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Induced Smectic Mesomorphism in Mixtures of *p*-Cyano-*p'*-pentylbiphenyl and *p*-Pentylbenzoic Acid

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The phase diagram of *p*-cyano-*p'*-pentylbiphenyl (CPB) and *p*-pentylbenzoic acid (5BA) shows a maximum value of the nematic-isotropic transition temperature at ~equimolar concentrations of CPB and the *dimer* of 5BA (D5BA). Two eutectic points occur at concentrations of D5BA of 8 and 65 mole %, respectively, and an induced smectic phase occurs in the concentration range of 15 to 65 % D5BA. Dielectric properties and the spontaneous homeotropy of some of the mixtures can best be understood by considering the phases to consist primarily of D5BA and CPB, with a small amount of free 5BA modulating the dielectric properties and promoting homeotropic alignment.

INTRODUCTION

Although the phase diagram of a binary mixture of nematic liquid crystals usually exhibits a simple eutectic, a number of systems show the induction of a smectic phase. Mixing nematogens containing a strongly polar terminal group such as —C≡N with terminal non-polar liquid crystals produces this behavior in a number of cases.[1] Park, Bak and Labes[2] attributed this behavior to a charge-transfer interaction between the components. Oh[3] proposed a lamellar model to account for the formation of smectic phases. Griffin *et al.*[4] found that mixing mesogens of which one component tended to form a bimolecular layer and the other a unimolecular layer showed induction of smectic mesomorphism. In this work, we wish to report that alkyl and alkoxy benzoic acids, when mixed with substituted cyanobiphenyls, show smectic phase induction and enhanced nematic-isotropic transition temperatures primarily via the interaction of an acid *dimer* with the cyanobiphenyl. While this work was in progress, Engelen *et al.*[1a] reported that *p*-*n*-heptyloxy- and *p*-*n*-octyloxybenzoic acid (8OBA) showed induced smectic phases when mixed with *p*-*n*-pentyl-*p*'-cyanoterphenyl and *p*-heptylcyanobiphenyl respectively, but the details have not as yet appeared. Engelen and Schneider[1b] have also reported the phase diagram of 8OBA with *N*-*p*-cyanobenzylidene-*p*-octyloxyaniline (CBOOA).

EXPERIMENTAL

CPB was purchased from British Drug House and used without purification. 5BA was purchased from Eastman Kodak Co. and purified by crystallization from ethanol, benzene and hexane. The crystal-nematic and nematic-isotropic transition temperatures of 5BA were 89 and 126°C, respectively. Transition temperatures for the phase diagram were measured by both hot stage microscopy and differential scanning calorimetry (Perkin-Elmer DSC–1B). Phase textures were characterized by using a Nikon polarizing microscope, and the enthalpies of the transitions were measured by using the DSC–1B. The enthalpy was calibrated with reference to 99.95% indium (United Mineral and Chemical Corp.) and spectral grade benzene. The enthalpy of the phase transitions of CPB were in good agreement with the literature value.[5]

Dielectric constants were measured by using a General Radio 1608A impedance bridge. The capacitor cell consisted of two tin oxide coated glass electrodes separated by a 12.7 μm Mylar spacer. The cell temperature was controlled by a brass housing, which has been described previously.[6] The voltage applied was 1 volt at 1 kHz. A General Radio 1312 decade oscillator was used for application of variable frequencies. Alignment of the sample was achieved by applying a 17 kG magnetic field. The dielectric constants measured for CPB were in good agreement with the literature.[7]

RESULTS AND DISCUSSION

Phase diagram

The phase diagram and total enthalpies of transition, ΔH_{total}, are plotted in Figure 1 as a function of mole % of D5BA in CPB. Each point on the phase diagram represents an average of both calorimetric and optical determinations, which agreed very well. The general features of the phase diagram and

