Liquid Crystal Formation in Binary Systems. IV.[1] Induction of Smectic Phases in Mixtures of *N*-(*p*-Nitrobenzylidene)-*p*-aminoazobenzene and Various Electron Donors of the Type *N*-(*p*-Substituted Benzylidene)-*p*-aminoazobenzene

Minoru Fukui and Yoshio Matsunaga*

Department of Chemistry, Faculty of Science, Hokkaido University, Sapporo 060

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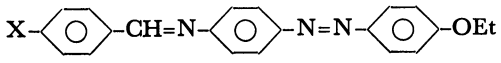
A study of the phase diagrams of binary systems consisting of nematogenic *N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene and various electron donors of the type *N*-(*p*-*X*-benzylidene)-*p*-aminoazobenzene revealed the induction of a smectic A phase in the cases where X=MeO, EtO, *n*-PrO, Me_2N, and Et_2N and of a smectic B phase as well in the cases where X=EtO and *n*-PrO. The extent of thermal stability enhancement of the smectic A phase is larger with non-nematogenic dialkylamino derivatives than with nematogenic alkoxy derivatives; this supports our postulate that the smectic phases are stabilized by the intermolecular interaction of the electron donor-acceptor type. The induction of smectic A phases was shown also in all the combinations of the *p'*-ethoxy derivatives, including the cases where X=H, Me, and Ph.

We reported earlier that nematic and smectic liquid crystals can be induced by mixing the *p*-dimethylamino and *p*-nitro derivatives of *N*-benzylideneaniline, which are both potentially mesogenic.[2] The induction of the mesophases in these binary systems was attributed to the stabilization of the parallel molecular arrangement by the interaction of the electron donor-acceptor type. In order to seek further correlation between the donor-acceptor interaction and the formation of smectic liquid crystals, we have applied the phase diagram approach to mixtures of nematogenic *N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene and various electron donors of the type *N*-(*p*-*X*-benzylidene)-*p*-aminoazobenzene. The latter compounds themselves are nematogenic or non-nematogenic depending upon the substituent X. The following substituents were selected purely from the standpoint of the electron-donor strength: H, Me, MeO, EtO, *n*-PrO (hereafter abbreviated PrO), Me_2N, and Et_2N. As the nature of each of these terminal substituents is so different, the influence on the thermal stability of mesophases of the component compounds may be quite variable. In addition, we worked on mixtures of the *p'*-ethoxy derivatives.



The appearance of a smectic phase has been noted by several research groups with a number of binary systems in which either one or both of the components are capable of giving nematic mesophases.[3-8] For instance, Schroeder and Schroeder have found the formation of a smectic phase in the system comprised of nematogenic 4,4'-bis(hexyloxy)azoxybenzene and non-nematogenic *N*-(*p*-methoxybenzylidene)-*p*-nitroaniline.[3] Engelen *et al.* have examined about thirty combinations and concluded that mixtures of terminal nonpolar and terminal polar nematogens usually induce a smectic phase of the type A.[5] While the nematogens with only alkyl and alkoxyl groups are considered to be nonpolar, the cyano and nitro derivatives are polar. A paper of Domon and Billard published a year later has referred to about ten systems which comprise two different nonpolar nematogens and yield smectic phases.[7] The donor-acceptor systems examined in our previous work consist of only polar components and markedly differ from theirs. Thus, it seems difficult to explain the role of terminal substituents and their dipole moments in the induction of smectic phases in binary mixtures. Recently, Sharma *et al.* have reported their work on the electron donor-acceptor complexes formed by two mesogenic component compounds and noted that the formation of smectic A phase is favored by such an interaction.[8] Their donor compounds are 4,4'-bis(alkylamino)biphenyls and the acceptors are various compounds carrying nitro, cyano, and/or carbonyl groups.

