Appendix 1

APPENDIX 1

ENHANCED SMECTIC A MESOPHASE IN MIXTURES OF TWO TERMINALLY POLAR COMPOUNDS

INTRODUCTION

Compounds having three phenyl rings and ester linkage groups with the dipoles opposing that of the end cyano or nitro groups 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, several homologues of nitro compounds similar to the above but with only two phenyl rings have been synthesized in our laboratory [4]. Though none of them is mesogenic, when the twelfth homologue is mixed with even a few percent 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 favour 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, described below, we find a considerable enhancement in T_{AN} before it turns around and starts decreasing. We have also measured the smectic layer spacings and the dielectric constants for a few compositions.

EXPERIMENTAL

The compound 5-(4-n-butylphenyl)-2-(4-cyanophenyl)-pyrimidine (4PCPP) was obtained from Hoffman-La Roche and was used without further purification. n-dodecyl-4-(4'-nitrobenzoyloxy) benzoate (12 NBOB) was synthesized 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 Fig. 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 1592 Hz using a Wayne Kerr (B642) bridge. The dispersion 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 about 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 normal 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-constanton thermocouple.

RESULTS AND DISCUSSION

As can be seen from the structural formula (Fig. 1), in 4PCPP 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 at 244.7°C. In 12 NBOB the two ester dipoles are opposed to that of the nitro end group. The compound is non-mesomorphic. 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 Fig. 2. Addition of even about 6% of 4 PCPP leads to the formation of a monotropic smectic A phase in 12 NBOB. The IA transition point increases with increase of 4 PCPP content, and it becomes enantiotropic at about 70% of 12 NBOB. By extrapolating the IA transition curve back to pure 12 NBOB, one gets a 'hidden' IA transition point at about 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 less than about 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 less than about 37% of 12 NBOB and the mixtures having just higher 12 NBOB content exhibit the reentrant nematic phase (N_R). The A - N_R transition is monotropic for all compositions. Both the NI and AI transitions are broad, with a considerable temperature range of coexistence of the two phases. On the other hand, the AN transitions are quite sharp. The initial

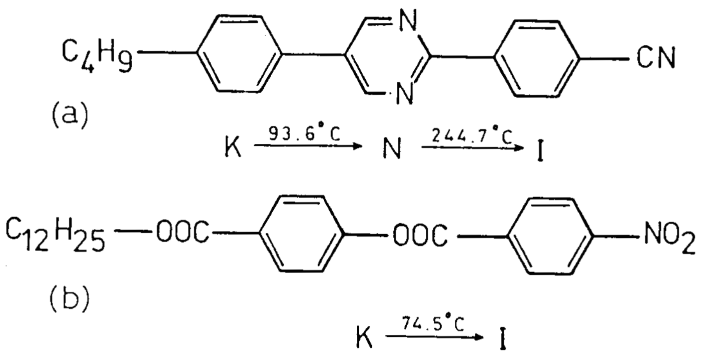

Fig.1. Structural formulae and transition temperatures of (a) 5-(4-n-butylphenyl)-2-(4-cyanophenyl)-pyrimidine(4 PCPP) and (b) n-dodecyl-4-(4'-nitrobenzoyloxy)bencoate (12 NBOB).