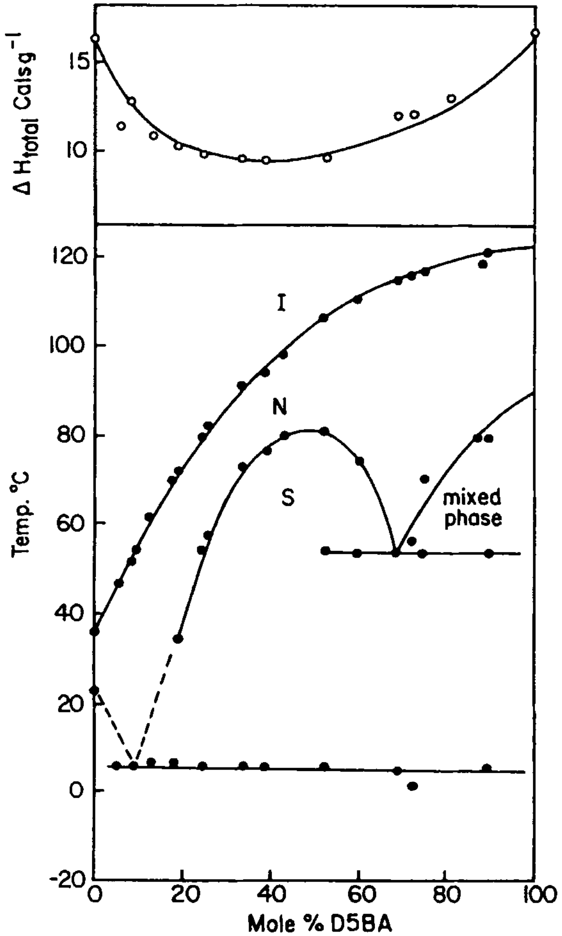

FIGURE 1 Phase diagram of D5BA in CPB, indicating isotropic (I), nematic (N) and smectic (S) phases. Upper curve indicates the total transitional enthalpies as a function of concentration. (Moles of "D5BA" are defined as mass of 5BA/M.W. of dimer).

enthalpic relationships indicate that dimeric benzoic acid behaves as an undissociated entity in its interaction with CPB.

If the phase diagram is plotted vs mole % of monomer, the maximum occurs at $\sim$67 mole % 5BA, and it is therefore more likely that dimeric D5BA is the entity interacting with CPB, producing a maximum at 50 mole %.

Carboxylic acids, in general, are dimeric in their pure state and dissociate only slightly in non-polar solvents. The extent of dissociation is very slight ($\sim$0.01 %) in solvents such as heptane or benzene,[8–10] but even in 1,2-dichloroethane with a dielectric constant of $\sim$10, dissociation is only $\sim$0.1 %.[11]

The nematic-isotropic transition temperature (T_{NI}) shows a pronounced positive deviation from the linear average of the two components, with the maximum deviation occurring at a 50–50 molar mixture of CPB and D5BA. The induced smectic phase is located in the concentration range from 15–65 mole % D5BA, with the maximum thermal stability also occurring at the equimolar concentration. ΔH_{total} correspondingly shows a minimum at the equimolar concentration point. As is typical of other phase diagrams showing induced smectic phases, two eutectics occur, in this case at 8 and 65 mole % D5BA. Optical observations of the texture indicated the induced phase to be smectic A.

While studying these mixtures, it was noted that adding 5BA to CPB resulted in a substantial improvement in the homeotropic alignment of pure CPB on clear glass when D5BA is below 50 mole %. As the concentration of 5BA is further increased, homogeneous textures are obtained, as is the case with pure 5BA. The tendency of D5BA to homogeneously align can be understood in terms of its most hydrophilic moiety being at the center of the molecular structure. Molecules such as CPB probably couple directly on the glass surface via the polar terminal group.[12,13] As one adds small amounts of 5BA, the monomeric form of the acid presumably couples very strongly with glass thereby enhancing homeotropy.[12,13]

A similar study was conducted of the phase diagram of 8OBA and CPB, showing induced smectic mesomorphism with the maximum thermal stability occurring at the 50–50 mole % point of dimeric 8OBA-CPB. These binary mixtures show the same tendency to spontaneous homeotropy as the D5BA-CPB system.

Although it is possible that there are hydrogen bonding interactions between CPB and 5BA, the phase diagram studies clearly indicate that the primary interaction is between dimer D5BA and CPB, although monomer 5BA seems to be responsible for a strong tendency to homeotropy. As to the question of the factors leading to phase induction, no evidence for charge-transfer complex formation[2] could be found in the present system. The presence of free 5BA also causes perturbations in the dielectric properties as will now be discussed.

