November, 1980] Bull. Chem. Soc. Jpn., 53, 3079—3084 (1980)

Liquid Crystal Formation in Binary Systems. II. Induction of Nematic and Smectic Phases by Electron Donor-Acceptor Interaction between the *p*-Dimethylamino and *p*-Nitro Derivatives of *N*-Benzylideneaniline

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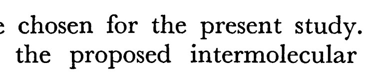
(Received February 28, 1980)

The formation of solid molecular complexes and the induction of nematic and smectic phases have been demonstrated with a number of binary mixtures of potentially-mesomorphic electron donors and acceptors of the type *N*-(*p*-X-benzylidene)-*p*-Y-aniline. One of the components contains a dimethylamino group as X or Y, and the other a nitro group as X or Y. The remaining substituents are methoxyl, ethoxyl, or propoxyl groups. The maximum temperature of the nematic phase induced in these electron donor-acceptor systems is higher by 23 to 45 °C than the straight line joining the latent transition temperatures of the two components. The tendency to form a solid complex and that to induce a nematic phase are both shown to a large extent by the propoxy derivatives, to a lesser extent by the methoxy derivatives, and least by the ethoxy derivatives. All the solid molecular complexes are reddish brown and exhibit an additional electronic absorption band located at about 500 nm. The mesophases are similarly colored. The enhanced thermal stability of the nematic and smectic phases in these binary mixtures is ascribed to the complex formation by an electron donor-acceptor interaction.

The liquid crystalline state is a state of matter intermediate between crystalline solids and isotropic liquids. Intermolecular attractions are supposed to be essential for producing the parallel molecular arrangement characteristic of such a state. If the interactions are not strong enough to produce the orientation, the compound may be monotropically mesomorphic. Upon heating such a compound, the crystalline solid melts to an isotropic liquid but the latter may undergo the transition to a liquid crystal if it is sufficiently supercooled. Even when the expected metastable liquid crystalline state is not achieved, the compound may be considered to be potentially mesomorphic. This paper deals mostly with the compounds of the last category. It seemed likely to us that the parallel molecular arrangement required by liquid crystal formation should become observable in the binary systems consisting of potentially mesomorphic compounds if the orientational cohesive forces were supplemented by an electron donor-acceptor interaction. This sort of intermolecular force may particularly suit the alignment of the planar component molecules. The enhancement of nematic-phase stability found by Park *et al.* with the binary system of *N*-(*p*-methoxybenzylidene)-*p*-butylaniline and 4-cyano-4′-pentylbiphenyl and several other, closely related systems is apparently in support of our postulate.[2,3] They have attributed the increased thermal stability to molecular complexing by a weak electron donor-acceptor interaction. A similar observation has been made by us with the azoxydianisole-*N*-(*p*-nitrobenzylidene)-*p*-anisidine mixtures.[1] It must be noted that both or one of the component compounds in these systems are enantiotropically mesomorphic, in contrast to those to be described in this paper.

Because of the simplicity of molecular structure and the ease of preparations, *N*-(*p*-X-benzylidene)-*p*-Y-ani-



lines were chosen for the present study. In order to maximize the proposed intermolecular attraction, a dimethylamino group was introduced to one of the components, which is regarded as the electron donor, and a nitro group to the other, which is regarded as the electron acceptor. The remaining terminal groups were selected from short alkoxyl groups: namely, methoxyl, ethoxyl, and propoxyl groups, to avoid making the component compounds themselves mesomorphic.

Experimental

Materials. The *N*-benzylideneanilines listed in Table 1 were prepared by a condensation reaction between a *p*-X derivative of benzaldehyde and a *p*-Y derivative of aniline, and were purified by repeated recrystallization from a suitable solvent and by sublimation in a vacuum if necessary. Hereafter, the compounds are represented by their terminal groups (X,Y). Binary mixtures in known proportions were melted in small test tubes, shaken well to insure homogeneity, and then rapidly cooled.