Experimental

Materials. The condensation reaction between *p*-X-substituted benzaldehyde and *p*-aminoazobenzene yields *N*-(*p*-X-benzylidene)-*p*-aminoazobenzene, as reported by Vorländer and Schuster.[9] The *p'*-ethoxy derivatives were similarly prepared. Hereafter, the component compounds are represented by their terminal substituents: that is, [X, H] in the first series and [X, EtO] in the second series. *p*-Amino-*p'*-ethoxyazobenzene needed for the latter series was prepared by the rearrangement of *p*-ethoxydiazoaminobenzene obtained by the coupling of benzenediazonium chloride with *p*-phenetidine.[10] Binary mixtures in known proportions were melted in small test tubes, shaken well to ensure homogeneity, and then rapidly cooled.

Measurements. The calorimetric curves were recorded on a Rigaku Denki differential scanning calorimeter, Model 8001 SL/C, during the processes of heating and cooling. The heating rate in the present work was 5 °C min^{-1}. The liquid crystals were identified by examining their texture with the aid of a polarizing microscope and/or by studying the continuous miscibility with a reference mesogen.

Results and Discussion

The [H, H] and [Me, H]–[NO_2, H] Systems. The acceptor compound [NO_2, H] has a nematic phase stable between 181 and 228 °C. The combination with non-mesogenic [H, H] yields no smectic phase (see Fig. 1a). A eutectic point is located at 122.5 °C and 14.5 mol% of [NO_2, H] and a peritectic point at 161 °C and 81 mol%.

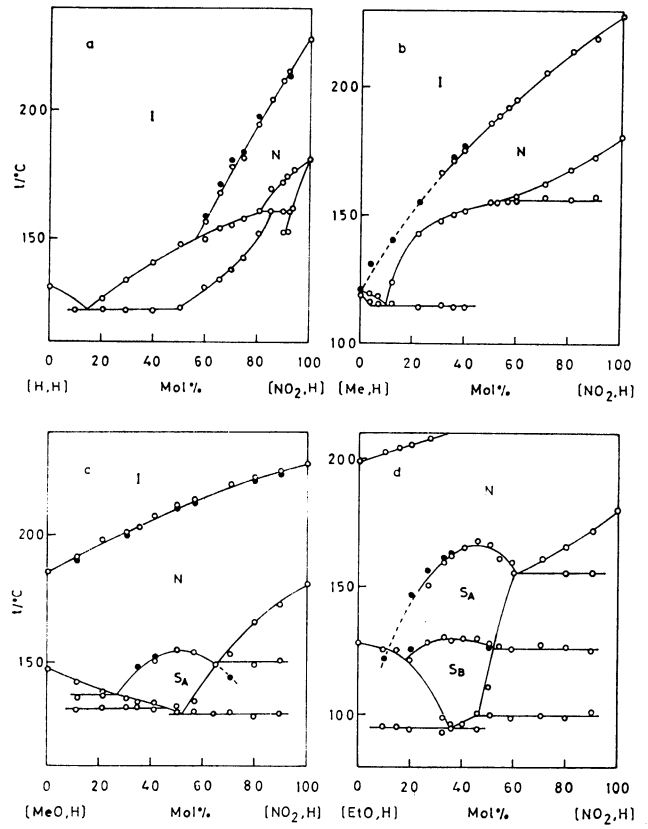


Fig. 1. Phase diagrams of (a) the *N*-benzylidene-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene, (b) *N*-(*p*-methylbenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene, (c) *N*-(*p*-methoxybenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene, and (d) *N*-(*p*-ethoxybenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene systems. The open and shaded circles are transitions observed in the processes of heating and cooling respectively.

The nematic liquid crystal-isotropic liquid (N-I) transition curve is met by the freezing point curve at 150 °C and 56.5 mol%. The extrapolation of the N-I transition curve, which is almost straight, to 0 mol% of the acceptor indicates that [H, H] has a latent N-I transition temperature around 50 °C. This temperature is far below its melting point, 131 °C.[9]

The compound [Me, H] exhibits a nematic phase stable between 118.5 and 120.5 °C. This temperature range is so narrow that the N-I transition is not detectable on the calorimetric curve recorded in the process of heating; however, the transition is well established in the process of cooling because of the delayed solidification. The N-I transition curve in the [Me, H]–[NO_2, H] system is slightly convex upwards (see Fig. 1b). A eutectic point is found at 114.5 °C and 10 mol% of [NO_2, H]. As the phase change at the former temperature is detected only below 50 mol%, the solid molecular compound melting incongruently at 156 °C may be of a 1 : 1 mole ratio. No smectic phase is induced in this system.

