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Liquid Crystal Formation in Binary Systems. III.[1] Effect of the Central Double Bond Linkage on the Induction of Nematic Liquid Crystals

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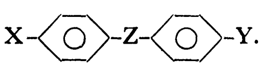
The effect of central double bond linkage on the induction of liquid crystals has been examined employing eight binary mixtures of potentially mesomorphic electron donors and acceptors of the type 4-X–C_6H_4–Z–C_6H_4–OC_2H_5-4. The central linkage Z is –N=N–, –CH=N–, or –CH=CH– group. The terminal substituent X is a dimethylamino group in the donor compounds and a nitro group in the acceptor compounds. A stable nematic liquid crystal is observable with the systems of azo-azo and azo-azomethine compounds. When the acceptor is the nitro derivative of stilbene, a 2 : 3 molecular complex is formed and no liquid crystal can be found, irrespective of whether the partner is an azo or azomethine compound. The latent induction of nematic liquid crystals in these combinations has been proved by studies on the phase diagrams of the pseudo-binary systems with a reference nematogen, azoxydianisole. The nematic liquid crystal-isotropic liquid transition temperatures of both the component compounds and the equimolar mixtures depend on the central double bond linkage: the order is –CH=CH–>–N=N–>–CH=N–. On the other hand, the order of –N=N– and –CH=N– groups is reversed in the extent of the induction of nematic liquid crystals.

In an earlier paper of this series, we reported that nematic and smectic liquid crystals can be induced by mixing of electron donors and acceptors of the type 4-X–C_6H_4–CH=N–C_6H_4–Y-4.[1] The donor molecules with a dimethylamino group as X or Y and the acceptor molecules with a nitro group as X or Y were employed in that work. The remaining terminal substituents were selected from short alkoxyl groups. The component compounds themselves were designed to be not mesomorphic. Nevertheless, they should be considered potentially mesomorphic because a liquid crystal of variable composition appears in the mixtures. The extrapolation of the observed liquid crystal-isotropic liquid transition curve to 0 mol% or 100 mol% gives a finite temperature. In other words, the strength of orientational cohesive forces in the molten component compound is not sufficient to produce a liquid crystal where the long axes of the molecules are essentially parallel. The induction or the enhancement of the thermal stability of liquid crystals in the above-mentioned mixtures was found to be maximum at a mole ratio of 1 : 1. The molecular arrangement characteristic of liquid crystals in the mixture was supposed to be achieved by supplementing the orientational cohesive forces with an electron donor-acceptor interaction. This sort of intermolecular interaction is well known to produce the alignment of the planar component molecules in ordinary crystals.

The above-mentioned Schiff bases belong to the class of compounds of the least complex structure for mesogens: that is,



The variation of the nematic liquid crystal-isotropic liquid (N-I) transition temperatures of such single compounds with the nature of central double bond linkage Z is known to be fairly regular. The efficiency for central linkages in promoting N-I transition temperature was concluded by Knaak *et al.* to decrease in the order:

–CH=CH–>–N=N–>–CH=N–.[2]

We took up two azobenzenes and a stilbene in order to find out how the induction of liquid crystals in binary systems is affected by the central linkages. The terminal substituents other than dimethylamino and nitro groups in the present work were limited to the ethoxyl group. Only with this alkoxyl group did the induced nematic liquid crystals appear as stable single phases in the binary systems which comprise Schiff bases.[1]

Experimental

Materials. 4-Dimethylamino-4′-ethoxyazobenzene (DMAEA) was prepared by the method described by Vorländer and Wolferts: *p*-phenetidine was diazotized and coupled with *N*,*N*-dimethylaniline dissolved in acetic acid.[3] The supercooled melt was reported to be transformed into a liquid crystal, but neither the transition temperature nor the kind of the phase was given by them. 4-Ethoxy-4′-nitroazobenzene (ENA) was obtained by boiling 4-hydroxy-4′-nitroazobenzene in ethanolic solution with ethyl bromide and sodium ethoxide for about 1 h.[4] 4-Ethoxy-4′-nitrostilbene (ENS) was synthesized by the condensation reaction between *p*-nitrophenylacetic acid and *p*-ethoxybenzaldehyde in the presence of a small amount of piperidine. This is analogous to the preparation of the methoxy compound given by Pfeiffer.[5] The Schiff bases (azomethine compounds) were made by the condensation between *p*-X-benzaldehyde and *p*-Y-aniline. In contrast to the azobenzene and stilbene, these molecules are asymmetric and will be represented by their substituents (X, Y). Binary mixtures were prepared by the procedure given in our previous paper.[1]