Measurements. The calorimetric curves were recorded on a Rigaku Thermoflex differential scanning calorimeter during the processes of heating and cooling. The heating rate in this work was 2.5 °C min^{-1}. The temperature was calibrated as described in a previous paper.[1] The induced mesophases were identified by examining the texture with the aid of a polarizing microscope and/or by studying the continuous miscibility with a reference mesophase. The diffuse reflectance of the solid component compounds and molecular complexes was measured by means of a Beckman DK 2A spectroreflectometer. The spectrum was then plotted using the Kubelka-Munk function.

Results and Discussion

Methoxy Derivatives. The phase diagrams of all the possible electron donor-acceptor combinations of the methoxy derivatives are presented in Fig. 1. The open and shaded circles indicate the transitions found during the processes of heating and cooling respectively. Therefore, the phase appearing below the transition, indicated solely by shaded circles, is metastable. The shaded circles are omitted when they coincide exactly with the open circles. The systems of (dimethylamino, methoxy) with (nitro, methoxy) and also of (methoxy,

TABLE 1. MELTING POINTS AND ISOTROPIC LIQUID-NEMATIC LIQUID CRYSTAL TRANSITION TEMPERATURES OF *N*-(*p*-X-BENZYLIDENE)-*p*-Y-ANILINES

Substituents X	Y	Mp/°C	Tp/°C[a]
$(CH_3)_2N$	CH_3O	141[b]	(55)
NO_2	CH_3O	133[c]	(80)
CH_3O	$(CH_3)_2N$	143.5	(60)
CH_3O	NO_2	124[d]	(82)
$(CH_3)_2N$	C_2H_5O	147[e]	(97.5)
NO_2	C_2H_5O	122[f]	(85)
C_2H_5O	$(CH_3)_2N$	138	(102)
C_2H_5O	NO_2	114[g]	(90)
$(CH_3)_2N$	C_3H_7O	122	(75)
NO_2	C_3H_7O	103[h]	(50)
C_3H_7O	$(CH_3)_2N$	115	(75)
C_3H_7O	NO_2	110[i]	57.5[j]

a) The values in parentheses were estimated by studies on the binary systems with azoxydianisole. b) 140.2 °C Dave and Lohar (Refs. 4 and 8). c) 135.7 °C by Dave and Dewar (Ref. 5); 134.4—136 °C by Schroeder and Schroeder (Ref. 6); 135 °C by Malthete *et al.* (Ref. 7). d) 124.5—125 °C by Schroeder and Schroeder (Ref. 6); 124 °C by Malthete *et al.* (Ref. 7). e) 147.4 °C by Dave and Lohar (Ref. 4). f) 123.5 °C by Dave and Lohar (Refs. 4 and 8). g) 121 °C by Malthete *et al.* (Ref. 7). h) 105 °C by Malthete *et al.* (Ref. 7). i) 97 °C by Malthete *et al.* (Ref. 7). j) 62 °C by Malthete *et al.* (Ref. 7).

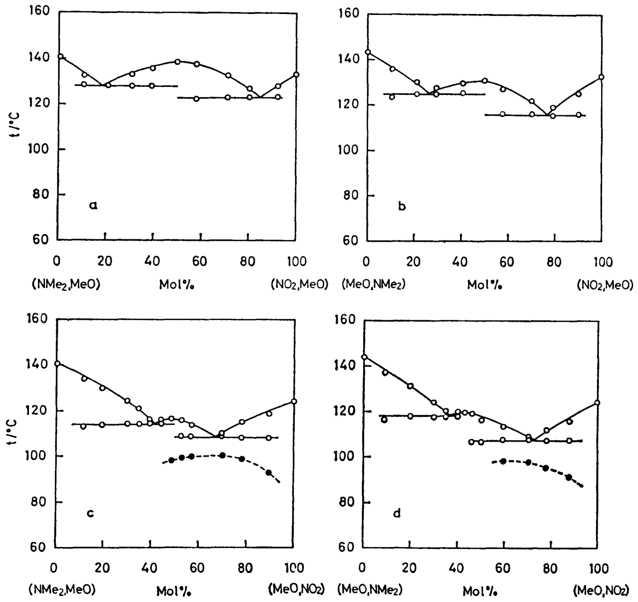


Fig. 1. Phase diagrams of (a) the *N*-[*p*-(dimethylamino) benzylidene]-*p*-anisidine–*N*-(*p*-nitrobenzylidene)-*p*-anisidine, (b) *N*-(*p*-methoxybenzylidene)-*p*-(dimethylamino)aniline–*N*-(*p*-nitrobenzylidene)-*p*-anisidine, (c) *N*-[*p*-(dimethylamino)benzylidene]-*p*-anisidine–*N*-(*p*-methoxybenzylidene)-*p*-nitroaniline,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