The [MeO, H], [EtO, H], and [PrO, H]–[NO_2, H] Systems. The donor [MeO, H] is nematogenic.[9] The liquid crystal is stable between 147.5 and 185.5 °C. The system [MeO, H]–[NO_2, H] gives a eutectic point located at 130 °C and 52 mol% of the acceptor. The N-I transition curve is convex upwards but only slightly. A smectic liquid crystal of the type A is induced and the maximum temperature of 154.5 °C is at 50 mol% (see Fig. 1c). The smectic liquid crystal-nematic liquid crystal (S-N) transition curve intersects the freezing point curve of the donor component at 137.5 °C and 27 mol% and that of the acceptor component at 150 °C and 65 mol%. The extrapolation of the S-N transition curve to 0 mol% gives a latent S_A-N transition temperature of donor at about 90 °C, while the extrapolation to 100 mol% yields a temperature of about 100 °C. Thus, the smectic phase is stabilized as much as 60 °C by the interaction between these two mesogens.

The nematic phase of [EtO, H] covers the temperature range from 128 to 199 °C. The system with [NO_2, H] shows a eutectic point at 95 °C and 36 mol% of [NO_2, H] and a peritectic point at 100 °C and 47 mol% (see Fig. 1d). There seems to be a solid molecular compound at 50 mol% with an incongruent melting point. Not only a smectic A phase but also a smectic B phase can be observed in this system. The maximum temperature of the former phase is about 167 °C and of the latter about 130 °C. The extrapolation of each transition curve to 0 mol% suggests that the donor has latent S_A-N and S_B-S_A transition temperatures at about 95 and 90 °C respectively. The existence of these two transitions has been confirmed by a study of the phase diagram of the system [EtO, H]–[NoO, H], *N*-(*p*-nonyloxybenzylidene)-*p*-aminoazobenzene. The reference compound gives a smectic B phase stable between 109.5 and 126 °C and a smectic A phase stable between 126 and 156 °C, in agreement with the data reported by Demus and Sackmann.[11] The freezing point curve of [EtO, H] is met by the S_A-N transition curve at 114 °C and 31 mol% of [NoO, H] and by the S_B-S_A transition curve at 105 °C and 44 mol% (see Fig. 2a). While the S_A-N transition curve above 31 mol% is convex upwards, the curve below this composition appears concave upwards. The extrapolation yields the latent transition temperatures of 95 and 89 °C which agree well with those suggested above. The latent S_B-S_A transition expected to be around 95 °C for [NO_2, H] is also supported by the phase diagram of the system with the same reference mesogen (see Fig. 2b). Here, the S_A-N transition curve is markedly convex upwards, as has been noted with the shorter alkoxy derivatives (see Figs. 1c and 1d). Passing the maximum at 177 °C and 60 mol% of [NoO, H], the transition curve is met by the freezing point curve of [NO_2, H] at 157.5 °C and 37 mol%. In contrast to the S_A-N transition curve, the curve separating the smectic A and B phases is slightly concave upwards. The intersection with the freezing point curve is found at 112 °C and 58 mol%. Consequently, the extents of stabilization of the smectic A and B phases in the [EtO, H]–[NO_2, H] system are estimated to be about 70 and 38 °C respectively.

