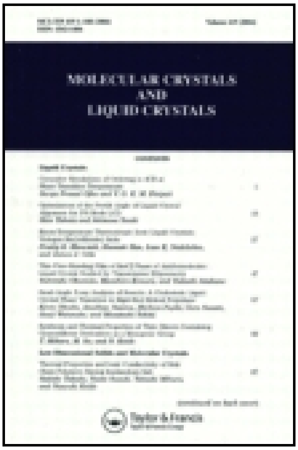

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Mesophases Induced in the Binary Systems Consisting of the 4-Dimethylamino-4-Alkoxy and 4-Nitro-4-Alkoxy Derivatives of N-Benzylideneaniline

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Mesophases Induced in the Binary Systems Consisting of the 4-Dimethylamino-4-Alkoxy and 4-Nitro-4-Alkoxy Derivatives of N-Benzylideneaniline

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The effect of terminal alkoxyl group on the induction of mesophases has been examined by preparing phase diagrams for binary systems of potentially mesogenic 4-dimethylamino and 4-nitro derivatives of N-benzylideneaniline. All the systems composed of the methoxy and ethoxy derivatives produce a nematic phase, while both a nematic and a smectic phases are found when at least one of the component compounds carries a propoxyl group. The only exception is N-[(4-dimethylamino)benzylidene]-4-ethoxyaniline-N-(4-nitrobenzylidene)-4-propoxyaniline system which exhibits a smectic phase alone. The maximum temperature of the nematic-isotropic transition point curve is not very sensitive to the exchange in the positions of the terminal groups, especially those in the donor molecules. On the other hand, the thermal stabilities of the induced smectic phase and solid complex are markedly affected by the positions of the terminal groups.

INTRODUCTION

Mixing of potentially-mesogenic electron donors and acceptors of the type N-(4-X-benzylidene)-4-Y-aniline often leads to the appearance of nematice and/or smectic behavior.[1,2] The terminal group X or Y in the donor molecules was a dimethylamino group, while that in the acceptor molecules was a nitro group. The other terminal groups for both the component molecules were chosen from short alkoxyl groups; namely, methoxyl, ethoxyl, and propoxyl groups. We reported earlier the phase diagrams only for the combinations of the component compounds carrying the same alkoxyl groups. The induction of nematic phases could be achieved with the methoxy and ethoxy derivatives. On the other hand, metastable smectic phases were observed with the propoxy derivatives. In addition, a nematic phase was produced in a narrow composition range on the acceptor-rich side. As a preliminary study on equimolar mixtures of all the possible combinations between the donor and acceptor compounds revealed that both nematic and smectic phases are frequently induced when the component molecules carry different alkoxyl groups,[2] we decided to examine the phase diagrams of the remaining twenty-four binary systems in order to gain more insight into the effects of such structural parameters.

EXPERIMENTAL

The N-benzylideneanilines were prepared by a condensation reaction between a 4-X derivative of benzaldehyde and a 4-Y derivative of aniline as described in our previous paper.[1] In this text, they are represented by the terminal groups in parentheses, (X, Y). The composition of binary mixtures is given by mol% of the acceptor compound. The calorimetric curves were recorded on a Rigaku Denki differential scanning calorimeter during the processes of heating and cooling at the rate of 3 °C min^{-1}. The induced mesophases were identified by examining the texture with the aid of a polarizing microscope. The observed smectic phase is of the A type.

RESULTS AND DISCUSSION

a) Combinations of the methoxy and ethoxy derivatives

The phase diagrams for four systems comprising (Me_2N, MeO) or (MeO, Me_2N) and (NO_2, EtO) or (EtO, NO_2) are given in Figure 1. When the acceptor compound is (NO_2, EtO), a solid complex of a 1:1 mole ratio is formed. The (Me_2N, MeO) complex melts at slightly lower temperature and its freezing point curve covers a narrower composition range compared to the (MeO, Me_2N) complex. The observation of metastable nematic-isotropic (N-I) transition point curves in these two mixtures is limited to the range from 50 to 80 mol%, the maxima being located at 110 and 112°C respectively. No solid complex is found in the (Me_2N, MeO)-(EtO, NO_2) system and

