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Mesophases Induced by Molecular Complexing

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By mixing of potentially-mesomorphic electron donors and acceptors of the type N-(p-X-benzylidene)-p-Y-aniline, nematic and smectic liquid crystals could be induced. In the present work, the donor molecules with a dimethylamino group as X or Y and the acceptor molecule with a nitro group as X or Y were employed. The remaining terminal substituents were selected from short alkoxyl groups; namely, methoxyl, ethoxyl, and propoxyl groups. The effect of the replacement of ethoxyl group by propyl group was also studied. The induced mesophases are more deeply colored than the component compounds owing to the appearance of intermolecular charge-transfer absorption near 500 nm.

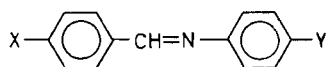
I INTRODUCTION

Contrary to real liquids where the molecules are randomly arranged, the long axes of the molecules lie essentially parallel in the nematic state, while the molecules show two-dimensional order in the smectic state. The ordering in mesophases is much less complete than in a crystal lattice regular in three dimensions; nevertheless, the strength of orientational cohesive forces is apparently crucial to produce liquid crystals. Bogojawlensky and Wino-gradow and also Walter studied a number of binary systems in which one or both compounds are mesomorphic and demonstrated that in many cases the transition curves separating the isotropic liquids and mesophases in the phase diagrams are nearly linear.^{1,2} When the interaction between the different component molecules is more attractive than that between like molecules, the transition curve is expected to become convex upwards. In other words, the mesophase in the binary mixtures is more stable than expected from the

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ideal linear relationship. Such an induction or an enhancement of the thermal stability of mesophases has been observed by Dave and Lohar in the system comprised of N-(*p*-methoxybenzylidene)-*p*-phenetidine and N-(*p*-nitrobenzylidene)-*p*-phenetidine and also by Park *et al.* in the system of N-(*p*-methoxybenzylidene)-*p*-butylaniline with 4-cyano-4'-pentylbiphenyl.^{3,4} If an additional intermolecular cohesion introduced by mixing of two kinds of molecules is sufficiently strong, the stabilization may be so significant that a mesophase is produced even with mixtures of non-mesomorphic compounds. As will be described below, the melt of such a component compound cannot be supercooled to the isotropic liquid-mesophase transition temperature without solidification occurring; nevertheless, the compound may be regarded as potentially mesomorphic.

In this paper, we wish to report that a number of binary systems consisting of potentially-mesomorphic compounds can be transformed into mesophases by intermolecular interactions of the electron-donor-acceptor type. The component compounds employed were N-(*p*-X-benzylidene)-*p*-Y-anilines,



because of the simplicity of molecular structure, of the readiness of preparations, and also of the structural relation to a number of the compounds known to be mesomorphic. The molecule designated to be an electron donor carries a dimethylamino group as X or Y and that designated to be an electron acceptor, a nitro group as X or Y. In order to ensure the potentially mesomorphic behavior of the compounds, the remaining terminal substituents were selected from methoxyl, ethoxyl, propoxyl, and propyl groups.

II EXPERIMENTAL

The N-benzylideneanilines were prepared by a condensation reaction between a *p*-X-benzaldehyde and a *p*-Y-aniline. Hereafter, the resulting Schiff bases are represented by their terminal groups (X, Y). The calorimetric curves were recorded on a Rigaku Denki Thermoflex differential scanning calorimeter during the processes of heating and cooling. The heating rate in this work was 2.5°C min⁻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. For this purpose, we employed azoxydianisole (PAA) forming a nematic liquid crystal stable between 117.5 and 135°C and N-(*p*-phenylbenzylidene)-*p*-ethoxycarbonylaniline (Ph, EtCO₂) forming a smectic A liquid crystal between 121.6 and 131°C.

