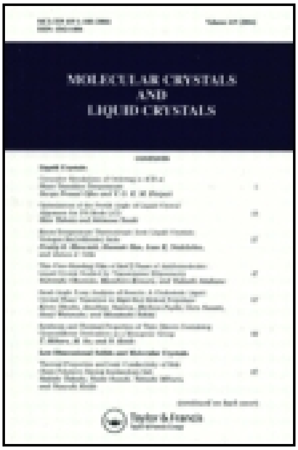

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BROADENING OF THE NEMATIC TEMPERATURE RANGE BY A NON-MESOGENIC SOLUTE IN A NEMATIC LIQUID CRYSTAL

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Abstract The general rule that addition of a non-mesogenic solute causes a sharp decrease in the nematic-isotropic transition temperature ($T_{N\to I}$) of a nematic solvent is not obeyed when the solute and solvent can enter into a donor-acceptor interaction. Addition of 4-aminobiphenyl to the nematic liquid crystal 4-cyano-4'-pentylbiphenyl (nematic range ∿ 25-35°) leads to an increase in $T_{N\to I}$ and a decrease in the crystal-nematic transition temperature. The maximum nematic range (21-38°) is achieved at ∿ 7 mole % solute.

In order to extend liquid crystalline temperature ranges, it is common to prepare a mixed system to take advantage of eutectic behavior. In a typical binary mixture, where the components are miscible in all proportions, the phase diagram shows a nearly linear dependence of the nematic→isotropic (N→I) transition, and a simple eutectic determined by heats of melting of the components in the crystal→nematic (C→N) transition.

In a previous paper,[1] we reported unusual phase diagrams of binary liquid crystalline mixtures between 4-cyano-4'-pentylbiphenyl (CPB) and Schiff base or azo type liquid crystals: for example, when N-(p-methoxybenzylidene)-p-n-butylaniline (MBBA) is mixed with CPB, a double eutectic is found in the C→N transition and the N→I transition temperature increases as one proceeds from either component to an ∿ equimolar mixture.

These unusual phase diagrams were attributed to a donor-acceptor type interaction between the constituent molecules. Further studies[2] of the MBBA-CPB system showed strong positive deviations in the dielectric anisotropies ($\Delta\varepsilon$) from a normal linear relationship, slight increases in the splay elastic constants, and marked decreases in the electro-optic response times of twisted nematic cells made from the mixtures.

It occurred to us that similar type phase diagrams and changes in properties could be achieved when a non-mesogenic solute is dissolved in a liquid crystalline solvent if the solute and solvent undergo a donor-acceptor interaction. In general, addition of a non-mesogenic solute leads to a sharp decrease in $T_{N\rightarrow I}$ of a mesogenic solvent.[3-7] Such a decrease can be understood in terms of the degree of disruption of nematic order caused by the solute, which are functions of the size, shape and flexibility of the solute, and to any changes in dipole-dipole interactions or dispersion forces in the solvent caused by the solute. The slope of the depression of $T_{N\rightarrow I}$ ($\partial T_{N\rightarrow I}/\partial_X$, where X is the mole fraction of solute) is a measure of this perturbation.

Contrary to this general rule, we find that when 4-aminobiphenyl (ABP),[8] a non-mesogenic donor type molecule, is added to CPB, $T_{N\rightarrow I}$ increases and $T_{C\rightarrow N}$ decreases with a maximum nematic range being achieved at ∿ 7 mole % ABP. As opposed to pure CPB, which has a nematic range of 25-35°, 93% CPB/7% ABP has a range of 21-38°. The phase diagram (Figure 1), determined by using polarized optical microscopy on a Mettler FP-2 hot stage,and differential scanning calorimetry (DSC),utilizing a Perkin-Elmer DSC 1-B, is another example of a two-component system forming a compound showing a congruent melting point at a 50:50 mixture, and exhibiting two eutectics in the melting point. Enthalpies (ΔH) of the C→N or C→I transitions for the binary mixture are plotted in Figure 2, showing virtually linear variations of the total enthalpies of melting with composition. The complexity of Figures 1 and 2 can be explained in terms of definite compositions in the stable solid phases.