With the [MeO, H]–[EtO, H] system, we have confirmed the ideal linear relationship of N-I transition

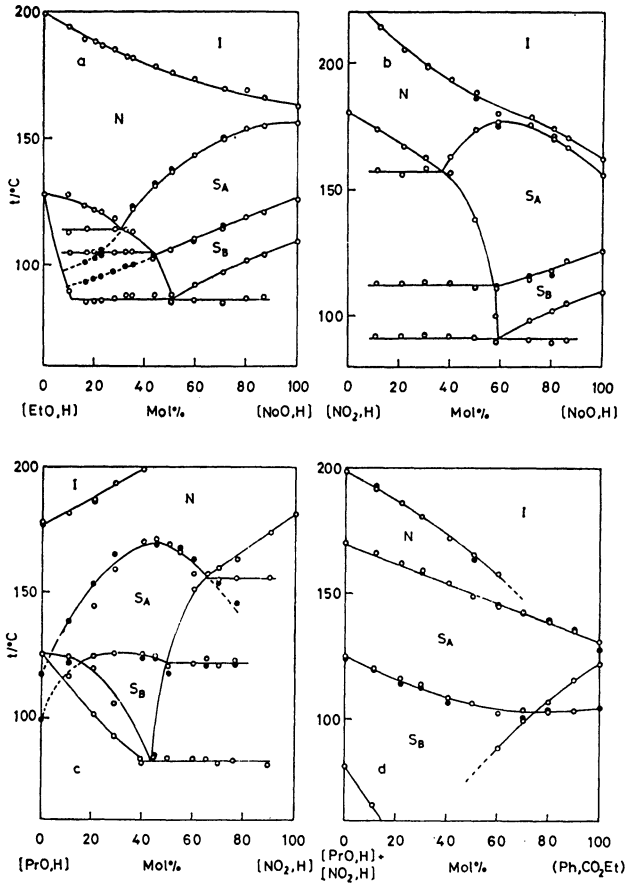
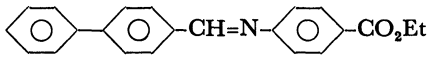


Fig. 2. Phase diagrams of (a) the *N*-(*p*-ethoxybenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nonyloxybenzylidene)-*p*-aminoazobenzene, (b) *N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nonyloxybenzylidene)-*p*-aminoazobenzene, and (c) *N*-(*p*-propoxybenzylidene)-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene) -*p*-aminoazobenzene systems and (d) the system consisting of *N*-(*p*-phenylbenzylidene)-*p*-(ethoxycarbonyl)aniline and the 6 : 4 mixture of *N*-(*p*-propoxybenzylidene)-*p*-aminoazobenzene and *N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene. As to the open and shaded circles, see the caption of Fig. 1.

temperatures in the absence of a particular interaction. The single eutectic point is located at 115 °C and 56 mol% of [EtO, H]. It is rather surprising to see that solid [EtO, H] can dissolve [MeO, H] up to 30 mol%. On the other hand, the solubility of [EtO, H] into solid [MeO, H] is less than 10 mol%.

The nematic phase of [PrO, H] makes an appearance at 125 °C and is stable up to 178 °C. This donor has metastable smectic A and B phases: that is, the supercooled nematic phase is transformed into a smectic A phase at 117 °C and then into a smectic B phase at 99 °C. When mixed with [NO_2, H], a eutectic point appears at 83 °C and 44 mol% of the acceptor (see Fig. 2c). The smectic A phase has a region of existence from 4 to 65 mol% and the smectic B phase from 15 to 50 mol%. The upper temperature limit of the former mesophase is located at about 170 °C, which is higher by 62 °C than the straight line joining the S_A-N transition temperatures of the components. When the composition is lower than 30 mol%, the S_A-N transition temperatures recorded in the process of heating were found to deviate significantly from those recorded in the process of cooling. The curve was drawn on the basis of the latter points which are in conformity with the transition temperature of pure [PrO, H]. In contrast to the smectic A phase, the maximum deviation from the ideal linear relationship in the smectic B phase apparently occurs at a composition far from a 1 : 1 mole ratio. This phase at 30 mol% is stabilized by about 28 °C.

The induced smectic A and B phases could be identified by their characteristic fan-shaped texture. In addition, the classification has been confirmed by the selective miscibility with the smectic A phase of *N*-(*p*-phenylbenzylidene) -*p*- (ethoxycarbonyl) aniline (Ph,



CO_2Et) which is stable between 121.6 and 131 °C.[12] Fig. 2d presents the diagram of the pseudo-binary system consisting of a mixture of [PrO, H] and [NO_2, H] at 40 mol% and the reference compound. The diagram is of the eutectic type. The N-I transition curve is slightly convex upwards and the nematic phase is not observable above 70 mol% of (Ph, CO_2Et). Doubtlessly the mesophases induced in the mixture at high temperatures form an uninterrupted series of mixed crystals with the smectic A phase of the reference compound. Another smectic phase appearing enantiotropically in the mixtures at lower temperatures is identical with the metastable smectic phase of (Ph, CO_2Et). The latter was classified into type B on the basis of its miscibility behavior with [NoO, H].