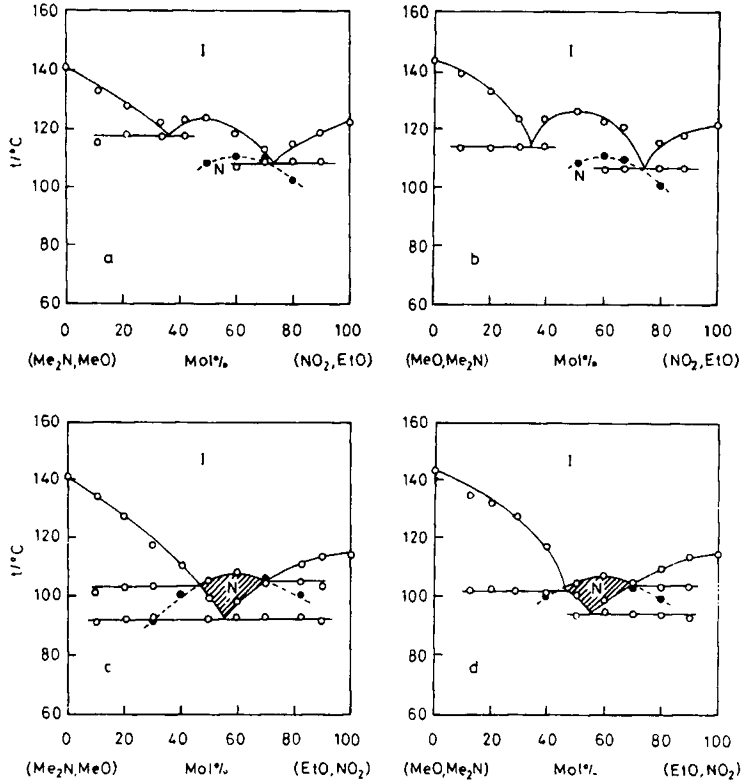

FIGURE 1 Phase diagrams of (a) (Me_2N, MeO)-(NO_2,EtO), (b) (MeO, Me_2N)-(NO_2, EtO), (c) (Me_2N, MeO)-(EtO, NO_2), and (d) (MeO, Me_2N)-(EtO, NO_2) systems. The open and shaded circles are transitions recorded in the processes of heating and cooling respectively.

a stable N phase is induced. The maximum clearing point is at 108°C and about 60 mol%. The replacement of the donor compound by (MeO, Me_2N) results in the formation of an incongruently-melting solid complex. In this system too, the stable existence of an N phase is noted. The maximum clearing point lies also at 108°C and about 60 mol%.

When the ethoxy derivatives are employed as donors, (EtO, Me_2N)-(NO_2, MeO) is the only combination which yields a solid complex (see Figure 2). This solid complex is thermally less stable than that shown in Figure 1b and melts at 121°C. The N phases produced by (NO_2, MeO) are monotropic and are formed in the range from 30 to 70 mol% with (Me_2N, EtO) and in the range from 10 to 70 mol% with (EtO, Me_2N) respectively. In the former system, the upper limit