dimethylamino) with (nitro, methoxy) yield only solid 1:1 molecular complexes (see Figs. 1a and 1b). The eutectic points in the former system are located at 128 °C and 18.5 mol% and at 123 °C and 84.5 mol% of the acceptor component. The melting point of the complex is 138.5 °C; this is a few degrees higher than the mean value of those of the components. In the latter system, the eutectic points are found at 125 °C and 26 mol% and at 115.5 °C and 77 mol%. The complex melts congruently at 131 °C. This temperature is several degrees below the straight line joining the melting points of the components. Disregarding small variations in the melting point of the component compounds, one may say that the higher the melting point and the wider the region of the existence of the solid complex (the composition difference between the two eutectics), the more stable is the complex.[9] Therefore, the solid complexes formed in the (dimethylamino, methoxy)–(methoxy, nitro) and (methoxy, dimethylamino)–(methoxy, nitro) systems shown in Figs. 1c and 1d are of considerably lower stability. Note that the composition of the complex in the last system is not 1:1 but 3:2. When the melts of these two systems are supercooled, the isotropic liquid-nematic liquid crystal (I-N) transition curves are partially observable. Since the latent I-N transition temperatures of (dimethylamino, methoxy) and (methoxy, nitro) were estimated as 55 °C and 82 °C respectively by the method to be mentioned in the last paragraph of this paper, the maximum deviation from linearity in the transition temperature is as much as 30 °C at 50 mol%. The corresponding value in the (methoxy, dimethylamino)–(methoxy, nitro) system is not available, but the deviation at 60 mol% is 25 °C. The flat maximum is indicative of a high degree of dissociation of molecular complex in the isotropic liquid phase. The I-N transition curve is observable only in the high mol% range of the acceptor compound. The large temperature difference between the freezing point curve and the metastable I-N transition curve may account for the solidification of supercooled melts without reaching the latter in the left half of the diagram.

Ethoxy Derivatives. As is shown in Fig. 2, all the combinations of the ethoxy derivatives can produce nematic phases. The I-N transition is monotropic in the system of (dimethylamino, ethoxy) with (nitro, ethoxy) but enantiotropic in the other three. The nematic liquid crystals are stable in the hatched areas in Figs. 2b, 2c, and 2d. The I-N transition curves are very much alike. The maximum is located near a 1:1 mole ratio, and is a little above 120 °C in the two systems with (nitro, ethoxy), but a little below 120 °C in the two systems with (ethoxy, nitro). One factor that should not be ignored is the fact that the latent I-N transition in the donor compound occurs at an appreciably higher temperature than that of the corresponding methoxy compounds. The thermal stability enhancement by mixing of the donor and acceptor compounds is therefore not large; it ranges from 23 to 32 °C.