III RESULTS AND DISCUSSION

a) Survey

Equimolar mixtures of all the possible combinations between the donor and acceptor compounds with alkoxy groups were examined to find out whether or not mesophases can be induced. The results are summarised in Table I

TABLE I

Mesophases induced in equimolar mixtures of electron donors and acceptors. N is for nematic and S for smectic and parentheses mean that the transitions are monotropic. The component compound, N-(*p*-X-benzylidene)-*p*-Y-aniline is represented by the terminal groups (X, Y) and is accompanied by its melting point in °C

	(Me ₂ N, MeO)	(MeO, Me ₂ N)	(Me ₂ N, EtO)	(EtO, Me ₂ N)	(Me ₂ N, PrO)	(PrO, Me ₂ N)
	141	143.5	147	138	122	115
(NO ₂ , MeO)						
133	---	---	(N)	(N)	(N)	(N, S)
(MeO, NO ₂)						
124	(N)	(N)	(N)	(N, S)	N, (S)	N, (S)
(NO ₂ , EtO)						
122	(N)	(N)	(N)	N	---	(S)
(EtO, NO ₂)						
114	N	N	N	N	N, (S)	N, (S)
(NO ₂ , PrO)						
103	(N)	(N)	(S)	(S)	---	(S)
(PrO, NO ₂)						
110	(N, S)	(N, S)	(N, S)	N, (S)	(S)	(S)

together with the melting points of the component compounds. With only four exceptions out of thirty-six combinations, we succeeded in observing a nematic liquid crystal, or a smectic liquid crystal, or both. They appear enantiotropically in ten combinations. In such cases, the observable liquid crystals are denoted by N, or S, or N, S in Table I. It must be noted that stable mesophases are obtainable with all the mixture of (EtO, NO₂). When the solid-mesophase transitions are monotropic, the mesophases are metastable and are denoted by (N), or (S), or (N, S). With (NO₂, MeO) and (NO₂, PrO), only metastable mesophases could be formed. As the first

step of the present series of works, we looked into the binary systems consisting of the component compounds with the same alkoxyl groups and studied their phase diagrams.

b) Methoxy derivatives

The combination of the electron donor and acceptor compounds gives a molecular compound with a congruent melting point in all the four. The composition is 1:1 except in the (MeO, Me₂N)–(MeO, NO₂) system where a 3:2 compound is formed. The molecular compounds appearing in the systems containing (NO₂, MeO) as electron acceptors are fairly stable. Their regions of existence (the composition difference between eutectic points) are 66 and 51 mol% respectively. On the other hand, the region is merely 22.5 mol% in the (Me₂N, MeO)–(MeO, NO₂) system and 36.5 mol% in the (MeO, Me₂N)–(MeO, NO₂) system. The acceptor-rich melts in the latter two systems could be supercooled to the isotropic liquid-nematic liquid crystal (I–N) transition temperatures. The flat maximum of the transition curve, suggesting a low degree of molecular association in the isotropic melt, is located approximately at 98°C in both the cases and is 9–10°C below the eutectic temperature on the acceptor-rich side of the diagram. The higher melting points of the donor compounds (see Table I) and the higher eutectic temperatures on the donor-rich side, 114 and 118°C in these two systems, may be the reason why the other halves of the I–N transition curves could not be reached by supercooling. When a solid molecular compound is of higher stability, the eutectic temperatures become higher, e.g., 123°C on the acceptor-rich side in the (Me₂N, MeO)–(NO₂, MeO) system. The failure to observe mesophases in the other two systems, (Me₂N, MeO)–(NO₂, MeO) and (MeO, Me₂N)–(NO₂, MeO), may be attributed to the stronger tendency to form crystalline solids preventing the appearance of metastable mesophases.

c) Ethoxy derivatives

As is shown in Figure 1, nematic liquid crystals are induced in all the combinations. The open and shaded circles indicate the transitions found during the processes of heating and cooling respectively. The shaded circles are omitted when they coincide exactly with the open circles. The phase appearing below the transition indicated by both open and shaded circles is stable. The area in which the mesophase is stable is hatched in Figure 1. The I–N transition curves are very much alike to each other and the maxima are located near a 1:1 mole ratio and 120°C. Consequently, the stability of the solid molecular compounds largely determines how large the hatched areas are. The most stable molecular compound is formed in the (Me₂N, EtO)–(NO₂, EtO)