Measurements. The calorimetric measurement and examination of the texture were carried out as described in our earlier work.[1]

Results and Discussion

Component Compounds. The melting points and N-I transition temperatures of the component compounds are listed in Table 1. It must be noted that the former values are higher than the latter in all the cases. The transition temperatures in this table have been deduced by the extrapolation of the N-I transition curves observed in the binary systems with mesomorphic

Table 1. Melting points (T_m) and nematic liquid crystal-isotropic liquid transition temperatures (T_t) of the component compounds

Compound	T_m/°C	T_t/°C
4-(Dimethylamino)-4′-ethoxyazobenzene	151.5[a]	117
4-Ethoxy-4′-nitroazobenzene	157[b]	110
4-Ethoxy-4′-nitrostilbene	145	115
N-[4-(Dimethylamino)benzylidene]-4-ethoxyaniline	147[c]	97.5
N-(4-Ethoxybenzylidene)-4-(dimethylamino)aniline	138	102
N-(4-Nitrobenzylidene)-4-ethoxyaniline	122[d]	85
N-(4-Ethoxybenzylidene)-4-nitroaniline	114[e]	90

a) 151 °C according to Vorländer and Wolferts (Ref. 3). b) 155 °C according to Baly *et al.* (Ref. 4). c) 147.3 °C according to Dave and Lohar (Ref. 6). d) 123.5 °C according to Dave and Lohar (Ref. 6). e) 121 °C according to Malthete *et al.* (Ref. 7).

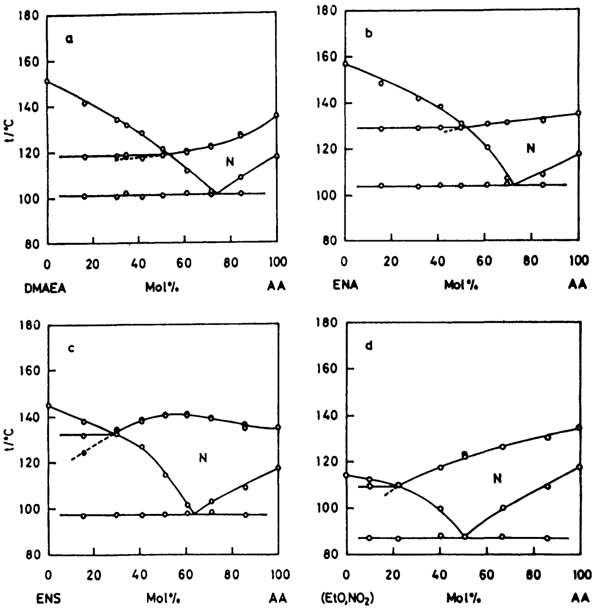


Fig. 1. Phase diagrams of (a) the 4-(dimethylamino)-4′-ethoxyazobenzene-azoxydianisole, (b) 4-ethoxy-4′-nitroazobenzene-azoxydianisole, (c) 4-ethoxy-4′-nitrostibene-azoxydianisole, and (d) *N*-(4-ethoxybenzylidene)-4-nitroaniline-azoxydianisole systems.

