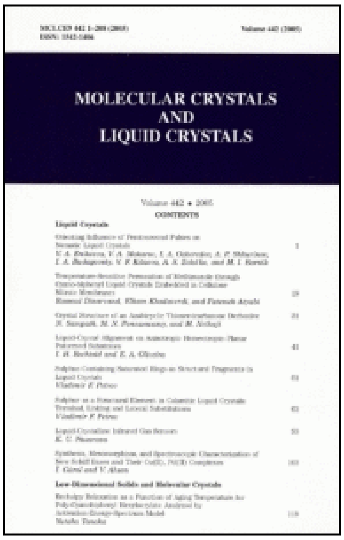

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Enhanced Smectic A Mesophase in Mixtures of Two Terminally Polar Compounds

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An enhanced smectic A phase has been observed in mixtures of two terminally polar compounds, viz, 5-(4-n butylphenyl)-2-(4-cyanophenyl)-pyrimidine (4 PCPP) and n-dodecyl-4-(4′-nitrobenzoyloxy) benzoate (12 NBOB). The former is a nematogen and the latter non-mesomorphic with a hidden smectic A-isotropic transition. The smectic A-nematic transition boundary shows a parabolic shape, but with an unusually large tilt angle between the axis of the parabola and the composition axis. Mixtures in some composition range exhibit the reentrant nematic phase. Xray diffraction studies indicate that the smectic phase is of the A_d type. Low frequency dielectric constants and dispersion measurements of $\epsilon_\parallel$ are also reported.

INTRODUCTION

Compounds having three phenyl rings and two ester linkage groups with the dipoles opposing that of the end cyano or nitro group are known to exhibit a variety of smectic A phases.[1,2,3] In order to study the effect of molecular structure on the mesomorphic properties, we have synthesised several homologues of nitro compounds similar to the above but with only two phenyl rings.[4] Though none of them is mesogenic, when the twelfth homologue is mixed with even a few per cent of other nematogens with polar end groups, a smectic phase is ‘induced.’

Induced smectic phases are usually formed when weakly polar nematogens are mixed with nematogens with highly polar end groups (HPEG).[5] Charge transfer complex formation between the two species appears to favor the formation of the layered phases.[6] The smectic

A phase exhibited by many compounds with HPEG is of the A_d type. In binary mixtures of these with purely nematogenic compounds having HPEG the AN transition boundary often has a parabolic shape, resulting in the occurrence of a reentrant nematic phase for certain composition ranges.[7,8] Usually in such systems the AN transition point T_{AN} decreases as the concentration of the pure nematogen is increased. But in the phase diagram of a similar system, to be reported in this paper, we find a considerable enhancement in T_{AN} before it turns around and starts decreasing. We also report the smectic layer spacings and dielectric measurements for a few compositions.

EXPERIMENTAL

The compound 5-(4-n-butylphenyl)-2-(4-cyanophenyl)-pyrimidine (4PCPP) was obtained from Hoffmann-La Roche and used without further purification. n-Dodecyl-4-(4'-nitrobenzoyloxy) benzoate (12 NBOB) was synthesised in our laboratory using standard procedures. It was first purified by column chromatography on silica gel using benzene as eluant. It was further purified by recrystallization from absolute ethanol. The structural formulae and the transition temperatures are given in Figure 1. The transition temperatures of the mixtures were determined using a Mettler FP52 hot stage and a polarizing microscope. The Xray studies were made on samples taken in Lindemann capillary tubes. Copper K_α radiation reflected off a bent quartz crystal monochromator was allowed to fall on the magnetically aligned sample. The diffraction patterns were recorded photographically. The low frequency principal dielectric constants were measured at 1592Hz using a Wayne Kerr (B642) bridge. The dis-

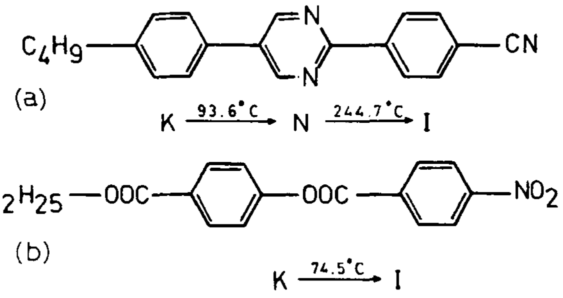

FIGURE 1 Structural formulae and transition temperatures of (a) 5-(4-n-butylphenyl)-2-(4-cyanophenyl)-pyrimidine (4 PCPP). (b) n-Dodecyl-4-(4'-nitro benzoyloxy)benzoate (12 NBOB).