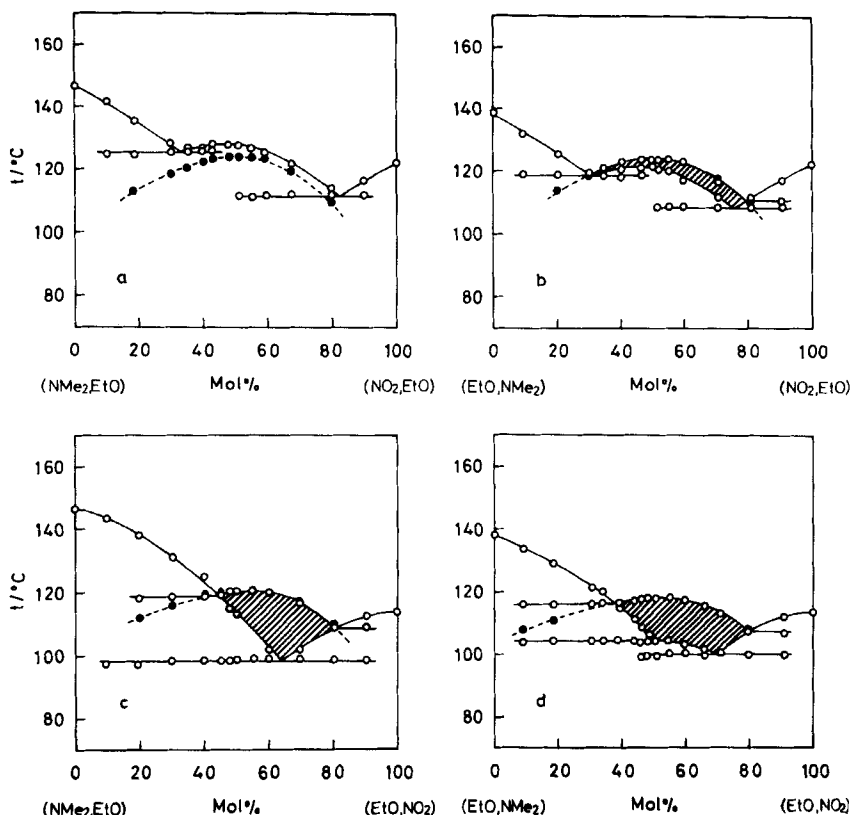


FIGURE 1 Phase diagrams of (a) the N-[p-(dimethylamino)benzylidene]-p-phenetidine-N-(p-nitrobenzylidene)-p-phenetidine, (b) N-(p-ethoxybenzylidene)-p-(dimethylamino)aniline-N-(p-nitrobenzylidene)-p-phenetidine, (c) N-[p-(dimethylamino)benzylidene]-p-phenetidine-N-(p-ethoxybenzylidene)-p-nitroaniline, and (d) N-(p-ethoxybenzylidene)-p-(dimethylamino)aniline-N-(p-ethoxybenzylidene)-p-nitroaniline systems. The open and shaded circles are transitions observed in the processes of heating and cooling respectively. In the hatched area, the nematic phase is stable.

system where the liquid crystal is monotropic. The stable mesophases occupy large areas in the systems containing $(\text{EtO}, \text{NO}_2)$ as electron acceptors because no solid molecular compound is formed in the system with $(\text{Me}_2\text{N}, \text{EtO})$ and the molecular compound in the system with $(\text{EtO}, \text{Me}_2\text{N})$, possibly of a 3:2 ratio, melts incongruently. It may be added that the solid molecular compounds are less stable than those of the corresponding methoxy derivatives. Even the most stable one has the region of existence not wider than 50 mol%. The phase diagram of the $(\text{Me}_2\text{N}, \text{EtO})$ -(NO_2 , EtO) system has been examined by Lohar.⁵ In contrast to our result, he has reported a diagram

of the eutectic type. The metastable nematic liquid crystal has not been recorded by him.