It must be added that the system (dimethylamino,

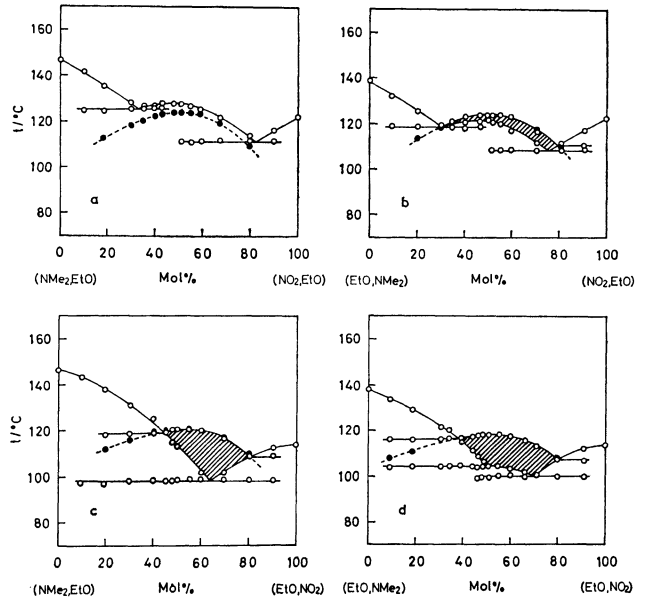


Fig. 2. Phase diagrams of (a) the *N*-[*p*-(dimethylamino)benzylidene]-*p*-phenetidine–*N*-(*p*-nitrobenzylidene)-*p*-phenetidine, (b) *N*-(*p*-ethoxybenzylidene)-*p*-(dimethylamino)aniline – *N*-(*p*-nitrobenzylidene)-*p*-phenetidine, (c) *N*-[*p*-(dimethylamino)benzylidene]-*p*-phenetidine–*N*-(*p*-ethoxybenzylidene)-*p*-nitroaniline, and (d) *N*-(*p*-ethoxybenzylidene)-*p*-(dimethylamino)-aniline–*N*-(*p*-ethoxybenzylidene)-*p*-nitroaniline systems. In the hatched area, the nematic phase is stable. As to the open and shaded circles, see the caption of Fig. 1.

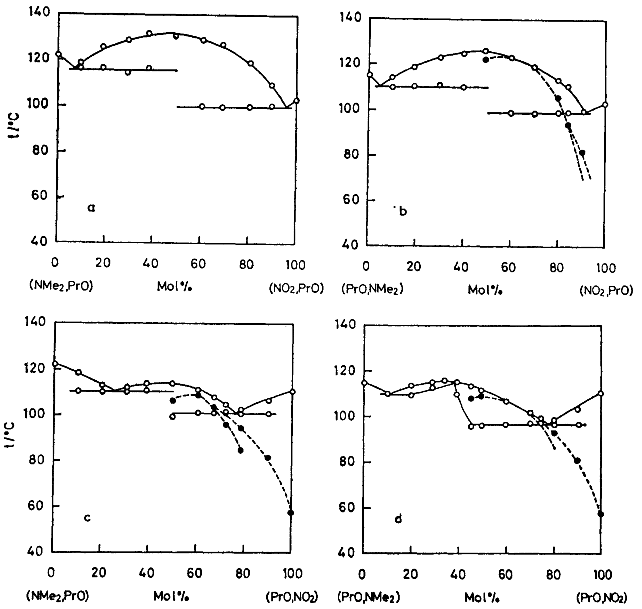


Fig. 3. Phase diagrams of (a) the *N*-[*p*-(dimethylamino)benzylidene]-*p*-propoxyaniline – *N*-(*p*-nitrobenzylidene)-*p*-propoxyaniline, (b) *N*-(*p*-propoxybenzylidene)-*p*-(dimethylamino)aniline – *N*-(*p*-nitrobenzylidene)-*p*-propoxyaniline, (c) *N*-[*p*-(dimethylamino)-benzylidene]-*p*-propoxyaniline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

ethoxy)–(nitro, ethoxy) shown in Fig. 2a has been studied by Lohar.[8] The agreement in the melting points of the component compounds is good and that in the freezing point curve above 60 mol% of the acceptor compound is fair. He has located a eutectic at 114.5 °C and 83 mol%. These values compare well with ours: namely, 111.5 °C and 82.5 mol%. However, Lohar's freezing point curve below 60 mol% is at significantly higher temperatures. The eutectic we found at 125.5 °C and 33 mol% is missing in his result. In addition, the metastable nematic phase has not been detected at all.

The tendency to form a solid complex is markedly diminished compared with that of the methoxy derivatives. While the region of the existence of the solid complex in the system of (dimethylamino, ethoxy) with (nitro, ethoxy) is 49.5 mol%, that in the system of the corresponding methoxy compounds extends over 66 mol% (compare Figs. 1a and 2a). The fact that the melting point of the complex, 127 °C, is several degrees below the mean value of those of the components reflects also a decreased stability of the solid complex. This tendency is shown most when (dimethylamino, ethoxy) is mixed with (ethoxy, nitro), as is illustrated in Fig. 2c. The resulting phase diagram is of the eutectic type, no solid complex being formed. The complex in the (ethoxy, dimethylamino)–(ethoxy, nitro) system shown in Fig. 2d is also not of high stability. It melts incongruently at 104 °C. Here again, the composition does not appear to be a 1:1 mole ratio.