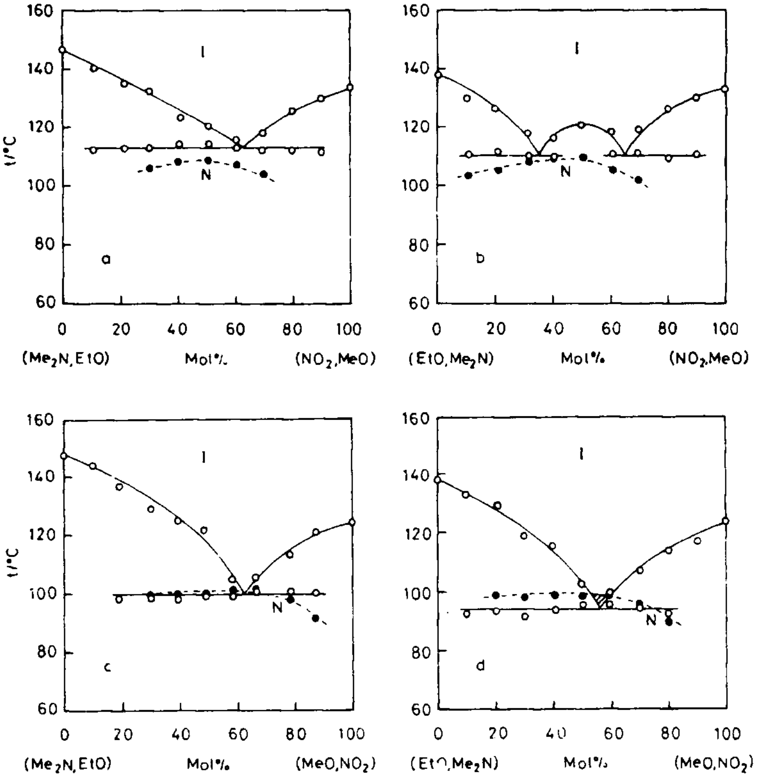

FIGURE 2 Phase diagrams of (a) (Me_2N, EtO)-(NO_2, MeO), (b) (EtO, Me_2N)-(NO_2, MeO), (c) (Me_2N, EtO)-(MeO, NO_2), and (d) (EtO, Me_2N)-(MeO, NO_2) systems. As to the open and shaded circles, see the caption of Figure 1.

of the existence is 109°C which is located 4°C below the eutectic. The maximum N-I transition point and two eutectics in the latter system are essentially at the same temperature, 110°C. The induced mesophases can be enantiotropic in small areas in the phase diagrams where (MeO, NO_2) is used as an acceptor. The N-I transition in the (Me_2N, EtO)-(MeO, NO_2) system is detectable in the range from 30 to 90 mol%. The curve is flat on the donor-rich side and reaches its maximum, 102°C, around 60 mol%. This part is within a few mol% from the eutectic composition and the transition temperature exceeds the eutectic by 2°C. The N phase in the (EtO, Me_2N)-(MeO, NO_2) system appears in the range from 20 to 80 mol% and can be stable in a larger area, the maximum clearing point being located 5°C above the eutectic.

b) Combinations of the methoxy and propoxy derivatives

All the eight systems in this classification produce an N phase as well as a smectic (S) phase. The diagrams obtained with the donors carrying a methoxyl group and the acceptors carrying a propoxyl group are presented in Figure 3. The acceptor (NO_2, PrO) forms a solid 1:1 complex. Its thermal stability depends appreciably upon the donor compound. The (Me_2N, MeO) complex melts at 110°C and the (MeO, Me_2N) complex at 122°C. Nevertheless, the maximum temperatures of the clearing point curves are almost the same; that is, 102°C in the former system and 104°C in the latter. The difference in the S-N transition point curve is relatively large, the maxima being at 93°C and 99°C respectively, Thus, the thermal stability is more affected by the structural change if the molecular order characteristic of a