d) Propoxy derivatives

This alkoxyl group stabilizes most solid molecular compounds among the examined terminal substituents. A congruently melting molecular compound is found in all the phase diagrams shown in Figure 2. In the $(\text{Me}_2\text{N}, \text{PrO})$ – $(\text{NO}_2, \text{PrO})$ system where the region of existence of the molecular compound

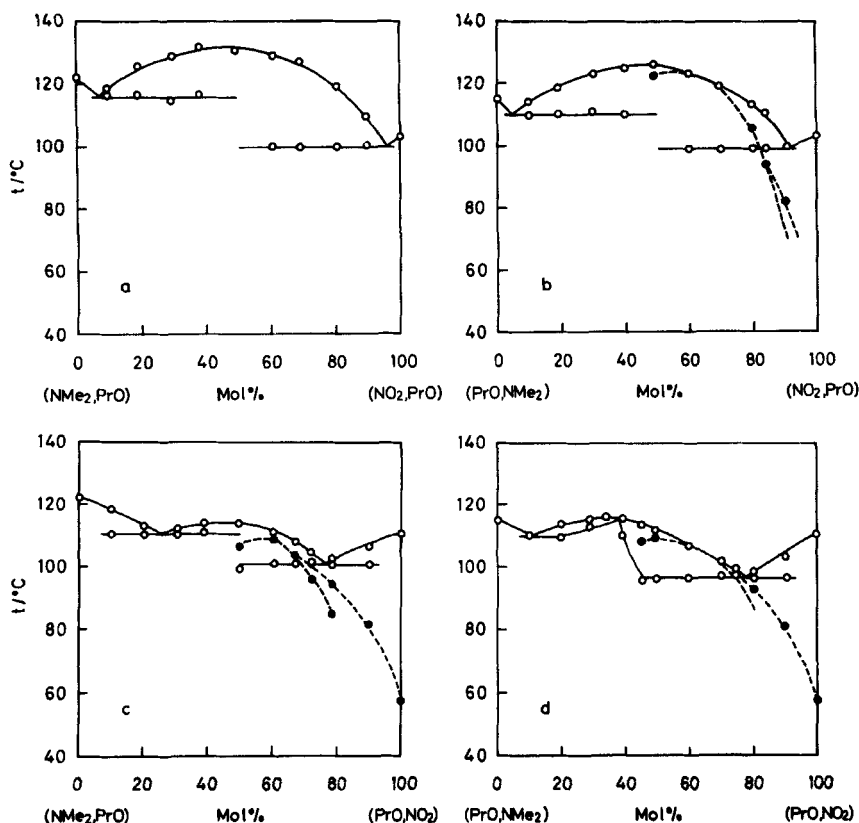


FIGURE 2 Phase diagrams of (a) the N -[p -(dimethylamino)benzylidene]- p -propoxyaniline- N -(p -nitrobenzylidene)- p -propoxyaniline, (b) N -(p -propoxybenzylidene)- p -(dimethylamino)aniline- N -(p -nitrobenzylidene)- p -propoxyaniline, (c) N -[p -(dimethylamino)benzylidene]- p -propoxyaniline- N -(p -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 Figure 1.

is as wide as 89 mol%, no mesophase is observable, while the other three systems yield not only the metastable smectic liquid crystals indicated in Table I but also metastable nematic liquid crystals. We note that the induced mesophases can be found only on the acceptor-rich side. As the maximum of the isotropic liquid-smectic liquid crystal (I-S) transition curve is located at a higher temperature than the extrapolation of the I-N transition curve, the normal sequence of transition in the process of cooling, $I \rightarrow N \rightarrow S$, is found only in the composition range relatively rich in the acceptor compound. (PrO, NO₂) is the only component compound in this work the I-N transition of which is observable. The temperature difference between the melting point and the I-N transition temperature is more than 50°C. The latent I-S or N-S transition temperature is supposed to be located at a further lower temperature.