Propoxy Derivatives. Among the examined alkoxyl groups, the propoxyl group is the substituent which best stabilizes a solid complex. The diagrams illustrated in Fig. 3 indicate the formation of a congruently melting molecular complex in all the systems. The one formed in the (dimethylamino, propoxy)–(nitro, propoxy) system is the most stable, melting at 132 °C (see Fig. 3a). While this value is lower than the melting point of the complex formed in the (dimethylamino, methoxy)–(nitro, methoxy) system shown in Fig. 1a, it is higher by 17 °C than the mean value of those of the components. The eutectic points are at 115.5 °C and 7 mol% and at 100 °C and 96 mol%. As the result, the freezing point curve of the complex occupies a large part of the diagram. No liquid crystalline phase is observed in this system, while the other three systems yield not only nematic but also smectic phases. The difference between the latent I-N transition temperature and the melting point in the acceptor compound is larger than that in the donor compound; nevertheless, the mesophases were found solely on the nitro derivative-rich side. (Propoxy, nitro) is the only compound in this work whose liquid phase could be cooled to the I-N transition temperature without solidification occurring. The melt, which is relatively rich in the donor component, is directly transformed into the smectic phase. In other words, only the isotropic liquid-smectic liquid crystal (I-S) transition curve is observable in such a composition range. The maximum temperatures of nematic and smectic phases in the system containing (propoxy, nitro) as the acceptor component do not differ much from each other (see Figs. 3c and 3d). These nematic phases are stabilized as much as 40 °C near the maximum with respect to the ideal linear relationship. The latent nematic liquid crystal-smectic liquid crystal (N-S) transition temperatures of the component compounds are not known, but they are certainly located below the I-N transition temperatures. The extrapolation of the N-S transition curve in Fig. 3c to 100 mol% of (propoxy, nitro) suggests that the latent transition temperature of this acceptor compound is not higher than 20 °C.

The thermal stability enhancement of a smectic phase has been reported by several workers in binary mixtures in which both or one of the components give stable nematic liquid crystals.[6,10-12] For example, a paper by Schroeder and Schroeder has referred to the appearance of a smectic phase by mixing of mesomorphic 4,4′-bis(hexyloxy)azoxybenzene and non-mesomorphic (methoxy, nitro).[6] Engelen *et al.* have proposed that such phases be called induced smectic phases.[11] They have concluded that mixtures of terminal polar with terminal nonpolar nematic liquid crystals usually induce smectic phases. While nitro and cyano derivatives are considered to be polar, the derivatives carrying only alkyl and alkoxyl groups are nonpolar. Contrary to these authors' conclusion, Domon and Billard have shown recently that the existence of a strong terminal dipole for only one of the components is not always correlated with the induction of smectic phases.[12] Among the twenty-eight systems listed by them, over ten have been shown to yield an induced smectic phase without a terminal polar compound. Our systems are entirely different from theirs; that is, all our component molecules bear a dimethylamino or nitro group and are strongly polar. Secondly, the nematic phases of the components are metastable with respect to the crystalline phases at any temperature.

General Remarks. As the whole, the tendency of a solid complex formation decreases in the following order:

(dimethylamino, alkoxy)–(nitro, alkoxy) > (alkoxy, dimethylamino)–(nitro, alkoxy) > (alkoxy, dimethylamino)–(alkoxy, nitro) > (dimethylamino, alkoxy)–(alkoxy, nitro).

Among the compounds examined, this tendency is shown to a large extent by the propoxy derivatives, to a lesser extent by the methoxy derivatives, and least by the ethoxy derivatives.

The latent I-N transition temperatures of the ethoxy derivatives are higher than those of the methoxy and propoxy derivatives, thus making the observation of the induced mesophases easiest. The effects of dimethylamino and nitro groups on the transition temperature are also appreciable. Consequently, the order is ethoxy > propoxy > methoxy for the donor compounds, while ethoxy > methoxy > propoxy for the acceptor compounds.