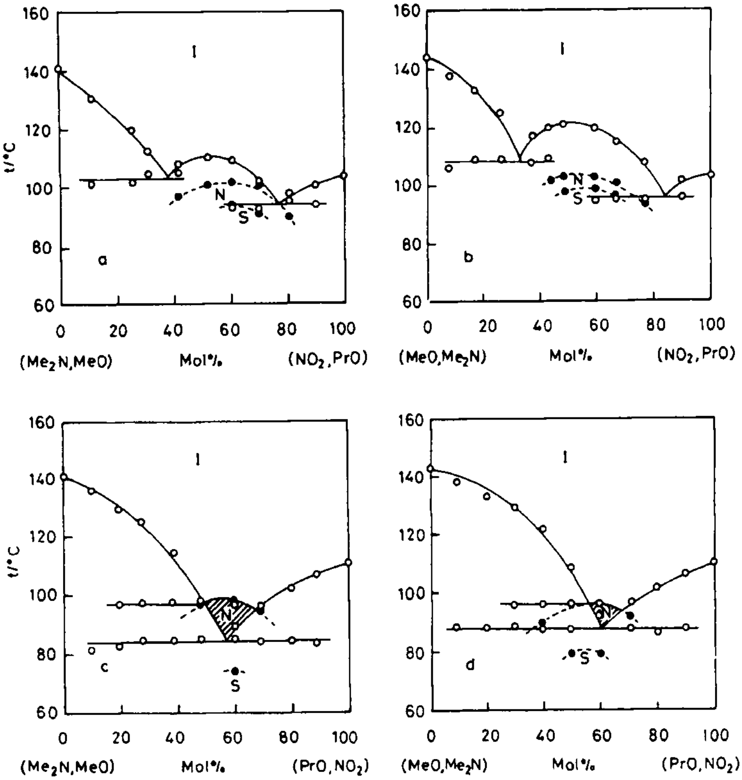

FIGURE 3 Phase diagrams of (a) (Me_2N, MeO)-(NO_2, PrO), (b) (MeO, Me_2N)-(NO_2, PrO), (c) (Me_2N, MeO)-(PrO, NO_2), and (d) (MeO, Me_2N)-(PrO, NO_2) systems. As to the open and shaded circles, see the caption of Figure 1.

phase is higher. When (PrO, NO_2) is employed as an acceptor, no solid complex is formed and the induced N phase is enantiotropic in an area above the eutectic (see Figures 3c and 3d). The clearing point curve passes through its maximum at 99°C if it is mixed with (Me_2N, MeO) and at 96°C with (MeO, Me_2N). The highest S-N transition temperature is located at 74°C in the former mixture and 80°C in the latter. Consequently, the separation between the N-I and S-N transition point curves increases in this sequence:

(MeO, Me_2N)-(NO_2, PrO) < (Me_2N, MeO)-(NO_2, PrO)

< (MeO, Me_2N)-(PrO, NO_2) < (Me_2, MeO)-(PrO, NO_2)

As one will see in the rest of this paper, the sequence is essentially determined by the positions of dimethylamino and nitro groups.

In Figure 4, the propoxy derivatives are donors and the methoxy derivatives are acceptors. A solid 1:1 complex is formed only when (NO_2, MeO) is the component compound. The interchange of the alkoxyl groups between the component molecules gives rise to an inversion of the relative thermal stability of the solid complexes (compare Figures 3a and 3b with Figures 4a and 4b). The melting point of the (Me_2N, PrO) complex is 114°C and that of the (PrO, Me_2N) complex is 108°C even though the freezing point curve of the latter covers a wider composition range. Contrary to the solid complex, the N phase is less stabilized in mixtures of (Me_2N, PrO)and (NO_2, MeO) than those of (PrO, Me_2N) and (NO_2, MeO). The maximum temperatures are 104 and 108°C respectively. Moreover, the mesophase can be stable above the eutectic point located on the acceptor-rich side of the latter system. With the acceptor (MeO, NO_2), the phase diagrams are of the eutectic type (see Figures 4c and 4d). The maxima of the S-N and N-I transition point curves and the eutectic point are nearly at the same composition in the (Me_2N, PrO)-(MeO, NO_2) system, the temperatures being 79, 100, and 92°C respectively, whereas the eutectic is widely separated from the maximum S-N transition point but the temperatures are not distinguishable from each other in the (PrO, Me_2N)-(MeO, NO_2) system. The N-I transition point curve reaches its maximum at about 99°C around 60 mol%. This point is further shifted to the acceptor-rich side compared with the maximum of the S-N transition point curve.

c) Combinations of the ethoxy and propoxy derivatives

These combinations exhibit a strong tendency to form solid complexes. When the donors are the ethoxy derivatives and the acceptors