Dielectric properties

Figure 2 shows the dielectric anisotropy ($\Delta\varepsilon$) and the parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) components of the dielectric constant as a function of D5BA concentration. The values are taken 10 degrees below T_{NI} for all the mixtures except those containing 60 and 75 mole % D5BA, which were measured up to 90°C and then linearly extrapolated to the corresponding temperatures. The dielectric constants of D5BA were measured at 94°C. Since

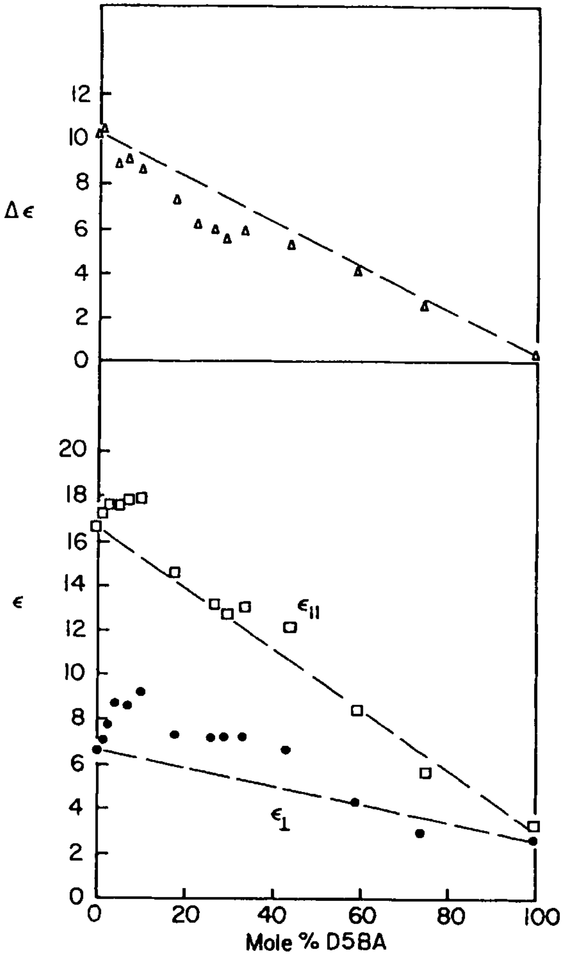

FIGURE 2 Dielectric anisotropy $\Delta\varepsilon$, parallel ($\varepsilon_{\parallel}$) and perpendicular ($\varepsilon_{\perp}$) dielectric constants of D5BA in CPB.

5BA exits in a dimeric configuration, the dipole moments would cancel each other resulting in a zero or small anisotropy. There has been some uncertainty regarding the sign of this anisotropy, since the value is small and is easily affected by impurities, as discussed by Carr.[14] Furthermore, there are monomers, open and closed dimers, polymers and possible cybotactic clusters involved in the alkyl and alkoxy benzoic acids which would complicate the dielectric properties.[14]

$\Delta\varepsilon$ increases linearly with the concentration of CPB. The values agree well with the linear average of the two components until an equimolar concentration is reached. If the concentration of CPB is increased further, $\Delta\varepsilon$ shows a negative deviation from the linear average. When D5BA is present at high concentration, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ show negative deviations from the linear average, but the values of these deviations are about the same and therefore cancel in the $\Delta\varepsilon$ term. The origin of these negative deviations is somewhat uncertain. Firstly, there could be a coupling between the CPB molecule with dimeric 5BA. Secondly, there could be an open and closed dimer equilibrium of D5BA.[8,15,16] Thirdly, as reported by Leadbetter *et al.*,[17] cyanobiphenyl nematogens have a repeat distance 1.4 times the molecular length in the nematic phase, indicating that CPB could form a dimeric configuration through a head-to-head overlap of the cyanobiphenyl moieties. This molecular association could persist in the isotropic phase.[17] If this is true, then the dielectric constants measured result from the effective dipole moments due to molecular association. This molecular association should be a function of temperature and dependent on the medium. In the mixture of CPB and 5BA, the molecular association of CPB would be strongly affected if there were indeed an energetically more favorable coupling between CPB and 5BA. Qualitatively speaking, the lowering in $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ for mixtures with low concentration of CPB could be due to the disruption of the molecular association of CPB and a coupling of CPB and D5BA.