The observations made with the ethoxy derivatives suggest that the thermal stability enhancement of nematic phases is larger in the first two combinations of the donor and acceptor compounds: namely, (dimethylamino, alkoxy)–(nitro, alkoxy) and (alkoxy, dimethylamino)–(nitro, alkoxy). Concerning the effects of alkoxyl groups, the comparison is possible with the other two combinations, as listed in Table 2. The order of the alkoxy derivatives in the thermal stability enhancement of nematic phases agrees exactly with that of the tendency of a solid complex formation: that is,

propoxy > methoxy > ethoxy.

TABLE 2. THERMAL STABILITY ENHANCEMENT OF NEMATIC PHASES: THE DEVIATION AT 50 mol% FROM A LINEAR RELATIONSHIP BETWEEN THE TRANSITION TEMPERATURES OF THE COMPONENT COMPOUNDS

(The values in parentheses were estimated by the extrapolation of the I-N transition curves.)

Combination	Methoxy deriv.	Ethoxy deriv.	Propoxy deriv.
(Dimethylamino, alkoxy) + (nitro, alkoxy)	(33 °C)	32 °C	(45 °C)
(Alkoxy, dimethylamino) + (nitro, alkoxy)	(32 °C)	31 °C	(40—45 °C)
(Dimethylamino, alkoxy) + (alkoxy, nitro)	30 °C	27 °C	(40 °C)
(Alkoxy, dimethylamino) + (alkoxy, nitro)	(27 °C)	23 °C	(40 °C)

Qualitatively speaking, therefore, the effects of substituents on the formation of a solid complex and the induction of mesophases are dependent on each other. The special feature of smectic phase is its stratification. This structure makes the phase to be much closer to the crystalline state than is the nematic phase. The appearance of smectic phase in the mixtures of the propoxy derivatives seems to be correlated with the fact that the tendencies to form a solid complex and to induce a mesophase are both high.

The solid molecular complexes are reddish brown, while the component compounds are yellow. A study of the diffuse reflection spectra has revealed the appearance of an additional electronic absorption band due to complexing. As is exemplified by the combination of (dimethylamino, ethoxy) and (nitro, ethoxy) in Fig. 4, the maximum is located around 20×10^3 cm^{-1} (500 nm). This band is assigned to the charge-transfer transition associated with the electron donor-acceptor pairs. The persistence of color in mesophases is considered as the evidence that the molecular complexing in them is also of the electron donor-acceptor type. Naturally, the loss of color is seen when the separation of donor and acceptor molecules into two phases occurs by the solidification.

Estimation of Latent Transition Temperatures. The failure to observe mesophases in the systems (dimethylamino, methoxy)–(nitro, methoxy), (methoxy, dimethylamino)–(nitro, methoxy), and (dimethylamino, propoxy)–(nitro, propoxy), shown in Figs. 1a, 1b, and 3a respectively, must be attributed to the strong tendency to form a crystalline solid, which overshadows the transformation of the melt to a metastable mesophase. The existence of such a induced mesophase has been confirmed by a study of the phase diagram of

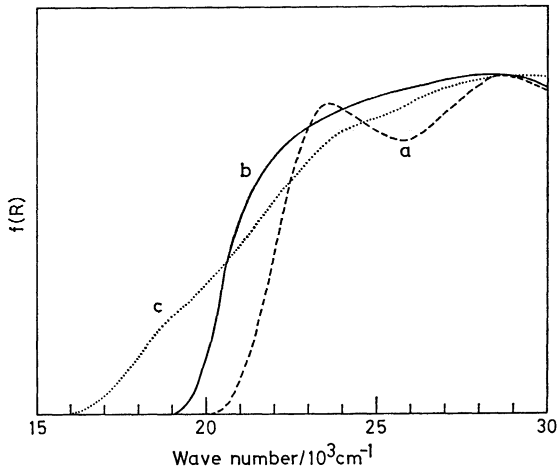


Fig. 4. Diffuse reflection spectra of (a) *N*-[*p*-(dimethylamino)benzylidene]-*p*-phenetidine, (b) *N*-(*p*-nitrobenzylidene)-*p*-phenetidine, and (c) their 1:1 complex.

