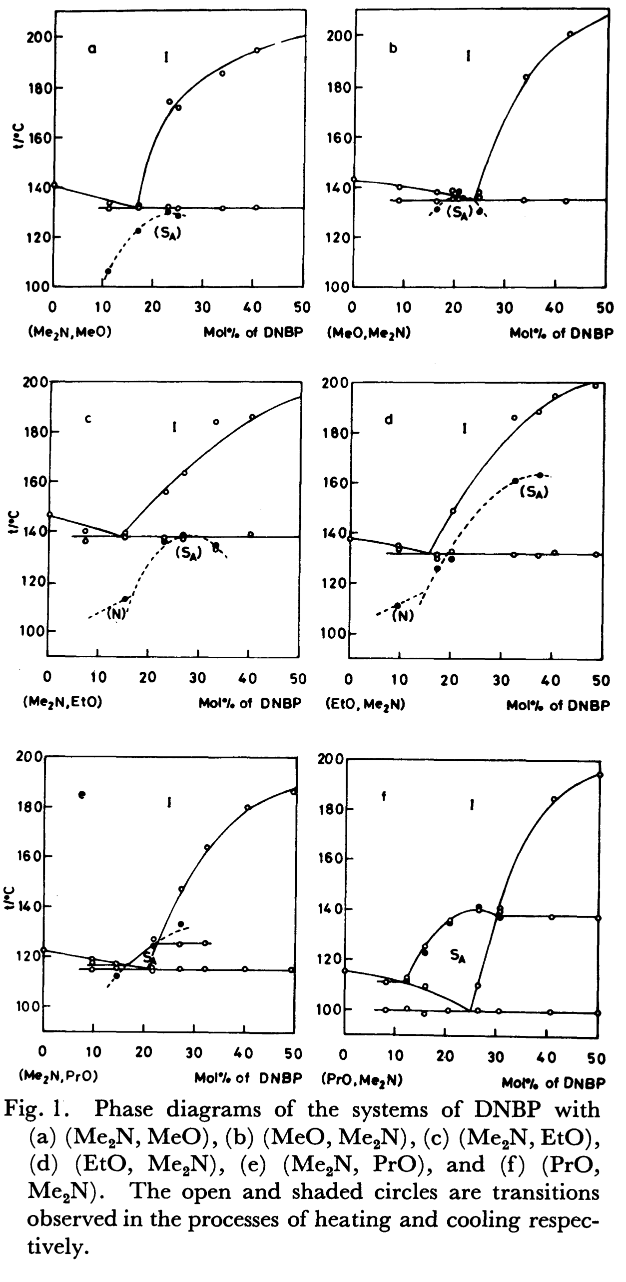

Fig. 1. Phase diagrams of the systems of DNBP with (a) (Me_2N, MeO), (b) (MeO, Me_2N), (c) (Me_2N, EtO), (d) (EtO, Me_2N), (e) (Me_2N, PrO), and (f) (PrO, Me_2N). The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

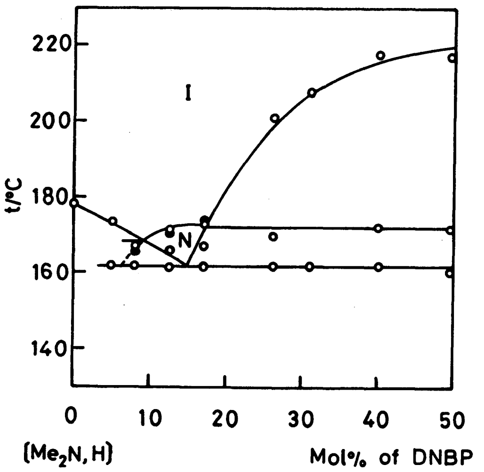

Fig. 2. Phase diagram of the [Me_2N, H]–DNBP system. As to the open and shaded circles, see the caption of Fig. 1.

freezing point curve on the DNBP-rich side at 125 °C and 23 mol%. The mesophase produced by mixing with (PrO, Me_2N) is more significantly stabilized (see Fig. 1f). The S–I transition curve meets the freezing point curve of the donor compound at 111 °C and 12 mol%, passes through the maximum at 140 °C and 26 mol%, and then meets the other freezing point curve at 138 °C and 30 mol%.