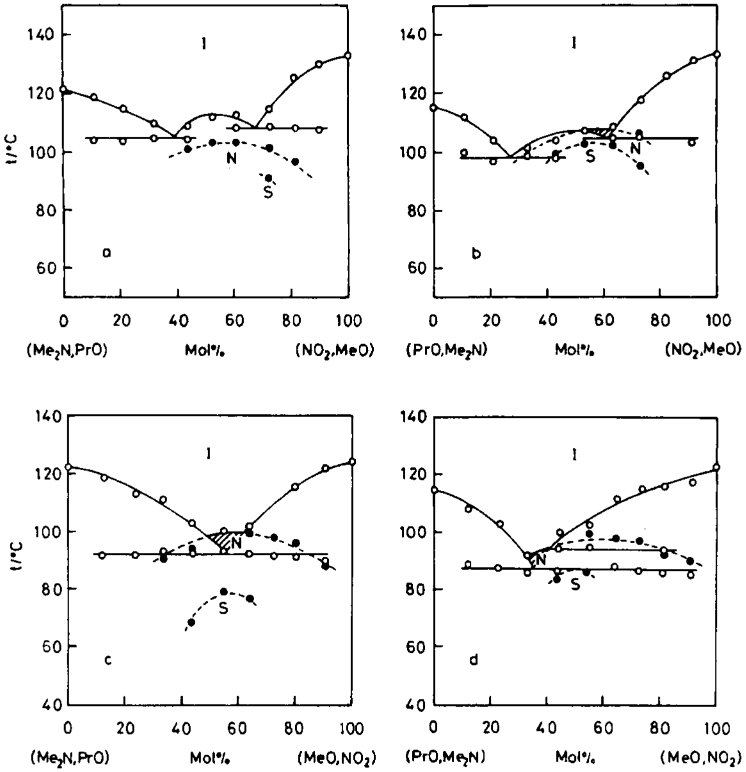

FIGURE 4 Phase diagrams of (a) (Me_2N, PrO)-(NO_2, MeO), (b) (PrO, Me_2N)-(NO_2, MeO), (c) (Me_2N, PrO)-(MeO, NO_2),and (d) (PrO, Me_2N)-(MeO, NO_2) systems. As to the open and shaded circles, see the caption of Figure 1.

are the propoxy derivatives, the complexes of (NO_2, PrO) melt congruently and those of (PrO, NO_2) melt incongruently (see Figure 5). The solid 1:1 complex found in the (Me_2N, EtO)-(NO_2, PrO) system has the melting point of 131°C. Only an S phase is induced in the range from 50 to 70 mol% and the maximum temperature is 119°C. When (Me_2N, EtO) is replaced by (EtO, Me_2N), the melting point of the 1:1 complex is lowered to 124°C. The eutectic points are also depressed but the composition range covered by the freezing point curve remains almost the same. The induction of a metastable N phase can be observed in two ranges, a branch of the N-I transition point curve starts from 109°C and 20 mol% and ends near 118°C and 50 mol% and the other one from about 116°C and 60 mol% to 88°C and 80 mol%. Between 50 and 60 mol%, the isotropic melt is directly transformed into an S phase.

As is shown in Figure 5c, the (Me_2N, EtO)-(PrO, NO_2) system

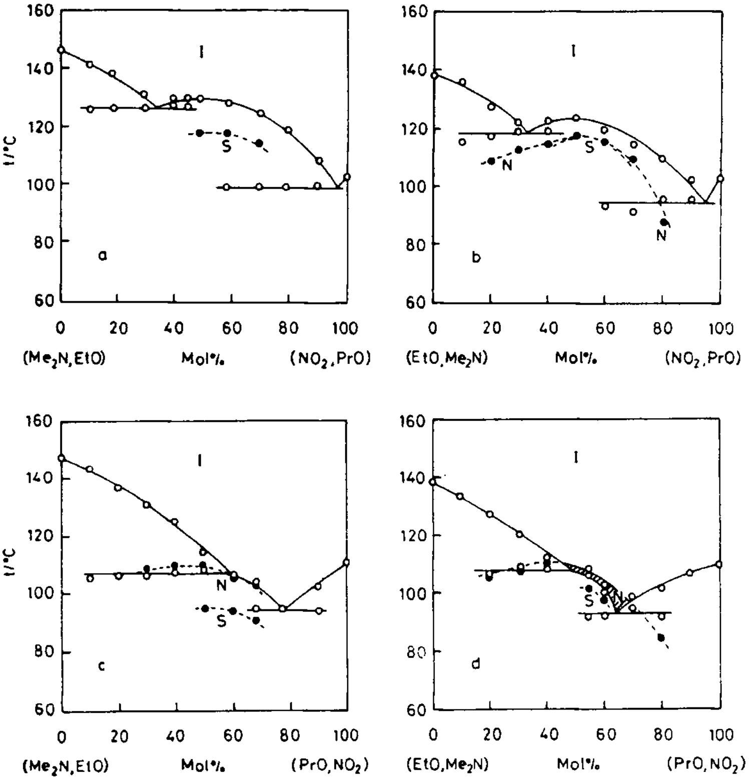

FIGURE 5 Phase diagrams of (a) (Me_2N, EtO)-(NO_2, PrO), (b) (EtO, Me_2N)-(NO_2, PrO), (c) (Me_2N, EtO)-(PrO, NO_2), and (d) (EtO, Me_2N)-(PrO, NO_2) systems. As to the open and shaded circles, see the caption of Figure 1.