The smectic B phase could be found also in the system comprising a 1 : 1 mixture of [MeO, H] and [NO_2, H] and the reference mesogen. The phase is stable in the composition range from 5 to 68 mol% of (Ph, CO_2Et). The extrapolation of the transition curve to 0 mol% gives a temperature only a few degrees below the eutectic temperature of the [MeO, H]–[NO_2, H] system.

The [Me_2N, H] and [Et_2N, H]–[NO_2, H] Systems. The donor [Me_2N, H] is non-mesogenic. A eutectic point is located at 142 °C and 75.5 mol% of [NO_2, H]. A peritectic point appears at 146 °C and 59 mol% because of the formation of an incongruently-melting molecular compound, possibly of a 1 : 1 mole ratio. The mixtures give rise to a smectic A phase, as is shown in Fig. 3a. The induced S_A-N transition curve is met by the freezing point curve of the donor component at 152 °C and 48 mol% and by that of the acceptor component at 166 °C and 87 mol%. The maximum may be located around 190 °C in the composition range between 60 and 70 mol%. The steep slope on the donor-rich side suggests that the latent S_A-N transition temperature of [Me_2N, H] is very low. This may be the reason why the maximum of the transition curve is found at an acceptor-rich composition. As this temperature is higher by 90 °C than the estimated S_A-N transition temperature of [NO_2, H], the extent of the stabilization of the smectic phase certainly exceeds 100 °C.

Replacement of a dimethylamino group by a diethyl-

amino group in the donor compound seems to lower markedly the latent N-I transition temperature. As is shown in Fig. 3b, the N-I transitions lie on an approximately straight line in the diagram. The extrapolation to 0 mol% of [NO_2, H] yields −12 °C. The line intersects the induced S_A-N transition curve at 167 °C and 72 mol%. The maximum temperature of the smectic A phase is found at 168 °C near 75 mol%. The extent of induction is at least 90 °C, because the latent S_A-N transition of [Et_2N, H] is expected to be lower than the latent N-I transition. It must be noted that the smectic A phase induced over the range of composition below 72 mol% is thermally more stable than the nematic phase. At 83 mol% and 164.5 °C, the S_A-N transition curve is met by the freezing point curve of the acceptor.

In summary, the maximum temperature of the induced smectic A phase in the present series decreases in the following order: [Me_2N, H]>[PrO, H]>[EtO, H]≃[Et_2N, H]>[MeO, H]. Even though these results arise from the complex interplay of different molecular parameters determining the thermal stability of smectic phases, the extents of the stability enhancement with more electron-donating dialkylamino derivatives are clearly larger than those with less electron-donating alkoxy derivatives, 60—70 °C, supporting our postulate that the ordered arrangement of molecules characteristic of smectic phases can be achieved by the interaction of the electron donor-acceptor type. In the latter derivatives, the sequence of the extents is [EtO, H] >[PrO, H]≃[MeO, H]. It must be emphasized that the maximum deviation of the nematic phases from the ideal linear relationship is merely several degrees in the above-mentioned systems. Moreover, the induction of the smectic A phases is about twice as large as that of the smectic B phases when observable. As no smectic phase could be found in the [H, H] and [Me, H]–[NO_2, H] systems, we decided to take up the second series, mixtures of the *p'*-ethoxy derivatives. The unsubstituted compound [H, EtO] is an isomer of [EtO, H] and has been found to be nematogenic by the work of Vorländer.[10]