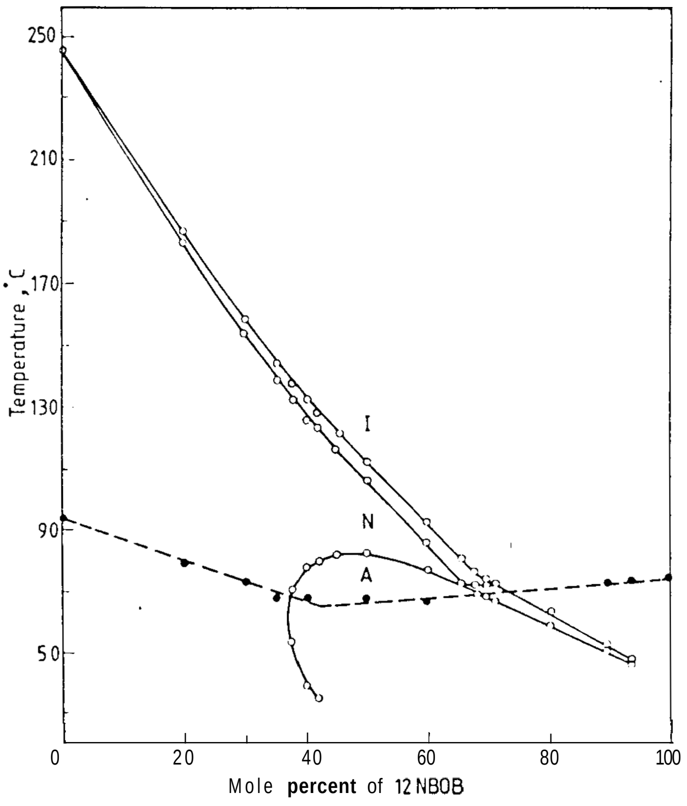

Fig.2. The phase diagram of mixtures of 4 PCPP and 12 NBOB. The melting curve is shown in dashed lines. (The AN and AN_R coexistence ranges are less than 1°C).

enhancement in the thermal stability of the A phase with an increase in the 4 PCPP content, and the fact that T_{NA} attains the (broad) maximum value for the 50 mole percent mixture indicate that there may be specific interactions between the two types of molecules favouring 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 behaviour [6]. Therefore it is possible that charge-transfer complexes are formed in the system under study. The results of the dielectric. studies discussed later 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 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 (Fig. 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 variation of the layer spacings (d) in the A phase of several compositions are shown in Fig. 3. The mixture with 40% 12 NBOB which exhibits a reentrant nematic phase, has a small 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 13,121. The molecular length (l) of both the components were found using the 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} = 2°C in Fig. 4. It is about 1.23 for the mixture with 40% of 12 NBOB and increases with increase of 12 NBOB content up to about *60%* of the latter compound after which it saturates at about 1.32. We can compare the d/l values of the 12 NBOB rich mixtures with

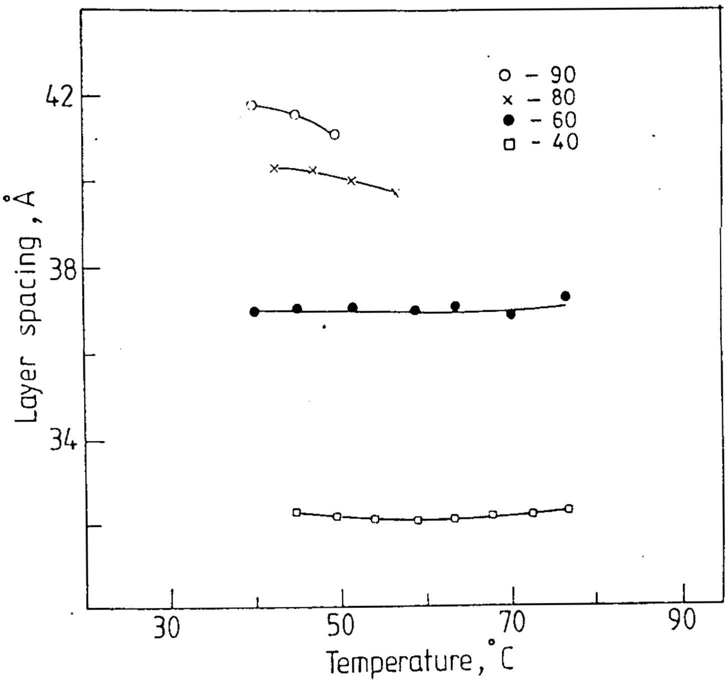

Fig.3. Temperature variation of the smectic layer spacing of a few mixtures of 4 PCPP and 12 NBOB. Numbers against the symbols indicate the mole percent of 12 NBOB.