persion studies up to 13 MHz were carried out with a Hewlett Packard L.F. impedance analyser (4192 A). Both the static and dispersion studies were made on samples taken between two aluminium coated glass plates separated by mylar spacers of ~ 125 μm thickness. A 14 KGauss magnetic field was used to align the samples so that the same sample could be used for measuring the principal dielectric constants parallel and perpendicular to the director. The cell was inserted into the heater assembly which was evacuated to remove any air bubbles present in the sample and then flushed with nitrogen. The temperature was recorded using a copper constantan thermocouple.

RESULTS AND DISCUSSION

As can be seen from the structural formula (Figure 1), in 4 PCPP the dipole moments of the pyrimidine bonds reinforce that of the cyano end group. The nematic-isotropic transition point of this compound is rather high (244.7°C). In 12 NBOB the two ester dipoles are opposed to that of the nitro end group. The compound is nonmesomorphic. We could supercool the isotropic phase down to only about 45°C.

The phase diagram of the binary mixtures of 4 PCPP and 12 NBOB is shown in Figure 2. Addition of even ~ 6% of 4 PCPP leads to the formation of a monotropic A phase in 12 NBOB. The AI transition point increases with increase of 4 PCPP content, and it becomes enantiotropic at ~ 70% of 12 NBOB. By extrapolating the AI transition curve back to pure 12 NBOB, one gets a 'hidden' AI transition point at ≃ 40°C. As mentioned earlier, we could not supercool the isotropic phase of 12 NBOB to this temperature. The N phase appears for compositions with <~ 65% of 12 NBOB and the NI transition temperature increases very steeply with further decrease of 12 NBOB content. At the same time, the AN transition boundary develops a curvature towards the composition axis and it becomes parabolic with the axis of the parabola tilted at a considerable angle. The A phase does not exist for <~ 37% of 12 NBOB and the mixtures having just higher 12 NBOB content exhibit the reentrant nematic phase (N_R). The N_RA transition is monotropic for all compositions. Both the NI and AI transitions are broad, with a considerable temperature range of coexistence of two phases. On the other hand, the AN transitions are quite sharp. The initial enhancement in the thermal stability of the A phase with an increase in the 4 PCPP content, and the fact that T_{AN} attains the (broad) maximum value for the 50 mole percent