When 4-cyanobiphenyl (CBP), which is structurally similar to ABP, but bears a cyano group instead of an amino group, is mixed with CPB, a normal phase diagram of a two-component system with $(\partial T_{N\rightarrow I}/\partial_X)_{X=0} = -50°$is obtained. Both ABP and CBP dissolved in nematic phase V (a eutectic mixture of p-methoxyazoxybenzenes which are p'-substituted with ethyl and n-butyl groups) induce sharp decreases in $T_{N\rightarrow I}$, giving $(\partial T_{N\rightarrow I}/\partial_X)_{X=0}$ values of -203 and -160° respectively. For a binary mixture between MBBA and CBP, $T_{N\rightarrow I}$ decreased approximately linearly with mole fraction of CBP with $(\partial T_{N\rightarrow I}/\partial_X)_{X=0} = -123°$. However, the melting point curve showed a slight negative deviation from a smooth line near the 50:50 mixture.[9]

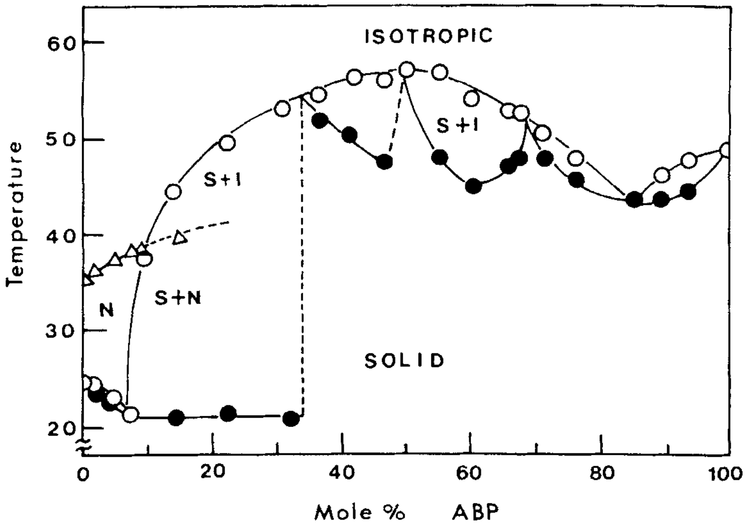

Figure 1. Phase diagram of CPB-ABP mixture: $T_{N\rightarrow I}(\Delta)$, melting point of last trace of solid (○), and melting point of excess components (●).

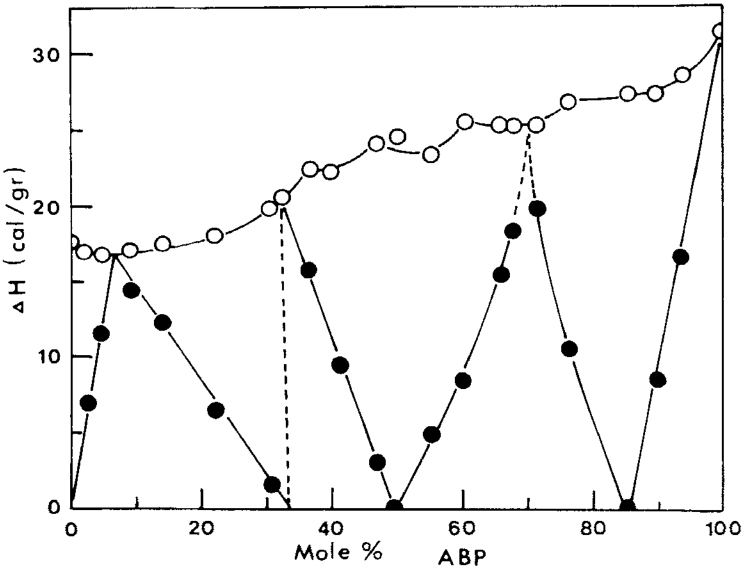

Figure 2. Heat of solid→nematic or liquid transition of CPB-ABP mixture: total heat of melting (○) and heat of melting of excess components (●).

These results clearly indicate that CPB and ABP form a complex. The complex may either be linear through the interaction between CN and NH_2 groups, or plate-like through the interaction between biphenyl rings. Either of these effects can lead to a $T_{N\rightarrow I}$ value higher than that of CPB itself. In the case of the MBBA-CBP mixture, a non-linear complex, which is not liquid crystalline, may be formed with substantially lower formation constants than those of MBBA-CPB or CPB-ABP. The lack of a long flexible hydrocarbon chain in CBP could cause the decrease in the stability of a complex in the highly ordered liquid crystalline and solid phases. Such an effect is unlikely in the MBBA-CPB and CPB-ABP systems.

Recently, Oh[10] has studied several other binary liquid crystalline systems, where one component bears a cyano group, and reports similar phase diagrams but with extended smectic ranges. He proposes a dipole-induced lamellar structure as an alternate model to explain the phase diagrams. Such a model may indeed be applicable in some situations, particularly in explaining the induced smectic mesomorphism. It is hard to see how such a model could explain the strong non-linearity in $T_{N\rightarrow I}$ in the case of the CPB-ABP mixtures studied in this work, where a donor-acceptor interaction appears so likely. Further studies on these unusual phase relationships should allow a mechanistic distinction as well as providing liquid crystals with wider mesomorphic ranges and modified electro-optic parameters.

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