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INDUCED PHASES IN MIXTURES OF TERMINAL POLAR LIQUID CRYSTALS-AMINES AND NITRILES

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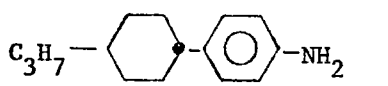
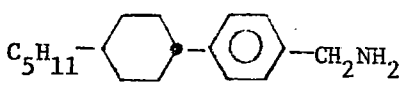
Although binary mixtures of mesogens usually exhibit phase diagrams of the simple eutectic type, there are a large number of exceptions which occur when mixing mesogens which are unalike in a significant structural way. Engelen et al[1] have proposed a classification scheme stating the requirement that induced smectic phases usually occur when mixing a terminal polar with a terminal non-polar structure. Domon and Billard[2] have pointed out that there are cases of induced smectic mesomorphism where both components do not have a strong terminal dipole. In this report, some cases are cited where mixtures of two terminal polar liquid crystals show phase induction with the special requirement that polar electron-donating and electron-accepting components to a π system be present.

To conduct the study, we employed a series of recently synthesized[3,4] terminal amino substituted liquid crystals and some closely related non-mesogens. Three of these compounds are substituted phenylcyclohexanes (I,II,III) and two are substituted biphenyls (IV,V).



I



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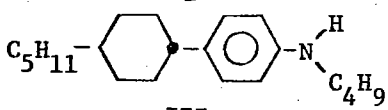

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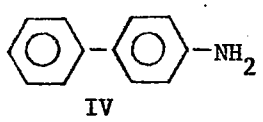

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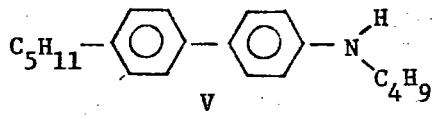

V

Obviously their mixtures with nitriles are almost ideal candidates for such a study in that essentially only the terminal polar moiety of the molecule is changed between the two components in most of the cases studied. I and II were mixed with trans-4-n-pentylcyclohexylbenzonitrile (5PCH-CN); whereas, IV and V were mixed with 4-n-pentyl-4'-cyanobiphenyl (CPB). Finally, III was mixed with CPB. The important results are summarized in Table I. All the substituted anilines, including the N-substituted members, showed induced smectic mesomorphism or an induced solid phase at higher concentrations, and expansions of the nematic range of the respective nitrile at concentrations of < 7 weight %. On the other hand, the methanamine II behaved in a "normal" way, i.e. depression of both K↔N and N↔I.

The phase diagram of the V-CPB system is given in Fig. 1. The mixed phase region is quite complicated and not completely analyzed at this time. For example, at 20 weight % V in CPB, one observes partial melting of the mixture at the nematic eutectic temperature, followed by partial conversion of the nematic regions to the isotropic phase at or near the normal melting point of the nematic phase. Both S_A and S_E phases are seen, together with a solid-like phase at concentrations of 60% V in CPB. For the 50-50 mixture, only a solid-like phase is observed.

Fig. 2 presents the phase diagram for the III-CPB binary system. Proceeding from either end of the phase

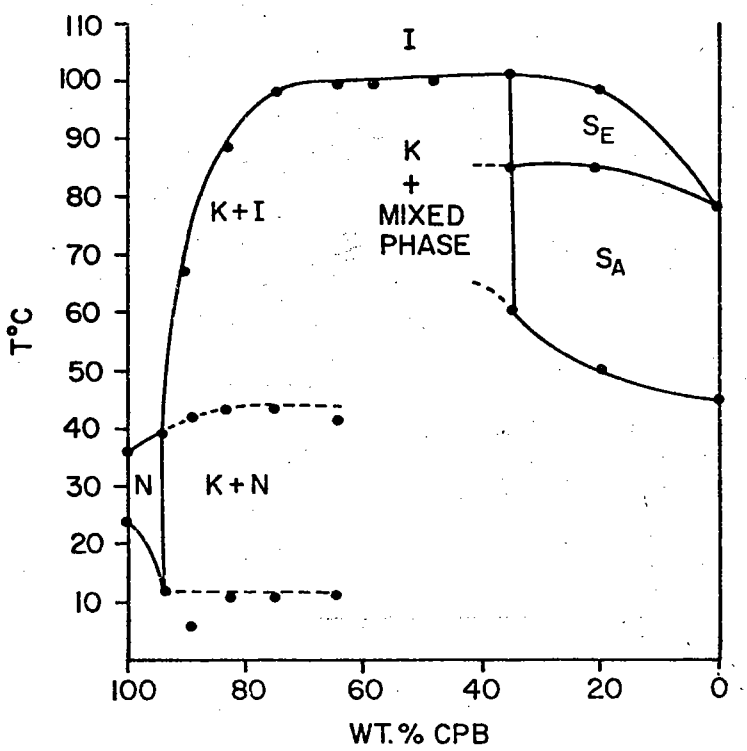

Figure 1. Phase Diagram for the Binary System CPB and V

diagram, the nematic range is enhanced by an increase in N→I and a suppression of K→N. At the 50-50 weight % mixture a maximum occurs for both K→N and N→I. The behavior in this example clearly indicates that two terminal polar nematogens can be mixed to yield induced phase behavior.

The behavior of mixtures of π donors and π acceptors is consistent with our earlier[6] suggestion of a charge transfer model for the interaction of unlike mesogens. This model is of considerable value in predicting phase induction in binary mixtures. Neither a charge transfer

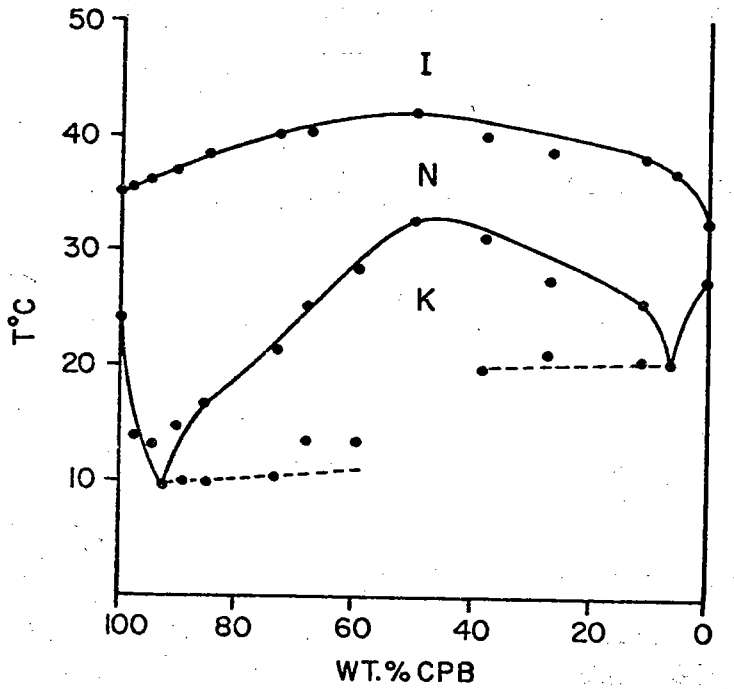

Figure 2. Phase Diagram for the Binary System CPB and III

model, nor the Engelen et al classification scheme, nor Oh's[7] model of a lamellar structure with sandwiched layers of terminal polar and non-polar mesogens is consistent with all the data on systems showing non-ideal phase diagrams. What is clear is that interactions between liquid crystalline molecules of an electronic nature can perturb the normal phase relationships whether these be of a dipole-dipole or charge transfer type.

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