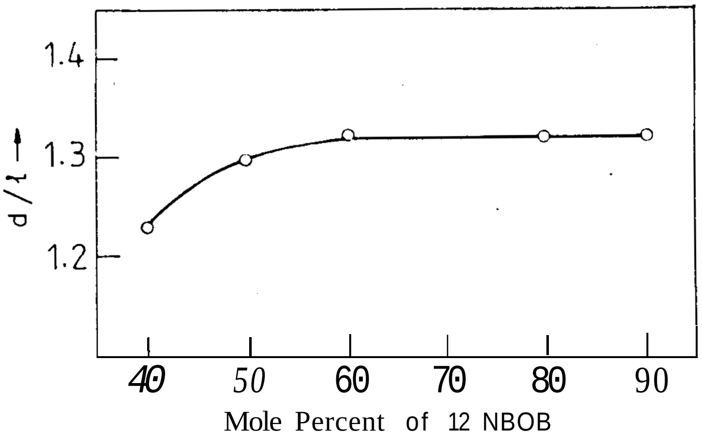

Fig.4. Variation of d/l ratio with the concentration of 12 NBOB. d value of each mixture corresponds to the temperature T □ T_{NA} - 2°C. The 1 values of the mixtures are calculated as the sum of the component values multiplied by the mole fractions.

those of similar compounds with three phenyl rings. DB8NO$_2$ which has an octyl chain shows an A_d phase with d/l ratio about 1.45 [13], while DB9ONO$_2$ with a nonyloxy chain exhibits a similar phase with d/l about 1.25 [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 Figs. 5 and 6 for two compositions. The mixture with 70% 4 PCPP has a large dielectric anisotropy (ϵ_a), as the 4 PCPP molecule has a large longitudinal dipole moment. The large NI coexistence range (Fig.2) results in a smooth variation of $\epsilon_\parallel$ and $\epsilon_\perp$ values across the broad transition region. ϵ_{is} increases with increase of temperature due to a reduction of antiparallel correlations between neighbouring molecules [14]. However, $\langle\epsilon\rangle = (\epsilon_\parallel + 2\epsilon_\perp)/3$ in the nematic phase shows a decrease with temperature, probably implying that the association between neighbours 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% 4PCPP (see Fig. 6) could not