The maximum transition temperatures observed in the above-mentioned six systems are compared with those of the systems containing (NO_2, NO_2) or 4,4′-dinitroazoxybenzene (DNAO) in Table 1. When the methoxy derivatives are employed as electron donors, smectic liquid crystals can be observed only with DNBP. The mesophases induced with DNBP are more thermally stabilized than those induced with the other two acceptors when the donors are the ethoxy derivatives. On the other hand, the smectic liquid crystal in the (Me_2N, PrO)–DNBP is least stable and the liquid crystal in the (PrO, Me_2N)–DNBP is of intermediate stability. Thus, the absence of a central double bond linkage favors the induction of mesophase with the methoxy and ethoxy derivatives of *N*-benzylideneaniline but not with the propoxy derivatives. If the donor molecule is much larger than the acceptor molecule, there might be some combinations where the charge-transfer interaction is too weak to induce a smectic phase but still enough to induce a less-ordered nematic phase. Such a condition seems to be achieved by the addition of DNBP to the dimethylamino derivative of *N*-(benzylidene)-4-aminoazobenzene [Me_2N, H]. As is shown in Fig. 2, a stable nematic liquid crystal is observable in this system. The nematic liquid crystal-isotropic liquid (N–I) transition curve meets the freezing point curve of the donor compound at 168 °C and 9 mol% of DNBP, and the other freezing point curve at 172 °C and 17.5 mol%. The maximum lies at 174 °C and 15.5 mol%. The donor [Et_2N, EtO] is nematogenic by itself. When this compound is mixed with DNBP, the N–I transition curve is found to be convex upwards, in agreement with the induction observed in Fig. 2. In addition, one can see a metastable smectic phase of the A type induced in the composition

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

Acceptor	Donor					
	(Me_2N, MeO)	(MeO, Me_2N)	(Me_2N, EtO)	(EtO, Me_2N)	(Me_2N, PrO)	(PrO, Me_2N)
DNBP	131	136	138	164	132	140
(NO_2, NO_2)	—	—	131.5	131	136	136.5
DNAO	—	—	136	139	140	143

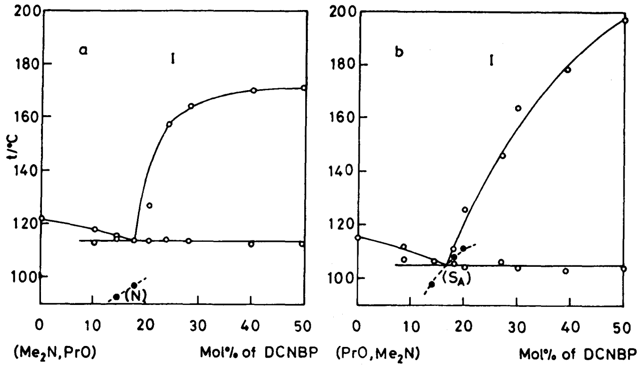

Fig. 3. Phase diagrams of the systems of DCNBP with (a) (Me$_2$N, PrO) and (b) (PrO, Me$_2$N). As to the open and shaded circles, see the caption of Fig. 1.

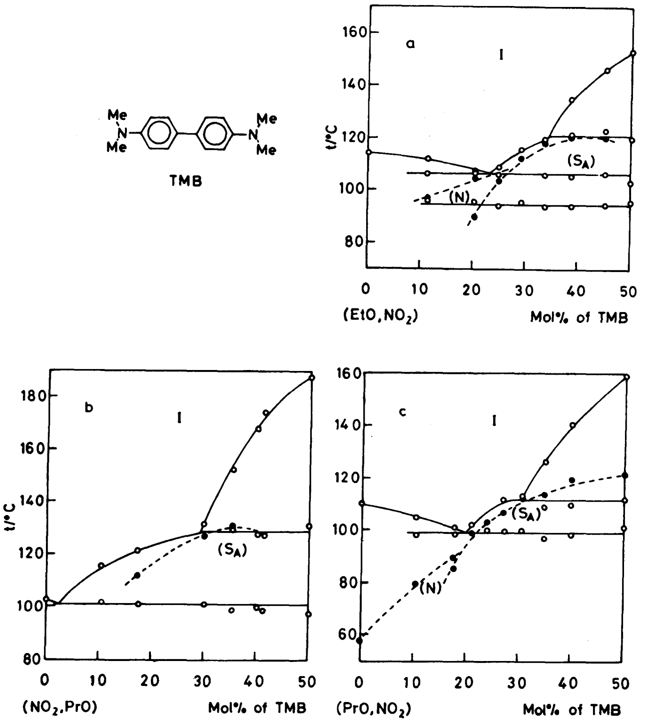

Fig. 4. Phase diagrams of the systems of TMB with (a) (EtO, NO$_2$), (b) (NO$_2$, PrO), and (c) (PrO, NO$_2$). As to the open and shaded circles, see the caption of Fig. 1.

range from 9 to 31 mol% of DNBP, the maximum being located at 136 °C and 23 mol%. This temperature is lower by 23 °C than the eutectic point. The induced metastable smectic phase is also noted in the system with nematogenic [Me$_2$N, EtO].