The emergence of a smectic liquid crystal in the binary mixtures, in which both or one of the component compounds exhibit stable nematic liquid crystals, has been reported by several workers.⁶⁻¹⁰ Recently, Domon and Billard have listed twenty-eight such systems.⁹ Among them, about two-thirds are mixtures of terminal polar with terminal nonpolar component compounds and the remaining systems have no terminal polar component compound. The present component molecules bearing a dimethylamino or a nitro group are strongly polar. Apparently, it is not the decisive factor for the induction of smectic liquid crystals whether the component molecules are polar or nonpolar.

e) Propyl derivatives

In order to compare the effects of the alkoxy and alkyl derivatives on the induction of mesophases, the alkoxy groups in the (Me₂N, EtO)-(NO₂, EtO) system were replaced one by one with the alkyl groups of the same length. The results are illustrated in Figure 3 repeating the diagram of the ethoxy derivatives for the sake of convenience. In the resulting three systems, the I-N transition curve is accompanied by the N-S transition curve running nearly in parallel. The maximum of the former transition curve is progressively lowered by the substitution with propyl groups. The stability of solid molecular compound is drastically lowered by the introduction of a propyl group in the place of one of the ethoxyl groups. In the system of (Me₂N, Pr)-(NO₂, EtO), the molecular compound presumably of 2:3 mole ratio decomposes at 75.5°C. With this system we obtained a stable nematic liquid crystal. Although a part of the N-S transition curve is located above the freezing point curve on the acceptor-rich side, the smectic liquid crystal appears only in the process of cooling. This observation is consistent with the absence of a horizontal transition line at the temperature of the intersection