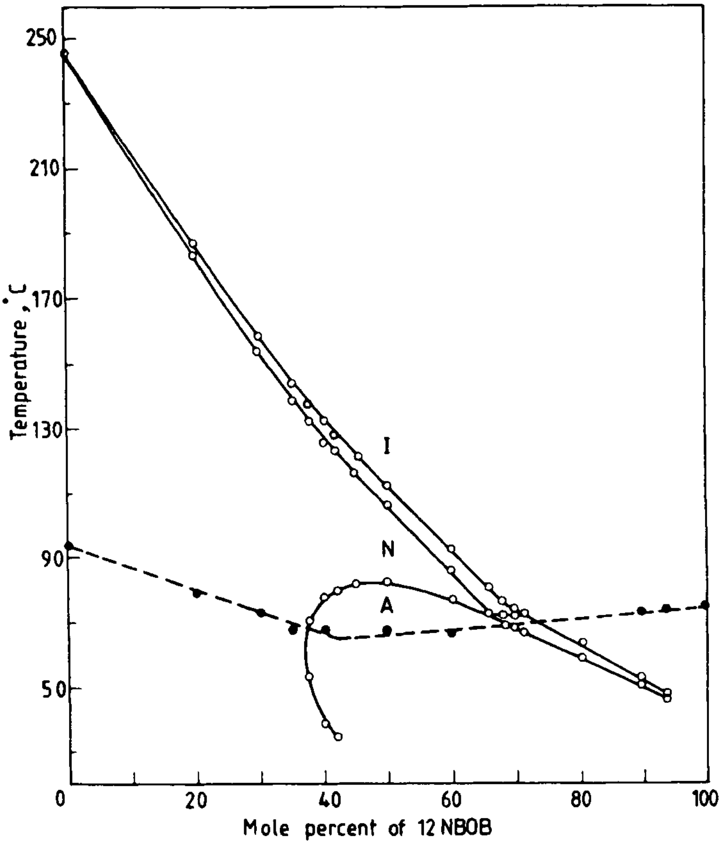

FIGURE 2 The phase diagram of mixtures of 4 PCPP and 12 NBOB. The melting curve is shown as dashed lines (The AN and AN_R coexistence ranges are less than 1°C).

mixture indicate that there may be specific interactions between the two types of molecules favoring the stability of the A phase. These features are usually observed in binary mixtures of highly (terminally) polar mesogens with weakly or nonpolar ones. Charge-transfer complex formation between the two types of molecules is responsible for this behavior.[6] Therefore it is possible that charge-transfer complexes are formed in the system under study. The results of the dielectric studies reported later in the paper further support this conclusion. Since both the components of this system possess highly polar end groups it is difficult to identify the donor and the acceptor. But the difference in the orientation of different dipoles in these two molecules may be of importance in this context. A nitro compound with a similar structure as 12 NBOB but with three phenyl rings and an alkoxy chain is known to exhibit two reentrant nematic phases.[9] The absence of the third phenyl ring in 12 NBOB apparently adversely affects its potential to form mesophases.

The most significant feature of the phase diagram (Figure 2) is the tilt of the axis of the parabolic AN transition curve. The 'enhancement' of the A phase may be a consequence of the steepness of the NI boundary. In this context it may be noted that Keyes[10] has recently developed a Landau theory of the reentrant nematic phase by including a term coupling the nematic and smectic order parameters. This would imply that the shape of the AN boundary would be strongly influenced by that of the NI boundary as found in the present investigation.

The temperature variations of the layer spacings (d) in the A phase of several compositions are shown in Figure 3. The mixture with 40% 12 NBOB which exhibits a reentrant nematic phase, has a small

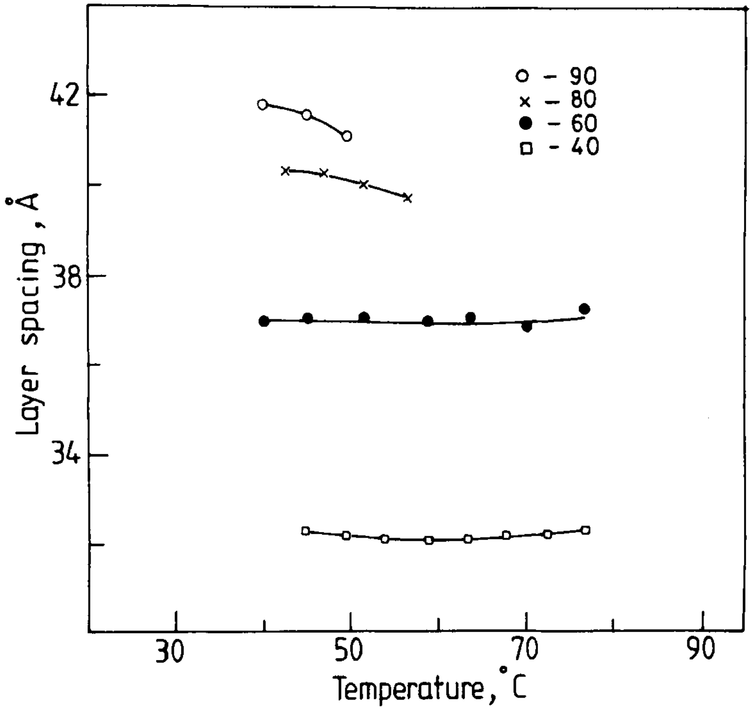

FIGURE 3 Temperature variation of the smectic layer spacing of a few mixtures of 4 PCPP and 12 NBOB. Numbers against the symbols indicate the mole percent of 12 NBOB.