azoxydianisole (AA). This reference mesogen exhibits a nematic liquid crystal which is stable between 117.5 and 135°C. The phase diagrams of the systems with DMAEA, ENA, ENS, and (EtO, NO$_2$) are presented in Fig. 1. The open and shaded circles show the transitions recorded on the calorimetric curves during the processes of heating and cooling respectively. The phase appearing below the transitions, indicated solely by shaded circles, is metastable. When the azobenzene has an electron-donating dimethylamino group, the N-I transition curve is slightly concave upwards (see Fig. 1a). The eutectic point in this system is located at 101 °C and 74 mol% of AA. The enantiotropic N-I transition curve meets the freezing point curve of the azobenzene at 118.5 °C and 53 mol% of AA. The transition to a nematic liquid crystal of the supercooled melt could be observed down to 35 mol% of AA. At this composition, the curve is almost horizontal. As mentioned above, Vorländer and Wolferts noted that a liquid crystal can be formed when the melt of DMAEA is sufficiently supercooled. We failed to observe this; however, the latent N-I transition temperature of DMAEA is located at about 117 °C, if we judge by the extrapolation of the transition curve.

When an electron-withdrawing nitro group is attached to one of the component molecules, the N-I transition curve tends to be convex upwards (see Figs. 1b, c, and d). The extrapolation to 0 mol% of AA gives about 110 °C for the latent transition temperature of ENA, 115 °C for that of ENS, and 90 °C for that of (EtO, NO$_2$). The phase diagram of the (NO$_2$, EtO)-AA system can be reproduced from the data given by Dave and Lohar.[6] The N-I transition temperatures, therefore, can be arranged in the following order:

$$\text{DMAEA} > (\text{EtO, Me}_2\text{N}) > (\text{Me}_2\text{N, EtO})$$

and

$$\text{ENS} > \text{ENA} > (\text{EtO, NO}_2) > (\text{NO}_2\text{, EtO}),$$

in agreement with the general order reported by Knaak *et al.*[2] The nonideality of the N-I transition curve is very remarkable in the ENS-AA system (see Fig. 1c). The transition at 50 mol% of AA deviates by about 16 °C from the line joining the transition temperatures of the component compounds. The degree of nonideality of the transition curve, which is the extent of the induction of liquid crystal at 50 mol% of AA, occurs in the following order:

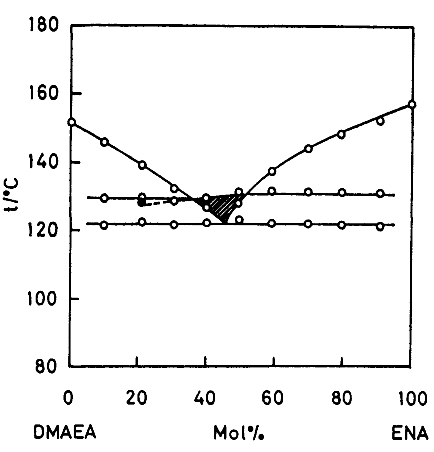


Fig. 2. Phase diagram of the 4-(dimethylamino)-4′-ethoxyazobenzene-4-ethoxy-4′-nitroazobenzene system. In the hatched area, the nematic liquid crystal is stable as a single phase.

$$\mathrm{ENS} \simeq (\mathrm{NO_2}, \mathrm{EtO}) > (\mathrm{EtO}, \mathrm{NO_2}) > \mathrm{ENA}.$$

The attractive interaction with AA is probably of the electron donor-acceptor type, as will be discussed later.

Systems with the Azobenzenes. The phase diagram of the DMAEA–ENA system is of the eutectic type, as is shown in Fig. 2. The eutectic point is found at 122 °C and 46 mol% of ENA. A nematic liquid crystal remains a single phase in the composition range from 36 to 52 mol% of ENA. The maximum transition temperature is 131.5 °C, observed at 60 mol%. Equilibrium diagrams such as the above have been reported by Lohar for the systems consisting of two Schiff bases: namely, (MeO, EtO) mixed with (NO_2, EtO), (Me_2N, EtO), or (MeCO, Me).[8] In his first system, the N-I transition curve is markedly convex upwards, suggesting the electron donor-acceptor interaction between the molecules of different kinds. On the other hand, the observed transitions vary more or less linearly with the composition in the remaining two systems. As the eutectic point is lowered with respect to the curve connecting the latent transition temperatures of the component compounds, a nematic liquid crystal is observable in these mixtures. Because of the strong tendency of the azobenzenes to crystallize, the transition curve observed in Fig. 2 is so short that one cannot say whether it is straight or curved. Considering the latent N-I transition temperatures given in Table 1, one can conclude that the nematic liquid crystal is induced as much as 18 °C by mixing. If there were no stability enhancement, the liquid crystal in this system would be metastable in the entire composition range.