At low concentrations of D5BA, $\varepsilon_{\parallel}$ and $\varepsilon_{\perp}$ show positive deviations from the linear average of the corresponding components. The enhancement of the $\varepsilon_{\perp}$ value is more pronounced than that of $\varepsilon_{\parallel}$ components and therefore results in a negative deviation in $\Delta\varepsilon$. I'haya ascribed the lowering of the dimerization equilibrium constant of benzoic acid in chloroform to the formation of a hydrogen bond between the proton of chloroform and the monomer carbonyl oxygen.[8] A similar effect could be expected in the present case, i.e. there might be a formation of a hydrogen bond between the nitrogen atom and the proton of the carboxylic acid. The formation of a hydrogen bond certainly affects the dipole moments and correspondingly the dielectric constants measured for these mixtures.[18,19]

Qualitatively one might expect a hydrogen bond formed via the coupling of a carboxylic acid proton and a cyano group to link these two molecules so as to enhance the dipole moment along the long axis. However, the free carbonyl group would enhance the dipole moment along a direction perpendicular to the long axis. The latter effects seem more pronounced than the former and results in a negative deviation of $\Delta\varepsilon$.

Figure 3 presents data on the frequency dependence of $\varepsilon_{\parallel}$ at low concentrations of D5BA in CPB, as well as the value of ε in the isotropic phase of one of these mixtures. The frequency dependence is more pronounced at higher temperatures and persists in the isotropic phase. The similarity of this dependence in the nematic and isotropic phases implies that the effect is

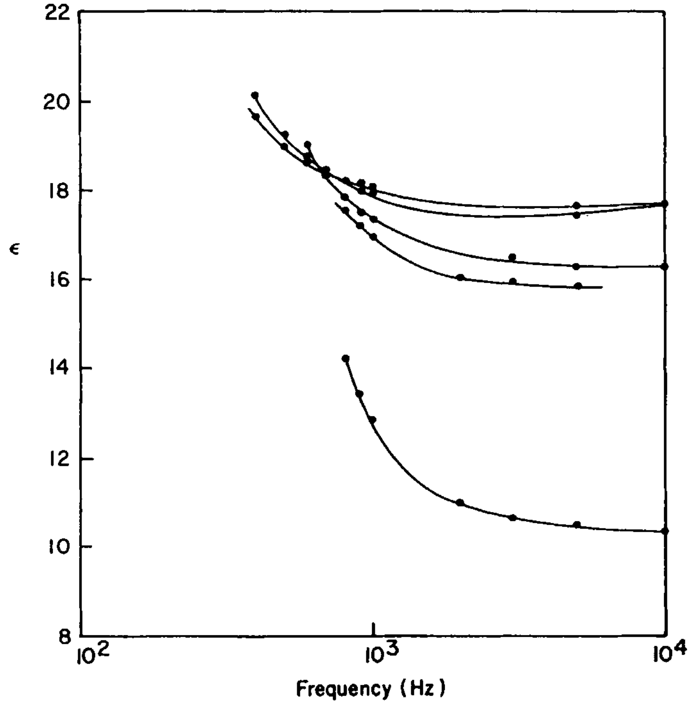

FIGURE 3 Dielectric constant ε as a function of log frequency (Hz). Reading from bottom to top, lower two curves: 2.61 mole % D5BA in CPB at 49° (isotropic, $\varepsilon_{\text{average}}$) and 38°C. Upper three curves: 2.08 mole % D5BA in CPB at 35°, 27° and 24°C, respectively.

due to short-range order effects,[20] that is, in some way involved with intermolecular association.

Leadbetter *et al.*[17] suggested that CPB molecules have a local order with a dimension of 100 molecules, and this local molecular order persists into the isotropic phase. Blumstein *et al.* reported an observation of cybotactic clusters in the nematic phase of *p*-*n*-octyloxy benzoic acid.[21] The presence of an induced smectic phase in mixing CPB and 5BA indicates that molecular association of CPB-D5BA occurs in addition to the CPB-CPB and D5BA-D5BA interactions. It is reasonable to expect this molecular association to persist in the isotropic state, and the extent of any molecular clusters to decrease with increasing temperature. Therefore, the frequency dependence may be due to the rotation of the effective dielectric components around the molecular axes coupled with the size of the molecular cluster and the viscosity of the material. A smaller extent of clustering and a a lower viscosity at a higher temperature give a narrower but more pronounced frequency dependence.

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