The [H, EtO] and [Me, EtO]–[NO_2, EtO] Systems. The compound [H, EtO] melts at 136 °C and has an enantiotropic nematic range up to 204 °C. The range is shifted upwards by several degrees compared with that of the isomeric [EtO, H]. When this donor is mixed with nematogenic [NO_2, EtO], a smectic A phase is produced in the composition range from 50 to 88 mol% of the acceptor (see Fig. 4a). At the latter composition, the induced S_A-N transition curve intersects the freezing point curve of the acceptor. The extrapolation of this transition curve to 100 mol% suggests that the acceptor has the latent transition temperature at about 155 °C. The smectic phase shows the maximum temperature of about 178 °C at 75 mol%. It must be added that the latent S_A-N transition temperature of pure [H, EtO] is apparently much lower than that of [EtO, H], which is located at 95 °C. This combination produces a congruently melting molecular compound, presumably at 33 mol%. Eutectic points are located at 118 °C and 22.5 mol% and at 127 °C and 47 mol%. The acceptor compound [NO_2, EtO] is transformed from a solid to a nematic liquid crystal at 177.5 °C.

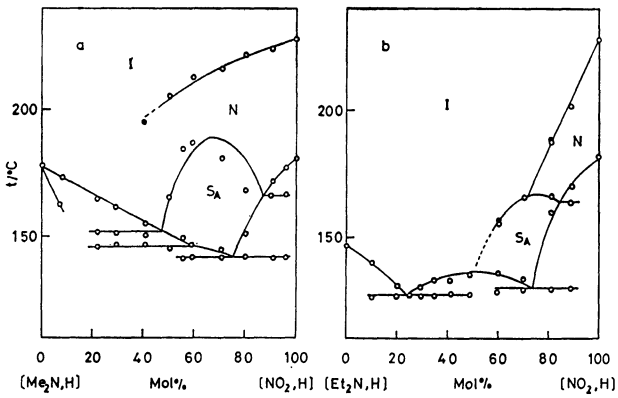


Fig. 3. Phase diagrams of (a) the *N*-[*p*-(dimethylamino)-benzylidene] - *p*-aminoazobenzene–*N* - (*p* - nitrobenzylidene)-*p*-aminoazobenzene and (b) *N*-[*p*-(diethylamino)benzylidene]-*p*-aminoazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-aminoazobenzene systems. As to the open and shaded circles, see the caption of Fig. 1.

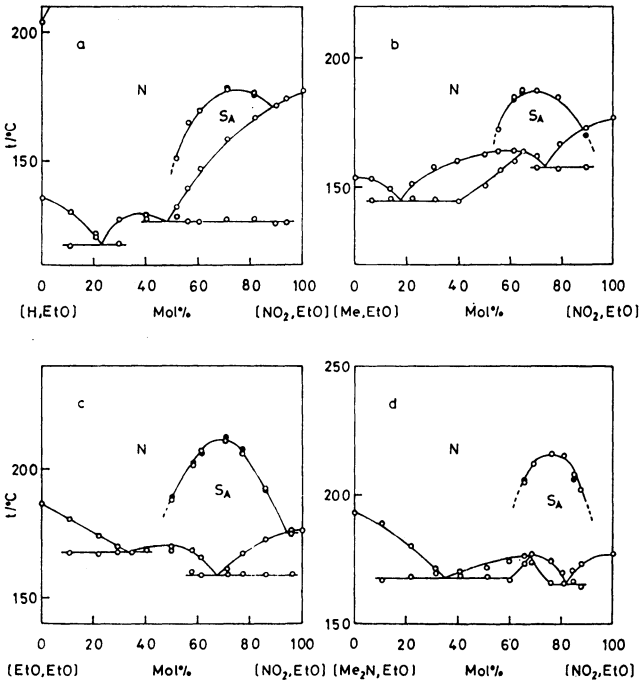


Fig. 4. Phase diagrams of (a) the *N*-benzylidene-*p*-amino-*p'*-ethoxyazobenzene–*N*- (*p*-nitrobenzylidene) -*p*-amino-*p'*-ethoxyazobenzene, (b) *N*-(*p*-methylbenzylidene)-*p*-amino-*p'*-ethoxyazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-amino-*p'*-ethoxyazobenzene, (c) *N*-(*p*-ethoxybenzylidene)-*p*-amino-*p'*-ethoxyazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-amino-*p'*-ethoxyazobenzene, and (d) *N*-[*p*-(dimethylamino)benzylidene]-*p*-amino-*p'*-ethoxyazobenzene–*N*-(*p*-nitrobenzylidene)-*p*-amino-*p'*-ethoxyazobenzene systems. As to the open and shaded circles, see the caption of Fig. 1.