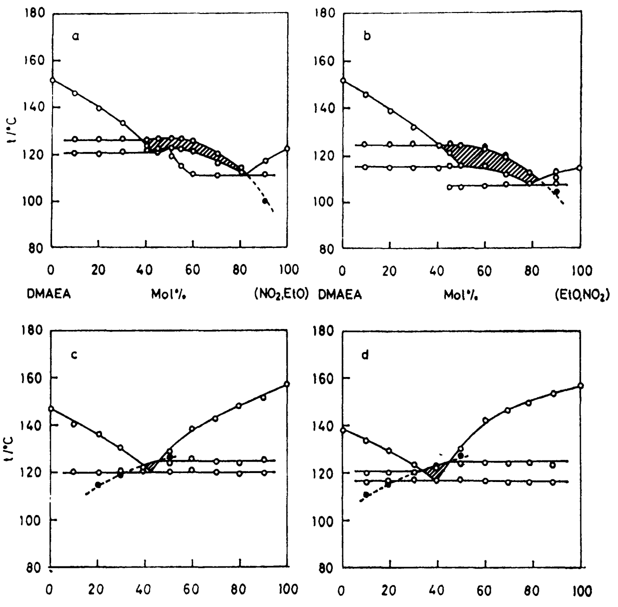


Fig. 3. Phase diagrams of (a) the 4-(dimethylamino)-4′-ethoxyazobenzene–*N*-(4-nitrobenzylidene)-4-ethoxyaniline, (b) 4-(dimethylamino)-4′-ethoxyazobenzene–*N*-(4-ethoxybenzylidene)-4-nitroaniline, (c) *N*-[4-(dimethylamino) benzylidene]-4-ethoxyaniline–4-ethoxy-4′-nitroazobenzene, and (d) *N*-(4-ethoxybenzylidene)-4-(dimethylamino)aniline–4-ethoxy-4′-nitroazobenzene systems. As to the hatched area, see the caption of Fig. 2.

The combination of DMAEA with (NO_2, EtO) or (EtO, NO_2) gives the diagram shown as Fig. 3a or b. The former system involves a congruently melting 1 : 1 molecular complex. The eutectic points are at 120.5°C and 42.5 mol% and at 111 °C and 82 mol% of the Schiff base. The molecular complex melts at 123 °C. The nematic liquid crystal appears as a stable single phase in the hatched area above the freezing point curve of the molecular complex. The area covers the composition range from 38 to 83 mol% of (NO_2, EtO). The maximum N-I transition temperature is located at 127 °C and 50 mol%. This temperature is higher by 26 °C than the mean value of the latent transition temperatures of the component compounds.

As is shown in Fig. 3b, a molecular complex is also formed in the system with (EtO, NO_2), but it is obviously less stable than that mentioned above. A peritectic point appears at 115 °C and 50 mol% and a eutectic point at 107 °C and 79 mol% of (EtO, NO_2). At the former temperature, the molecular complex decomposes, leaving the solid azobenzene and the melt of a 1 : 1 mole ratio. The composition of the solid molecular complex is not 1 : 1 mole ratio but possibly 3 : 2 or 2 : 1. A single phase nematic liquid crystal appears in the composition range from 41 to 83 mol% of the Schiff base. The maximum temperature is 124 °C. The extent of the induction is estimated to be 21 °C.