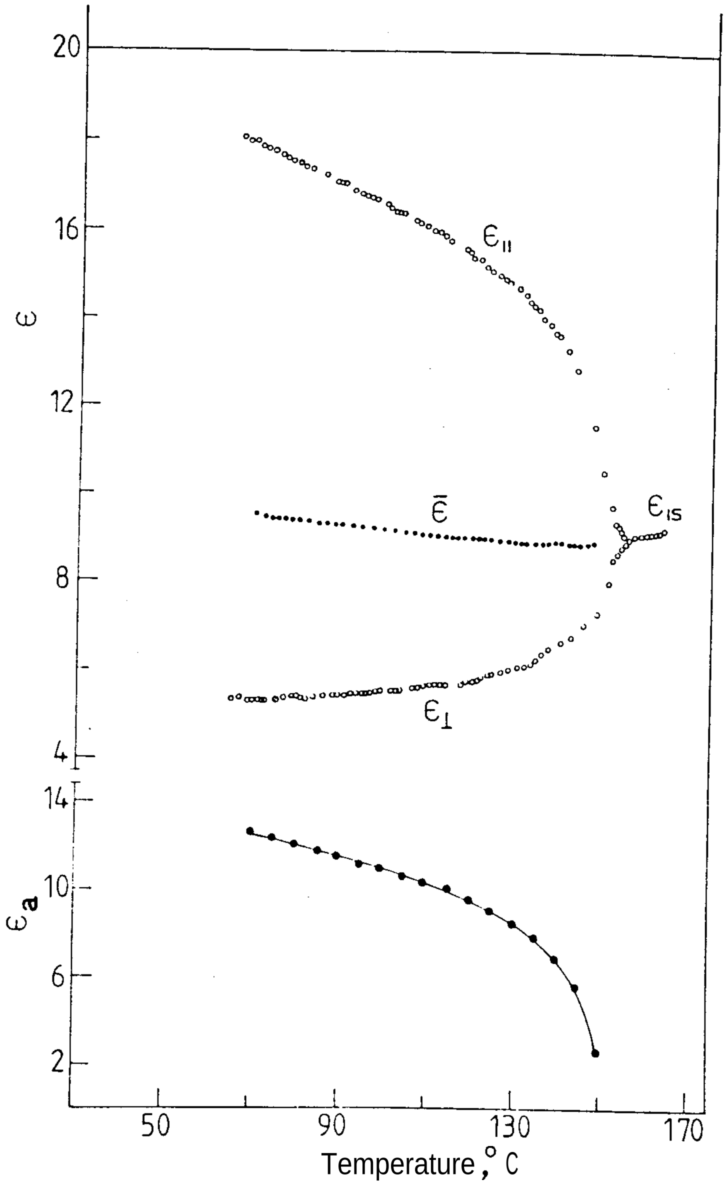

Fig.5. The low frequency principal dielectric constants and the dielectric anisotropy at 1592 Hz of the 70% 4 PCPP mixture as a function of temperature.

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 Fig. 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 plot gives good semicircular plots, with the centres lying only slightly below the ϵ' axis. We have listed in table 1 the relaxation frequencies (f_R) at $T_{NI} - T = 25°C$ and the activation energies of mixtures with 30, 40 and 50 mole percent 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 AC field [16]. The activation energies have values typical of similar systems and as is observed for