shows a peritectic point and a eutectic point. The N-I transition point curve overlaps the freezing point curve between these two singular points and extends to 30 mol% passing through the maximum of 110°C located around 45 mol%. An S phase appears in the range from 50 to 70 mol% and the highest temperature of 95°C is found at the former composition. The exchange of the positions of the terminal groups in the donor molecule modifies a little the phase diagram. The N-I transition point curve observable in the range from 20 to 80 mol% intersects the freezing point curve of (EtO, Me_2N) and that of (PrO, NO_2). In other words, the induced N phase can be enantiotropic between these two intersections. The S phase is detectable only between 55 and 60 mol%, the temperature at the former point being 102°C.

The phase diagrams of the binary systems composed of the propoxy derivatives as donors and the ethoxy derivatives as acceptors are shown in Figure 6. As (Me_2N, PrO) and (NO_2, EtO) melt at the same temperature, the diagram given by these two component compounds is nearly symmetrical. The solid 1:1 complex has the melting point of 134°C. However, the mesophases are observable only in the range between 60 and 80 mol%. The isotropic melt of the former composition is transformed into an S phase at 118°C and that of the latter into an N phase at 105°C. Between these two compositions, one can see the I-N and N-S transitions. The 1:1 solid complex appearing in the (PrO, Me_2N)-(NO_2, EtO) system melts at a temperature 10°C lower than that just described above. The S-I transition occurs at 120°C in the composition range from 50 to 60 mol%. The S phase induced in the (Me_2N, PrO)-(EtO, NO_2) system is thermally least stable among the systems given in Figure 6. Nevertheless, a

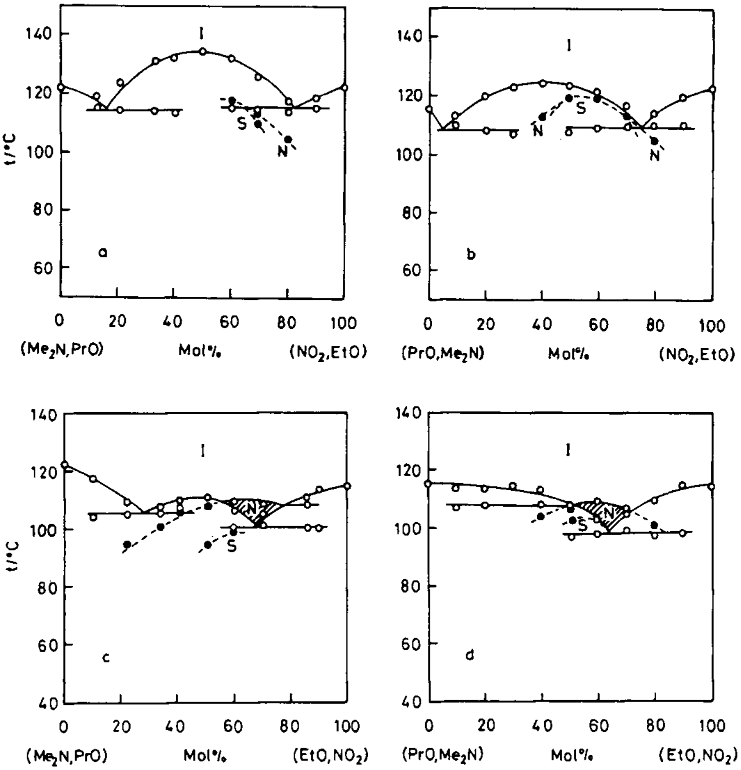

FIGURE 6 Phase diagrams of (a) (Me_2N, PrO)-(NO_2, EtO), (b) (PrO, Me_2N)-(NO_2, EtO), (c) (Me_2N, PrO)-(EtO, NO_2), and (d) (PrO, Me_2N)-(EtO, NO_2) systems. As to the open and shaded circles, see the caption of Figure 1.

congruently-melting solid complex is formed. The stability of the solid complex is naturally not high. It melts at 111°C and covers only the range from 30 to 65 mol%. The N-I transition point curve detectable in a rather wide composition range meets the freezing point curve of the solid complex and also that of the acceptor compound. The S phase is found at 50 and 60 mol%. The N-S transition temperature at the latter composition is 99°C.