The (Me_2N, EtO)–ENA and (EtO, Me_2N)–ENA systems yield no solid molecular complex (see Figs. 3c and d). The eutectic points are located at 120 °C and 42.5 mol% and at 117 °C and 39 mol% of ENA respectively. The nematic liquid crystal is stable as a single phase in a very limited area. In the former system, the composition range is only from 39 to 46 mol% and in the latter from 33 to 45 mol% of ENA. The N-I transitions at 50 mol% occur at 126 and 127 °C respectively. The stability of the liquid crystal is enhanced by 22 °C in the former system and by 21 °C in the latter. These values are a little bit larger than the 18 °C found with the system comprising only the azobenzenes. In Fig. 3c, a horizontal transition line is supposed to exist; this extends from the point of intersection between the N-I transition curve and the freezing point curve of the Schiff base. However, no peak due to this transition could be recorded because of overlapping with a much larger peak at the eutectic temperature.

Systems with 4-Ethoxy-4′-nitrostilbene. When the stilbene is the acceptor in binary systems, a stable 2 : 3 molecular complex is formed in all the examined systems and no liquid crystal is observable (see Figs. 4a, b, and c). The regions of existence of the solid molecular complexes (the composition difference between the two eutectic points) are as follows: 69 mol% with DMAEA, 74.5 mol% with (Me_2N, EtO), and 82 mol% with (EtO, Me_2N). The stability of solid molecular complex may be considered to increase in this order. While the stilbene is yellow and (Me_2N, EtO) is pale yellow, the molecular complex is orange, suggesting the appearance of a charge-transfer absorption band. On the other hand, the color change by the molecular complex formation is hardly noticeable when the orange-colored

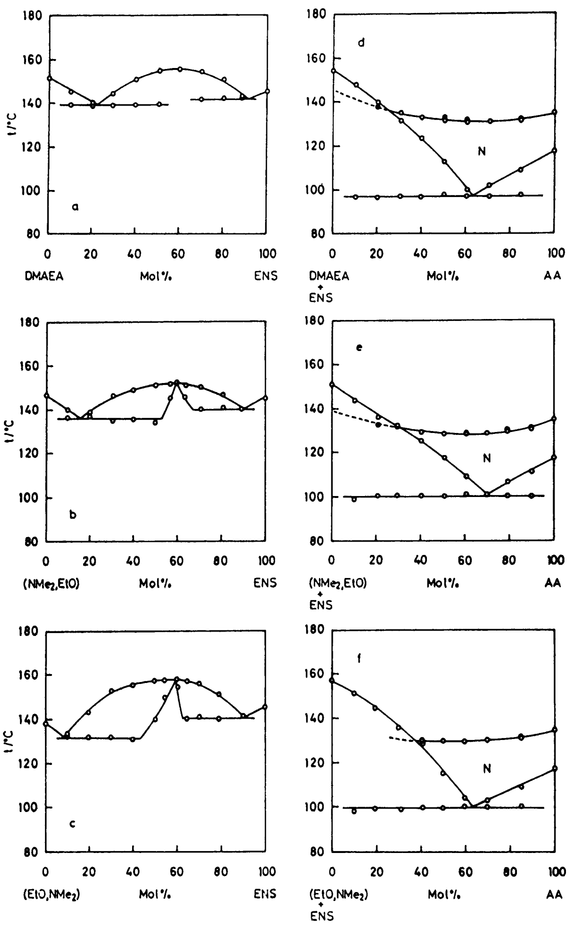


Fig. 4. Phase diagrams of (a) the 4-(dimethylamino)-4′-ethoxyazobenzene-4-ethoxy-4′-nitrostilbene, (b) *N*-[4-(dimethylamino)benzylidene]-4-ethoxyaniline-4-ethoxy-4′-nitrostilbene, and (c) *N*-(4-ethoxybenzylidene)-4-(dimethylamino)aniline-4-ethoxy-4′-nitrostilbene systems, (d) the system consisting of azoxydianisole and the equimolar mixture of 4-(dimethylamino)-4′-ethoxyazobenzene and 4-ethoxy-4′-nitrostilbene, (e) the system consisting of azoxydianisole and the equimolar mixture of *N*-[4-(dimethylamino)benzylidene]-4-ethoxyaniline and 4-ethoxy-4′-nitrostilbene, and (f) the system consisting of azoxydianisole and the equimolar mixture of *N*-(4-ethoxybenzylidene(-4-(dimethylamino)-aniline and 4-ethoxy-4′-nitrostilbene.

azobenzene is one of the components.