the pseudo-binary system consisting of the 1:1 complex and a mesomorphic compound. We employed for this purpose azoxydianisole (AA), which exhibits a nematic phase stable between 117.5 and 135 °C, and *N*-(*p*-phenylbenzylidene)-*p*-ethoxycarbonylaniline (phenyl, ethoxycarbonyl), which exhibits a smectic phase stable between 121.6 and 131.0 °C.[13] The diagrams displayed in Fig. 5 are of the eutectic type and clearly prove the latent induction of mesophases in all the three systems. The I-N transition temperature in the (dimethylamino, methoxy)–(nitro, methoxy) complex is estimated by the extrapolation of the transition curve to 0 mol% of AA to be 101 °C (see Fig. 5a). This temperature is higher by 33 °C than the straight line joining the latent transition temperatures of the two components of the complex. As the matter of fact, the molten complex solidifies at 112.5 °C, thus making the I-N transition not detectable. In the case of the (methoxy, dimethylamino)–(nitro, methoxy) complex shown in Fig. 5b, the I-N transition temperature obtained by the extrapolation is 102 °C, which is 32 °C above the mean value of those of the two components. It must be emphasized that the thermal stability enhancement in these two complexes is larger than that in the other two systems of the methoxy derivatives, in agreement with the order of tendency of a solid-complex formation.

The (dimethylamino, propoxy)–(nitro, propoxy) complex is expected to have latent I-N and I-S transition temperatures. The former temperature is located at about 107 °C by the diagram with AA and the latter at 119 °C by the diagram with (phenyl, ethoxycarbonyl), as are shown in Figs. 5c and 5d. The stability enhancement of the nematic phase is about 45 °C, the largest among all the examined combinations. The diagram shows that the induced mesophase is of the type smectic A. When the smectic A phase of (phenyl, ethoxycarbonyl) is supercooled, another smectic phase appears at 106 °C (see Fig. 5d). The eutectic point of this pseudo-binary system is considerably lower than this transition curve; therefore, the new smectic phase becomes enantiotropic in the range of 50 to 70 mol% of (phenyl, ethoxycarbonyl).

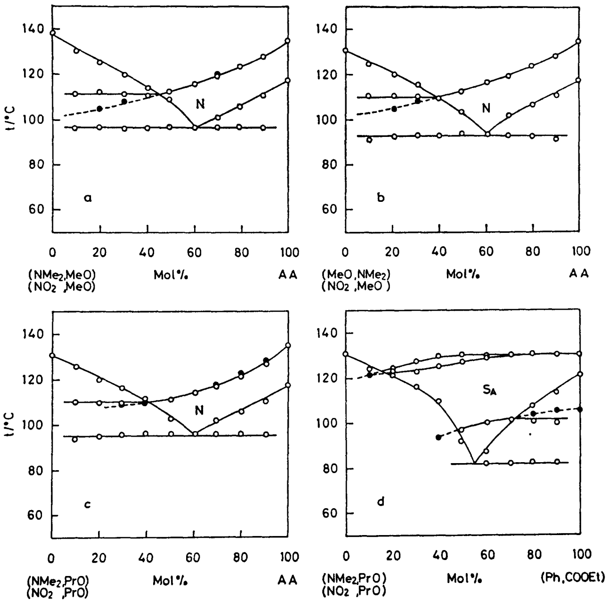


Fig. 5. Phase diagrams of (a) the system consisting of the *N*-[*p*-(dimethylamino)benzylidene]-*p*-anisidine–*N*-(*p*-nitrobenzylidene)-*p*-anisidine (1:1) complex and azoxydianisole, (b) the system consisting of the *N*-(*p*-methoxybenzylidene)-*p*-(dimethylamino)aniline–*N*-(*p*-nitrobenzylidene)-*p*-anisidine (1:1) complex and azoxydianisole, (c) the system consisting of the *N*-[*p*-(dimethylamino)benzylidene]-*p*-propoxyaniline–*N*-(*p*-nitrobenzylidene)-*p*-propoxyaniline (1:1) complex and azoxydianisole, and (d) the system consisting of the *N*-[*p*-(dimethylamino)benzylidene]-*p*-propoxyaniline–*N*-(*p*-nitrobenzylidene)-*p*-propoxyaniline (1:1) complex and *N*-(*p*-phenylbenzylidene)-*p*-ethoxycarbonylaniline. As to the open and shaded circles, see the caption of Fig. 1.