thermal variation of *d* but shows a broad minimum in the middle of the smectic range, in agreement with earlier studies on some reentrant compounds.[11] When the 12 NBOB content is more than 80%, the layer spacing decreases with temperature, as in compounds with basically similar structure.[3,12] The molecular lengths (*l*) of both the components were found using Dreiding models. It is 21.8 Å for 4 PCPP and 32 Å for 12 NBOB. The *d/l* ratio is plotted as a function of composition at $T_{AN} - T = 2°C$ in Figure 4. It is ~1.23 for the mixture with 40% 12 NBOB and increases with increase of 12 NBOB content, up to ~60% 12 NBOB, after which it saturates at ~1.32. We can compare the *d/l* value of the 12 NBOB rich mixtures with those of similar compounds with three phenyl rings. 4-n-Octyl-phenyl-4′-(4″-nitrobenzoyloxy)benzoate ($DB8NO_2$) shows an A_d phase with *d/l* ~ 1.45,[13] while 4-n-nonyloxyphenyl-4′-(4″-nitrobenzoyloxy)benzoate ($DB9ONO_2$) exhibits a similar phase with *d/l* ~ 1.24,[9] the latter compound exhibiting a rich polymesomorphism. The reduction of the number of phenyl rings to two reduces the smectic-isotropic transition temperature so strongly as to make it unobservable in pure 12 NBOB.

The low frequency dielectric constants are shown in Figures 5 and 6 for two compositions. The mixture with 70% 4 PCPP has a large dielectric anisotropy ($\Delta\epsilon$), as the 4 PCPP molecule has a large longitudinal dipole moment. The large NI coexistence range (Figure 2) results in a smooth variation of $\epsilon_{\parallel}$ and $\epsilon_{\perp}$ values across the broad

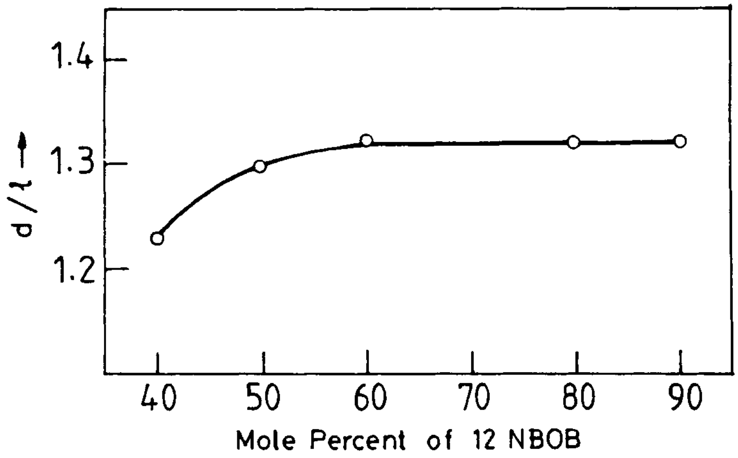

FIGURE 4 Variation of *d/l* ratio with concentration of 12 NBOB. *d* value of each mixture corresponds to the temperature $T = T_{NA} - 2°C$. The *l* values of the mixtures are calculated as the weighted sum of the component values.