The compound [Me, EtO] is nematogenic and melts at 154 °C. The mixtures with [NO_2, EtO] in the composition range from 55 to 90 mol% of [NO_2, EtO] yield a smectic A phase (see Fig. 4b). The maximum temperature of 188 °C is found at 70 mol%. The molecular compound formed in this system has a 1 : 2

mole ratio and melts congruently at 164 °C. Eutectic points are located at 145 °C and 18 mol% and at 158 °C and 74 mol%.

The [MeO, EtO], [EtO, EtO], and [PrO, EtO]–[NO_2, EtO] Systems. All the donor compounds are nematogenic. The donor [MeO, EtO] melts at 161 °C. When mixed with [NO_2, EtO], a smectic A phase is induced in the composition range from 55 to 88 mol%. The S_A-N transition curve has a maximum at 192 °C and 73 mol% and is met at 88 mol% by the freezing point curve of the acceptor. As the donor molecule has electron donating groups at the *p* and *p'* positions, the molecular complex formed in the smectic phase may be, at least, partly of a 1 : 2 mole ratio. A solid molecular compound is found at a 1 : 2 mole ratio and is stable up to its melting point, 164 °C. A eutectic point on the donor-rich side is located at 161 °C and about 48 mol%; therefore, the freezing point curve below this point is flat. Another eutectic point is found at 158 °C and 74 mol%.

The phase diagram of the [EtO, EtO]–[NO_2, EtO] system is presented in Fig. 4c. The donor compound has a nematic phase stable above 186 °C. The smectic mesophase appears in the range from 50 to 93 mol% of the acceptor. The upper temperature limit of the mixture's smectic range is found at 211.5 °C and 68 mol%. The equimolar solid molecular compound formed by the present combination melts at 170 °C. Eutectic points are located at 168 °C and 32 mol% and at 159 °C and 67 mol%.

The diagram of the [PrO, EtO]–[NO_2, EtO] system bears a similarity to the afore-mentioned one. The nematogenic [PrO, EtO] melts at 167 °C. The induced smectic A mesophase can be seen in the composition range from 45 to 90 mol%. The maximum in smectic phase stability occurs at 226 °C and 65 mol%. The intersection between the S_A-N transition curve and the freezing point curve on the acceptor-rich side may be at 176 °C and 93 mol%. The 1 : 1 molecular compound melts at 165°C. As this melting point and the eutectic temperature are not distinguishable from each other, the latter location could not be determined. Another eutectic point is at 150 °C and 67 mol%.

The [Me_2N, EtO], [Et_2N, EtO], and [Ph, EtO]–[NO_2, EtO] Systems. Contrary to [Me_2N, H], the donor [Me_2N, EtO] gives a stable nematic liquid crystal above 193 °C. As is shown in Fig. 4d, a smectic A phase is induced in the mixtures with [NO_2, EtO]. The maximum for the S_A-N transition is located at about 216 °C and 75 mol%. This combination yields a 1 : 2 molecular compound with a congruent melting point of 177.5 °C. Two eutectic points are at 168 °C and 35 mol% and at 165 °C and 82 mol%.

The compound [Et_2N, EtO] has a nematic range from 159.5 to 198.5 °C. The reduction of the enantiotropic N-I transition temperature by replacement of a dimethylamino group with a diethylamino group is in accordance with the trend suggested for the latent N-I transitions in [Me_2N, H] and [Et_2N, H]. The induced smectic A phase in the system with [NO_2, EtO] covers a wide composition range. One end of the S_A-N transition curve is the intersection with the freezing point curve of the donor located at 144 °C and 29 mol% and the other is the intersection with the freezing point curve of the acceptor, possibly around 98 mol%. The maximum temperature of 239 °C is found at about 77 mol%. The solid 1 : 2 molecular compound in this system is of lower stability and ceases to exist stably at 146 °C, producing a peritectic point at 64 mol%. The eutectic is at 138.5 °C and 34 mol%.