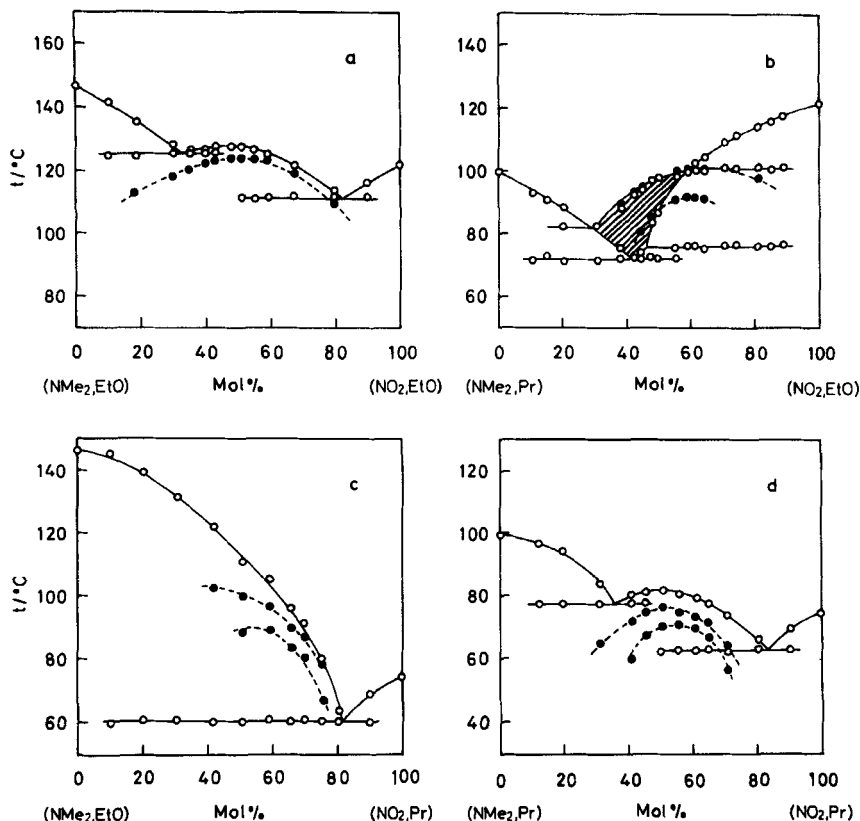


FIGURE 3 Phase diagrams of (a) the N-[p-(dimethylamino)benzylidene]-p-phenetidine-N-(p-nitrobenzylidene)-p-phenetidine, (b) N-[p-(dimethylamino)benzylidene]-p-propylaniline-N-(p-nitrobenzylidene)-p-phenetidine, (c) N-[p-(dimethylamino)benzylidene]-p-phenetidine-N-(p-nitrobenzylidene)-p-propylaniline, and (d) N-[p-(dimethylamino)benzylidene]-p-propylaniline-N-(p-nitrobenzylidene)-p-propylaniline. As to the open and shaded circles and hatched area, see the caption of Figure 1.

between the N-S transition and freezing point curves. The phase diagrams of the $(\text{Me}_2\text{N}, \text{EtO})-(\text{NO}_2, \text{Pr})$ system is of the eutectic type. However, the I-N and N-S transition curves are located underneath the freezing point curve on the donor-rich side and the mesophases are naturally monotropic. When either of the donor and acceptor molecules carry propyl groups, the 1:1 molecular compound becomes fairly stable and the whole diagram resembles that of the corresponding ethoxy derivatives.

The identification of the induced smectic liquid crystal has been attempted by a phase-diagram study on the pseudo-binary system comprising of the 1:1 molecular compound in the $(\text{Me}_2\text{N}, \text{Pr})-(\text{NO}_2, \text{Pr})$ system and a reference

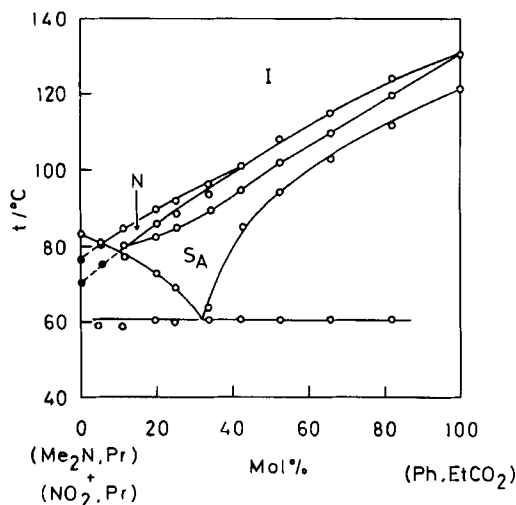


FIGURE 4 Phase diagram of the system consisting of the N-[p-(dimethylamino)benzylidene]-p-propylaniline-N-(p-nitrobenzylidene)-p-propylaniline (1:1) complex and N-(p-phenylbenzylidene)-p-ethoxycarbonylaniline. As to the open and shaded circles, see the caption of Figure 1.

compound (Ph, EtCO₂). As is shown in Figure 4, the induced smectic liquid crystal is of the type A. The nematic liquid crystal of the molecular compound becomes stable above 5 mol % of (Ph, EtCO₂) and continues to exist up to about 42 mol %.

f) The extent of induction of nematic phases

The diagrams in Figures 1–3 clearly suggest that the component compounds employed here have latent I–N transition temperatures. Such transition temperatures may be deduced by the extrapolation of the I–N transition curves observed in the binary systems with mesomorphic PAA. For the following five compounds, such diagrams have been studied by Dave and Lohar: (Me₂N, MeO), (NO₂, MeO), (MeO, Me₂N), (Me₂N, EtO), and (NO₂, EtO).^{11,12} We have worked on all the other systems. The I–N transition temperatures presented in Table II were thus estimated and are in good agreement with those located from the phase diagrams in Figures 1–3. Then, the extent of induction of a nematic liquid crystal may be represented by the deviation of the I–N transition curve at 50 mol % from a straight line joining the latent transition temperatures of the donor and acceptor compounds. The results in Table II show the extent of induction decreases with the alkoxy groups in the following order:

propoxyl > methoxyl > ethoxyl.

TABLE II

Isotropic liquid-nematic phase transition temperatures of the component compounds and extent of induction in the equimolar mixtures in °C. The latter values are in parentheses.