With the exception of (propoxy, nitro), the I-N transition of the component compounds could not be observed by supercooling of the melt. Consequently, the transition temperatures listed in Table 1 have been deduced by the extrapolation of the transition curves observed in the binary systems with mesomorphic AA. Such systems have been extensively studied by Dave and Lohar and the diagrams with the following five compounds can be reproduced from their data:[4,5] (dimethylamino, methoxy), (nitro, methoxy), (methoxy, dimethylamino), (dimethylamino, ethoxy), and (nitro, ethoxy). Especially for the last two, the transition temperatures have been estimated by Lohar to be 97.5 °C and 85 °C respectively.[8] We have worked on all the other systems. The diagrams are of the eutectic type. When the Schiff base is a dimethylamino derivative, the I-N transition curve deviates negatively from the ideal linear relationship. In other words, the curve is slightly concave upwards. On the other hand, the transition curve is markedly convex upwards with the nitro derivative, indicating the attractive interaction between the Schiff base and AA molecules. The I-N and solid-liquid transition temperatures read from the phase diagrams are summarized in Table 3

TABLE 3. ISOTROPIC LIQUID-NEMATIC LIQUID CRYSTAL TRANSITION TEMPERATURES IN THE BINARY SYSTEMS WITH AZOXYDIANISOLE
(Monotropic transitions are given in parentheses.)

Substituents		Mol% of azoxydianisole								
X	Y	10	20	30	40	50	60	70	80	90
CH_3O	NO_2	(93.0)	(100.5)	(107.0)	112.0	116.0	119.8	123.6	127.4	131.2
C_2H_5O	$(CH_3)_2N$			(105.5)	(108.0)	110.5	114.0	118.7	124.0	129.2
C_2H_5O	NO_2		(107.5)	112.8	117.0	121.5	124.7	127.3	129.5	132.3
$(CH_3)_2N$	C_3H_7O			(86.5)	(91.5)	97.5	104.5	112.3	120.2	128.0
NO_2	C_3H_7O	(76.5)	(93.5)	102.5	111.0	117.7	122.5	126.3	129.7	132.5
C_3H_7O	$(CH_3)_2N$			(85.0)	(90.2)	96.3	103.5	110.7	118.0	126.5

TABLE 4. SOLID-LIQUID TRANSITION TEMPERATURES IN THE BINARY SYSTEMS WITH AZOXYDIANISOLE

Substituents		Mol% of azoxydianisole									Eutectic	
X	Y	10	20	30	40	50	60	70	80	90	Mol%	Temp/°C
CH_3O	NO_2	118.5	113.8	108.5	103.0	91.5	97.5	103.0	106.7	112.3	51.0	90.0
C_2H_5O	$(CH_3)_2N$	135.0	130.2	124.7	118.5	110.5	102.0	102.0	107.8	113.0	64.0	98.0
C_2H_5O	NO_2	112.0	109.5	106.0	99.5	88.5	95.3	101.5	107.0	112.0	51.0	87.0
$(CH_3)_2N$	C_3H_7O	118.7	115.0	110.5	104.0	95.5	101.5	106.5	111.0	114.5	50.0	95.5
NO_2	C_3H_7O	101.0	96.5	92.5	86.0	89.5	96.5	102.0	107.5	112.5	43.5	82.5
C_3H_7O	$(CH_3)_2N$	110.5	105.7	100.5	93.5	94.0	98.5	102.7	107.5	112.5	43.0	89.5

and 4 respectively. The latent I-N transition temperatures of the Schiff bases presented in Table 1 were obtained by the extrapolation of the transition curves to 0 mol% of AA. They are in good agreement with those located from the phase diagrams of the binary mixtures of the Schiff bases given in Figs. 1, 2, and 3.

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