It seemed highly likely that the transition of the melt to a metastable nematic liquid crystal is overshadowed by the strong tendency to form a solid molecular complex; therefore, a study on the phase diagram of pseudo-binary system comprising AA and the mixture of the component compounds was undertaken. We employed equimolar mixtures instead of the solid molecular complexes because the nematic liquid crystal of the former composition is expected to be more stabilized than that of the latter composition. Such features are exemplified by the DMAEA-(EtO, NO_2) system presented in Fig. 3b. The diagrams of the pseudo-binary systems are displayed in Figs, 4d, e, and f. The latent induction of nematic liquid crystals is clearly proved in all three. The N-I transition temperature in the mixture of DMAEA and ENS is estimated by the extrapolation of the transition curve to 0 mol% of AA to be 145 °C. The deviation from the mean value of the latent transition temperatures of DMAEA and ENS is 29 °C. The induction of a nematic liquid crystal is even larger in the (Me_2N, EtO)-ENS and (EtO, Me_2N)-ENS systems: namely, 33 and 32 °C respectively.

The N-I transition temperature at 50 mol% and the extent of the induction are summarized in Table 2. For a given electron donor, the temperature varies with electron acceptor in the following order:

$$\text{ENS} > \text{ENA} > (NO_2, \text{EtO}) > (\text{EtO}, NO_2).$$

With a given acceptor, DMAEA gives a higher transition temperature than the Schiff bases do. These results conform to the order of the latent N-I transition temperatures of the component compounds; therefore, they conform also to the order of central double bond linkages reported by Knaak *et al.*[2] Of as great importance as the N-I transition temperatures, however, are the extents of the induction of nematic liquid crystals. In contrast to the transition temperature themselves, the extents of the induction are found more pronounced with the Schiff bases than with the azobenzenes: that is,

$$(Me_2N, \text{EtO}) \simeq (\text{EtO}, Me_2N) > \text{DMAEA}.$$

As to the electron acceptors, the order is consistently

$$\text{ENS} > (NO_2, \text{EtO}) > (\text{EtO}, NO_2) > \text{ENA}.$$

The coincidence between the latter series and the order of the induction of nematic liquid crystals in the systems with AA supports our proposition that AA acts as an electron donor in the examined mixtures. In summary, the order of the induction efficiency of central double bond linkages may be

$$\text{-CH=CH-} > \text{-CH=N-} > \text{-N=N-}.$$

It must be emphasized that the above order agrees

Table 2. NEMATIC LIQUID CRYSTAL-ISOTROPIC LIQUID TRANSITION TEMPERATURE AT 50 mol% AND THE DEVIATION FROM THE MEAN VALUE OF THE TRANSITION TEMPERATURES OF THE COMPONENT COMPOUNDS
(The latter values are in parentheses)

Acceptor	Donor			
	DMAEA	(Me_2N, EtO)	(EtO, Me_2N)	AA
ENA	131 (18)	126 (22)	127 (21)	129 (6.5)
ENS	145 (29)	139 (33)	140 (32)	141 (16)
(NO_2,EtO)	127 (26)	123 (32)[a]	124 (31)[a]	125.5 (15.5)
(EtO, NO_2)	124 (21)	121 (27)[a]	119 (23)[a]	121.5 (9)

a) Taken from Ref. 1.

with that of the tendency of formation of solid molecular complexes in the systems studied here. As we see in Fig. 4, a stable molecular complex is formed in all the systems containing ENS as one of the components. Comparison of Fig. 2 with Figs. 3a and b undoubtedly leads to the conclusion that the tendency to form a solid molecular complex is higher with the Schiff base than with the azobenzene. Indeed, examining the effect of terminal alkoxyl groups in Schiff base molecules, we have found that the extent of the induction of nematic liquid crystals in binary systems is qualitatively related to the tendency of formation of solid molecular complexes.[1]

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