All the phase transitions in the (PrO, Me_2N)-(EtO, NO_2) system occur in a narrow temperature range; that is, between the eutectic temperature of 98°C and the melting point of the donor of 115°C. The horizontal line on the donor-rich side starts from the intersection of two transition point curves at 52 mol%. There must be the accidental coincidence between the intersection and the peritectic point because the observation of the other horizontal line is limited above 50 mol%. The N phase is stabilized as much as that appearing in Figure 6c. The N-S transitions found at 50 and 60 mol% are located at 103°C.

d) General remarks

The mesophases induced in the donor-acceptor systems including those reported earlier are summarized in Table I. Parentheses mean that the transition is monotropic. The component compounds represented by the terminal groups are accompanied by their latent N-

TABLE I

Mesophases induced in the donor-acceptor systems and the extent of induction of nematic phase in the equimolar mixtures in °C

Donor[a] Acceptor	(Me_2N,MeO) 55		(MeO,Me_2N) 60		(Me_2,N,EtO) 97.5		(EtO,Me_2N) 102		(Me_2N,PrO) 75		(PrO,Me_2N) 75	
(NO_2,MeO) 80					(N)[b]	20	(N)	19	(N) (S)	27	N (S)	30
(MeO,NO_2) 82	(N)	30	(N)	--	N	11	N	7	N (S)	22	N (S)	17
(NO_2,EtO) 85	(N)	38	(N)	37	(N)	32	N	31	(N) (S)	--	(N) (S)	40
(EtO,NO_2) 90	N	33	N	30	N	27	N	23	N (S)	26	N (S)	26
(NO_2,PrO) 50	(N) (S)	49	(N) (S)	49	(S)		(N) (S)	42			(N) (S)	--
(PrO,NO_2) 57.5	N (S)	43	N (S)	37	(N) (S)	33	N (S)	30	(N) (S)	--	(N) (S)	--

[a] The component compound is accompanied by its latent N-I transition temperature.
[b] Phases in parentheses are metastable.

I transition temperatures in °C. They were deduced by the extrapolation of the N-I transition point curves observed in the binary systems with nematogenic azoxydianisole.[1] The symbol N for nematic phase is followed by the extent of induction of this mesophase defined by the deviation of the transition point curve at 50 mol% from a straight line joining the latent transition temperatures of the donor and acceptor compounds. It is of interest to note the following tendencies:

1. The extent of induction of an N phase increases with an increase of the alkoxyl chain length when a given donor compound, say (Me_2N, EtO), is combined with the acceptors of a given type, say (RO, NO_2).
2. When the alkoxyl group carried by the acceptor molecule is longer than that by the donor molecule, the induction of an N phase is more remarkable than that in the combination where the alkoxyl groups are interchanged. For example, compare the (Me_2N, MeO)-(NO_2, PrO) system with the (Me_2N, PrO)-(NO_2, MeO) system.
3. The extent of induction of an N phase by the acceptor compound of the type (NO_2, RO) is larger than that by the compound of the type (RO, NO_2).

We turn our attention now to the thermal stability of solid complexes. The general conclusion reached from our results is that the solid complexes formed with the acceptor of the type (NO_2, RO) are thermally more stable than those formed with the acceptor of the type (RO, NO_2). Considering the results presented earlier,[1,2] one may add that the combinations of the donor and acceptor molecules with the same alkoxyl groups lead to solid complexes more stable compared to the combinations of molecules with different alkoxyl groups. Finally, it may be emphasized that the stable existence of an induced N phase is mostly associated with the absence of a solid complex or the formation of a complex of low thermal stability.

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