As described in one of our earlier papers, the present observations may imply that DNBP is potentially smectogenic.[3] It may be interesting to add that 4,4‴-dinitro-*p*-quaterphenyl has been reported by Vorländer to be a mesogenic substance.[8]

4,4′-Dicyanobiphenyl (DCNBP) as an Electron Acceptor. The electron acceptor strength of DCNBP is less than that of DNBP; therefore, the induced mesophase could be found only in the systems with (Me$_2$N, PrO) and (PrO, Me$_2$N). The mesophase in the former system is nematic and its appearance is limited to a narrow composition range (see Fig. 3a). A metastable smectic liquid crystal is present in the latter system. The monotropic S–I transition curve covers the range from 14 to 20 mol%, passing near the eutectic point located at 105 °C and 16.5 mol% (see Fig. 3b).

N,N,N′,N′-*Tetramethylbenzidine (TMB) as an Electron Donor.* Smectic liquid crystals are induced in the systems with (MeO, NO$_2$), (EtO, NO$_2$), (NO$_2$, PrO), and (PrO, NO$_2$). The mesophase produced by mixing with the first acceptor is so unstable that the phase diagram approach failed to locate the existence region. Consequently, only the other diagrams can be presented here. In Figs. 4a and c, nematic liquid crystals are also observable. Thus, TMB is more efficient in the induction of mesophases than (Me$_2$N, Me$_2$N) and 4,4′-bis(dimethylamino)azoxybenzene (BDMAAO), which can induce smectic liquid crystals only in the systems with (NO$_2$, PrO).[2]

The metastable nematic mesophase in the system with (EtO, NO$_2$) is stabilized up to 110 °C at about 28 mol% of TMB. The N–I transition curve passes near the eutectic point located at 106 °C and 23 mol%. The smectic mesophase is detectable in the composition range from 20 to 45 mol%. The maximum lies at 121 °C around 40 mol%. The horizontal line at 121 °C starting from the peritectic point at 34.5 mol% indicates the formation of a solid complex. at 50 mol% or higher. The other line at 94 °C may be due to a solid-solid transition of the complex.

The diagram of the (NO$_2$, PrO)–TMB system exhibits a metastable smectic phase in the composition range from 17 to 42 mol% of TMB. The maximum is located slightly above the peritectic temperature of 129 °C. It may be noted that the smectic liquid crystal is the most stabilized in this combination among those shown in Fig. 4. This finding is consistent with the previous results that smectic mesophases are induced only when (Me$_2$N, Me$_2$N) and BDMAAO are mixed with this Schiff base.[2] In the (PrO, NO$_2$)–TMB system, the whole examined range is covered by metastable nematic or smectic phase. The intersection between the I–N and I–S transition curves occurs at about 90 °C and 19 mol% of TMB. The latter curve reaches 121 °C at 50 mol%.

No liquid crystal is formed when TMB is replaced by *N,N,N′,N′*-tetraethylbenzidine in any of these binary systems.

The addition of TMB to [NO$_2$, H] resulted in the formation of a congruently melting solid complex at 33 mol% of TMB and the induction of a smectic A phase in the range from 42 to 50 mol%, the temperature at the latter composition being 152 °C. The acceptor itself is nematogenic. As the I–N transition lowers linearly with the mol% of TMB and is observable up to 45 mol%, there is no thermal stabilization of this phase by TMB. No new mesophase appears when TMB is added to nematogenic [NO$_2$, EtO].

The maximum of the I–S transition curve lies between 20 and 50 mol% of DNBP or TMB. The exact composition is supposed to depend upon the extent of the formation of the 2 : 1 complex in addition to the 1 : 1

complex and/or upon the difference in the latent I–S transition temperature between the component compounds.

As the smectic layers consist of molecular complexes, the thickness is dependent on how the donor and acceptor molecules are stacked and could be larger than the average length of the component molecules. In order to check this possibility, the interlayer spacing in the stable smectic phase of the A type induced in the (PrO, Me_2N)–DNBP mixture at 19.7% was measured. The observed spacing of 1.80 nm is in good agreement with the weighted mean molecular length of 1.87 nm. The latter was estimated assuming 1.97 nm for the donor molecule and 1.46 nm for the DNBP molecule; these values were calculated by employing the bond lengths and the van der Waals radii compiled by Kitaigorodskii.⁹⁾ Thus, it seems quite certain that the mesophase induced in this particular mixture is a monolayer liquid crystal. In connection with this measurement, the smectic phases of the A and B types induced in mixtures of [PrO, H]–[NO_2, H], [Et_2N, H]–[NO_2, H], and [PrO, EtO]–[NO_2, EtO] were similarly examined. In all the cases, the monolayer model accounts for the observed thickness.

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