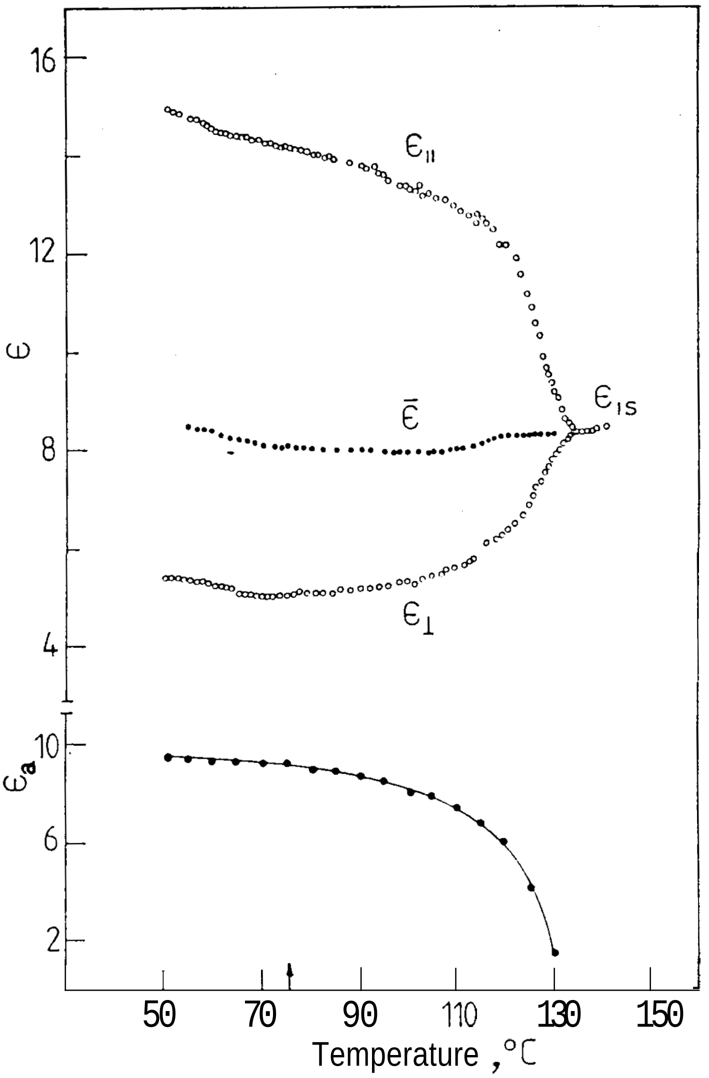

Fig.6. The low frequency principal dielectric constants and the dielectric anisotropy at 1592 Hz of the 60% 4 PCPP mixture as a function of temperature. The vertical arrow on the temperature axis indicates the nematic -smectic transition point.

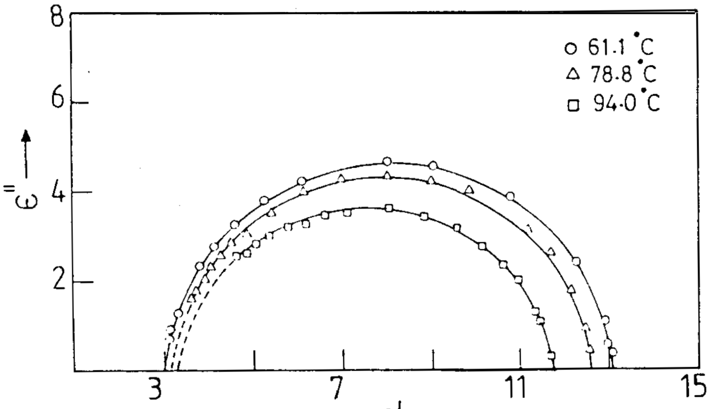

Fig.7. Cole - Cole plots for $\epsilon_{\parallel}$ relaxation in the 50% 12 NBOB mixture at three different temperatures.

TABLE 1

Mole % of 12 NBOB	Relaxation frequency at $T_{NI} - T = 25°C$ (MHz)	Activation Energy (eV)	
		Nematic Phase	Smectic A Phase
30	12.4 *	0.56	-
40	6.5	0.60	0.56
50	3.3	0.65	0.60

* Extrapolated

The relaxation frequency and the activation energies of a few mixtures of 4 PCPP and 12 NBOB.

several other compounds 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 4 PCPP 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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Appendix 2

APPENDIX 2

INDUCTION OF SMECTIC C PHASE IN BINARY MIXTURES OF COMPOUNDS WITH CYANO END GROUPS

INTRODUCTION

Mesomorphic compounds with strongly polar cyano end group exhibit a variety of interesting phenomena. Neighbouring molecules of such compounds tend to align with an antiparallel configuration [1,2] to minimize the mutual interaction energy. Generally this leads to the formation of bilayers, with an interdigitation of parts of neighbouring molecules [3,4]. The bilayer spacing depends upon the molecular structure of the compounds. In earlier studies in our laboratory, certain interesting properties were found in compounds with two ester linkages and a lateral methyl group in the aromatic core. For example, 12 CPMBB (Fig. la) has the ester dipole moments acting parallel to that of the cyano end group. The compound exhibits the reentrant nematic phase at temperatures lower than those corresponding to the stability of the smectic A phase [5]. Further, Xray studies [6] (Fig. 4) reveal that the bilayer spacing d ≈ 1.3 1 where 1 is the molecular length as calculated using Drieding models. If we now interchange the two end groups, the resulting 12 PMCBB (Fig. 1b) has the ester group dipole moments in an antiparallel alignment with reference to that of the terminal cyano group. **12 PMCBB** exhibits a very large bilayer spacing (≈ 1.7 1) at the lowest temperature of measurement, which decreases rapidly as the temperature is raised in the A phase [7]. Further, the layer spacing vs. temperature diagram exhibits a slope change indicative of a possible A_d-A_2 transition (Fig. 4).