In addition to the above-mentioned systems, the phase diagram has been prepared for the combination of [Ph, EtO] and [NO_2, EtO]. The donor [Ph, EtO] is transformed from a solid to a nematic liquid crystal at 199 °C. The diagram has a eutectic point at 159 °C and 64 mol%. In this system too, only a smectic A phase is induced. The S_A-N transition curve recorded in the range from 30 to 90 mol% reaches its maximum at 234 °C and 54 mol%. The smooth extrapolation to 0 mol% suggests that the donor has the latent transition a little below 150 °C. The extent of induction may be about 90 °C.

As described above, the smectic A phases induced in the second series are found to exhibit maxima beyond 50 mol% of [NO_2, EtO]. Except for the last donor, the latent S_A-N transition temperatures are expected to be considerably lower than that of the acceptor. The large mole percentages at the upper temperature limits may be ascribed to the low latent transition temperatures of the donor compounds and also to the formation of 1 : 2 molecular complexes. The observed upper temperature limits of the induced mesophases give the following sequence of the donors:

[Et_2N, EtO]>[Ph, EtO]>[PrO, EtO]>[Me_2N, EtO]>
[EtO, EtO]>[MeO, EtO]>[Me, EtO]>[H, EtO].

The extent of induction may be concluded to be less only when both the temperature limit and the composition are lower. Judging by such a condition, the donors may be partially arranged in order of their decreasing ability of inducing a smectic A phase: namely,

[Me_2N, EtO]>[MeO, EtO]>[Me, EtO],
[Et_2N, EtO]>[PrO, EtO],
[Me_2N, EtO]>[EtO, EtO], and
[Me_2N, EtO]>[H, EtO].

A plausible explanation for these features is that the stabilization is provided by the intermolecular electron donor-acceptor interaction.

No smectic B phase could be observed in the second series. As the molecular compounds found in this series are more stable than those in the first series, the freezing point may be too high to allow the observation of the S_B-S_A transition. This assumption has been supported by a study on the system consisting of a 3 : 7 mixture of [Me, EtO] and [NO_2, EtO] and the reference compound [NoO, H]. The composition of the mixture has been chosen to correspond to the upper temperature limit of the induced smectic A phase (see Fig. 4b). The diagram shown in Fig. 5 strongly suggests that the mixture has a latent S_B-S_A transition located around 120 °C, which is not very different from the transitions exhibited by mixtures of [EtO, H] and [NO_2, H]. The

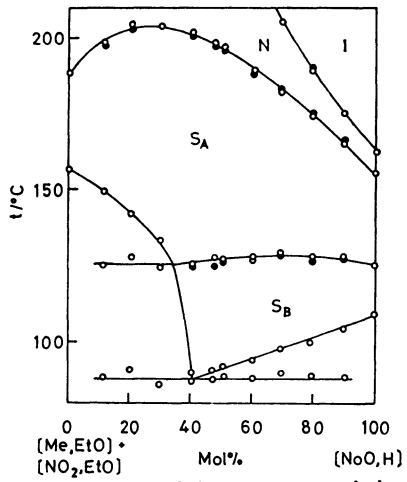


Fig. 5. Phase diagram of the system consisting of *N*-(*p*-nonyloxybenzylidene)-*p*-aminoazobenzene and the 3 : 7 mixture of *N*-(*p*-methylbenzylidene)-*p*-amino-*p'*-ethoxyazobenzene and *N*-(*p*-nitrobenzylidene)-*p*-amino-*p'*-ethoxyazobenzene. As to the open and shaded circles, see the caption of Fig. 1.

S_A-N transition curve is appreciably convex upwards and the maximum is located at about 25 mol% of [NoO, H]. These results imply that [NoO, H] is a better electron donor than [Me, EtO] is.

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