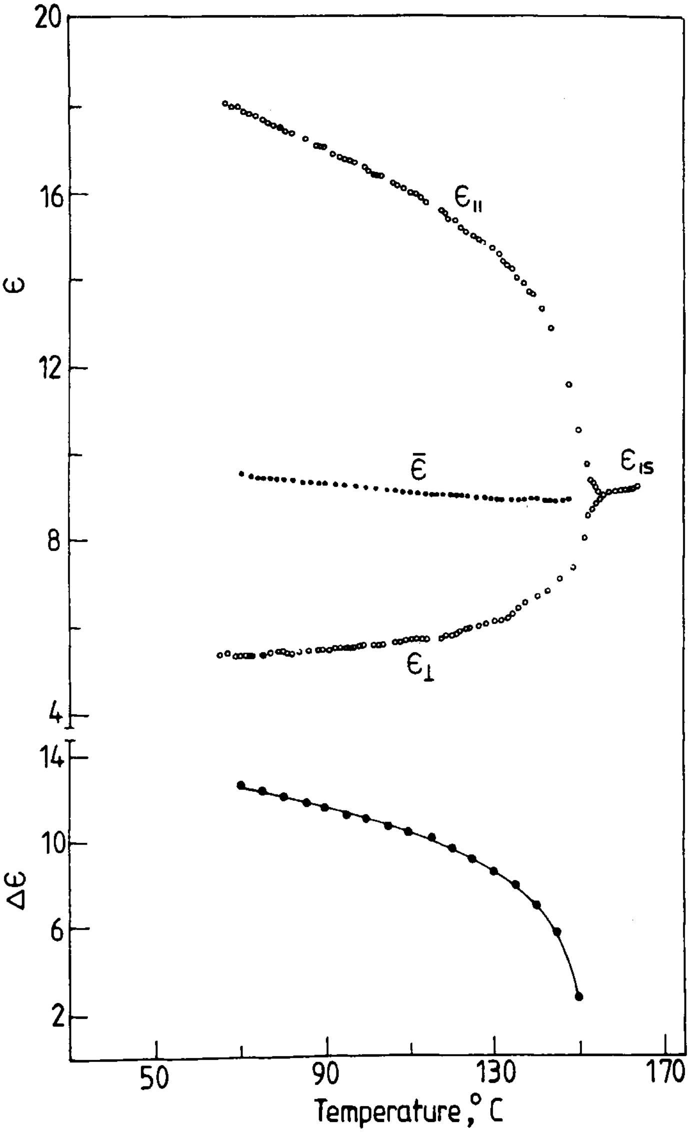

FIGURE 5 The low frequency principal dielectric constants and the dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) at 1592 Hz of the 70% 4 PCPP mixture as functions of temperature.

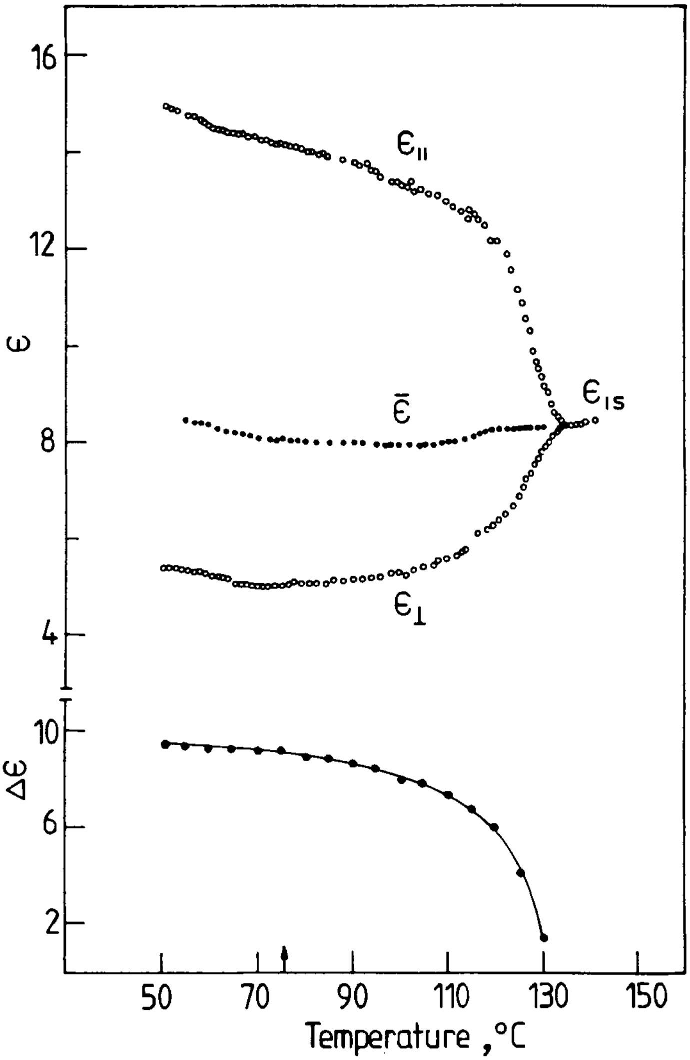

FIGURE 6 The low frequency principal dielectric constants and the dielectric anisotropy ($\Delta\epsilon = \epsilon_{\parallel} - \epsilon_{\perp}$) at 1592 Hz of the 60% 4 PCPP mixture as functions of temperature. The vertical arrow on the temperature axis indicates the nematic-smectic transition point.