A					
		X = Y =			
		MeO	EtO	PrO	
(Me ₂ N, Y)		55	97.5	75	
+		---	(32)	---	
(NO ₂ , Y)		80	85	50	
(X, Me ₂ N)		60	102	75	
+		---	(31)	(40-45)	
(NO ₂ , Y)		80	85	50	
(Me ₂ N, Y)		55	97.5	75	
+		(30)	(27)	(40)	
(X, NO ₂)		82	90	57.5	
(X, Me ₂ N)		60	102	75	
+		(27)	(23)	(40)	
(X, NO ₂)		82	90	57.5	
B					
(Me ₂ N, Pr)	25	(Me ₂ N, EtO)	97.5	(Me ₂ N, Pr)	25
+	(43)	+	(42)	+	(54)
(NO ₂ , EtO)	85	(NO ₂ , Pr)	20	(NO ₂ , Pr)	20

The ease of observation of mesophases with the ethoxy derivatives is apparently due to the fact that the latent I-N transition temperatures of these component compounds are higher than those of the other alkoxy derivatives. The above-mentioned order of the alkoxy groups exactly coincides with the tendency of a solid molecular compound formation. Therefore, the emergence of smectic liquid crystals, which are much closer to the crystalline state as compared to nematic liquid crystals, with the propoxy derivatives may not be independent of the high stability of solid molecular compounds.

It must be added that the largest extent of induction in the present work is 54°C found in the (Me₂N, Pr)-(NO₂, Pr) system. As is shown in Figure 3, the maximum temperature of the N-S transition curve never reaches that of the I-N transition curve in the mixtures. The tendency to form a solid molecular compound considerably weaker compared to that in the mixtures of the propoxy derivatives may be responsible to this result.

g) Electronic spectra

Although the donor and acceptor compounds are yellow, the resulting solid molecular compounds are reddish brown. The deeper coloration is due to the electronic absorption located around 500 nm which is not seen with either of the component compounds. The color persists in mesophases but disappears when the separation of the donor and acceptor molecules into two phases occurs upon solidification. The newly-appeared absorption in the molecular compounds may be assigned to the charge-transfer transition. Then, the transition moment is supposed to be in the direction connecting the donor and acceptor molecules; therefore, the mesophase is expected to be optically anisotropic in this region. The remarkable induction of mesophases found in this work may be attributed to the parallel arrangement produced by molecular complexing of the electron-donor-acceptor type.

The work on the remaining systems in Table I is being planned and will be the subject of a subsequent paper.

References

1. A. Bogojawlensky and N. Winogradow, *Z. Phys. Chem.*, **64**, 229 (1908).
2. R. Walter, *Ber.*, **58**, 2303 (1925).
3. J. S. Dave and J. M. Lohar, *Chem. and Ind.*, 1960, 494.
4. J. W. Park, C. S. Bak, and M. M. Labes, *J. Am. Chem. Soc.*, **97**, 4398 (1975).
5. J. M. Lohar, *J. de Phys. (Paris), Colloq.*, **36**, C1-393 (1975).
6. J. P. Schroeder and D. C. Schroeder, *J. Org. Chem.*, **33**, 591 (1968).
7. F. Hardouin, G. Sigaud, M. F. Achard, and H. Gasparoux, *Ann. de Phys. (Paris)*, **3**, 381 (1978).
8. B. Engelen, G. Heppke, R. Hopf, and F. Schneider, *Ann. de Phys. (Paris)*, **3**, 403 (1978).
9. M. Domon and J. Billard, *J. de Phys. (Paris), Colloq.*, **40**, C3-413 (1979).
10. L. J. Yu and M. M. Labes, *Mol. Cryst. Liq. Cryst.*, **54**, 1 (1979).
11. J. S. Dave and M. J. S. Dewar, *J. Chem. Soc.*, 4305 (1955).
12. J. S. Dave and J. M. Lohar, *J. Chem. Soc.*, A 1473 (1967).