transition region. ϵ_{is} increases with increase of temperature due to a reduction of antiparallel correlations between neighbouring molecules.[14] However, $\bar{\epsilon}$ $(=\epsilon_{\parallel}+2\epsilon_{\perp}/3)$ in the nematic phase shows a decrease with temperature, probably implying that the associations between neighbors in the highly polar 4 PCPP component is essentially unaffected by the increase of temperature in the orientationally ordered nematic phase.

The mixture with 60% 4 PCPP (see Figure 6) could not be supercooled below about 50°C in the dielectric cell. A curious result in this mixture is an *increase* of $\epsilon_{\perp}$ as the temperature is lowered in the A phase. This again may be attributed to the formation of charge-transfer complexes in the mixture which would increase the transverse polarizability.[15]

The dielectric dispersion of $\epsilon_{\parallel}$ is shown in Figure 7 for a mixture with 50% 12 NBOB, in the form of a Cole-Cole plot. It is interesting to note that even though the mixture has equal proportions of two different components with different molecular lengths the dispersion is characterized by a single relaxation time and the Cole-Cole plots give good semicircular plots, with the centres lying only slightly below the ϵ' axis. We have listed in table I the relaxation frequencies (f_R) at $T_{NI} - T = 25°C$ and the activation energies of mixtures with 30, 40 and 50 mole per cent of 12 NBOB. There is a reduction in f_R and an increase in the activation energies as the 12 NBOB content is increased (up to 50%). These trends appear to confirm that the two types of molecules have specific interactions like charge-transfer complex formation and indicate that the molecular complex responds as a unit to the external A.C. field.[16] The activation energies have values typical of similar systems and as is observed for several other com-

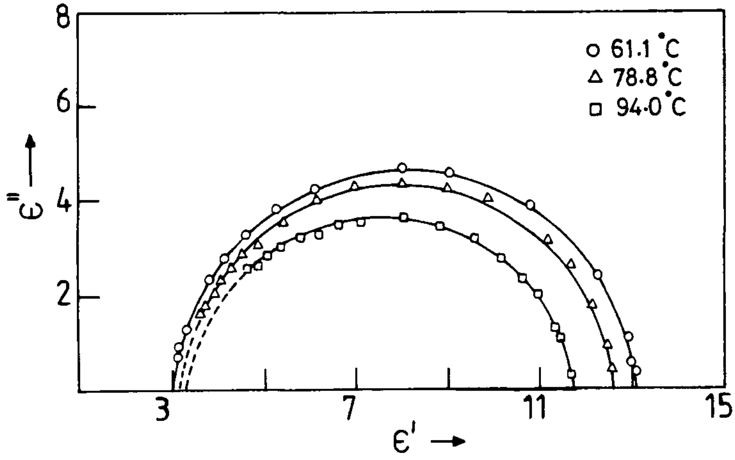

FIGURE 7 Cole-Cole plots for $\epsilon_{\parallel}$ relaxation in the 50% 12 NBOB mixture at three different temperatures.

TABLE I

The relaxation frequency (at $T_{NI} - T = 25°C$) and the activation energies of a few mixtures of 4 PCPP and 12 NBOB

Molar percent of 12 NBOB	Relaxation frequency in MHz at $T_{NI} - T = 25°C$	Activation energy eV	
		Nematic phase	Smectic phase
30	12.4[a]	0.56	-
40	6.5	0.60	0.56
50	3.3	0.65	0.60

[a] extrapolated

pounds and mixtures, it is lower in the smectic A phase than in the nematic phase.[17-19]

In conclusion, 12 NBOB has a hidden smectic A phase which becomes evident on mixing it with even a very small quantity of a second polar compound. Our studies on mixtures of the former with 4PCPP show some interesting features like a tilt of the axis of the parabolic AN phase boundary and also indicate the presence of specific interactions between the two types of molecules.

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