A physical model to account for these observations was proposed in Ref. 7 . While neighbouring **12 CPMBB** molecules would prefer to have interdigitation of the entire aromatic cores to minimize the interaction energy, such a structure would lead to a strongly repulsive dipolar energy between the cyano group and an ester group of the neighbouring molecules in the case of **12 PMCBB** (Fig. 5).

Our studies on mixtures of **12 CPMBB** with **12 PMCBB** are reported below. Unexpectedly, the mixtures exhibit an 'induced' smectic C phase over a fairly wide range of composition.

EXPERIMENTAL

The compounds were synthesized in our chemistry laboratory and the details of the synthesis are reported elsewhere [5,8]. The mixtures were made by weighing definite proportions of the compounds and physically mixing them in the isotropic phase. The transition temperatures were determined using a Mettler FP52 hot stage used in conjunction with 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 temperature of the sample was measured using a copper-constanton thermocouple.

RESULTS AND DISCUSSION

Many of the mixtures exhibit striped focal conic domains and the schlieren texture characteristic of the C phase when cooled from the A phase (Fig. 2). When observations are made between crossed polarizers on homeotropically aligned regions of the A phase, the A-C transition is heralded by the appearance of a faint whitish background, the intensity of the transmitted light increasing at lower temperatures. This is caused by the increase of the **tilt** angle of the molecules as the temperature is lowered in the C phase.

The phase diagram of the mixtures is shown in Fig. 3. All the transition temperatures correspond to those

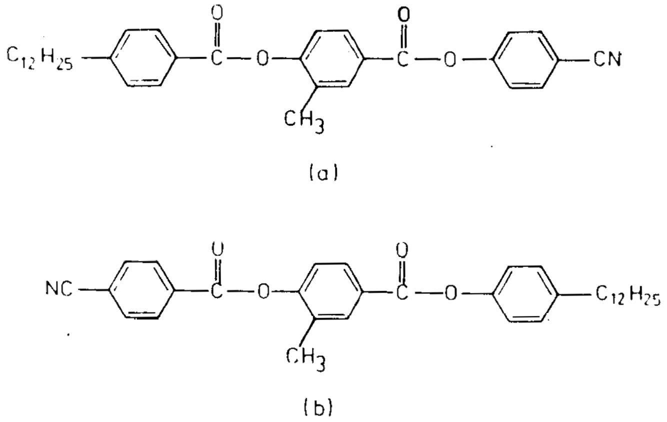

Fig.1. Structural formulae of (a) 4-cyanophenyl-3'-methyl-4'(4"-n-dodecylbenzoyloxy)benzoate (12 CPMBB) and (b) 4-n-dodecylphenyl-3'-methyl-4'(4"-cyanobenzoyloxy)benzoate (12 PMCBB).

Fig.2. The schlieren texture of the smectic C phase of the 50% mixture of 12 CPMBB and 12 PMCBB.

recorded while cooling the sample. It is seen that mixtures with about 10% to a little over 65% of 12 PMCBB exhibit the C phase. As we noted earlier, pure 12 CPMBB exhibits the reentrant nematic (N_R) phase. The AN_R transition point decreases as 12 PMCBB is added to this compound, and the mixture with about 10% of 12 PMCBB exhibits the sequence A - C - N_R as it is cooled. Beyond about 15% of 12 PMCBB, the sample crystallises before it can be supercooled sufficiently to observe the CN_R transition. The AC transition temperature (T_{AC}) goes up slowly as the proportion of 12 PMCBB is increased, attaining a broad maximum at about 55% of the latter compound. The mixture with 80% 12 PMCBB did not exhibit the C phase though the A phase could be supercooled right down to the room temperature. It is interesting to note that the AN transition boundary shows a shallow minimum for the composition for which the A, C and N_R phases coexist at a certain temperature even though T_{AN} occurs at about 80°C above that temperature.

The temperature variation of the layer spacings of 12 CPMBB (taken from ref. 6), 12 PMCBB (taken from ref. 7) and a few mixtures are shown in Fig. 4. 12 CPMBB shows a broad minimum in the curve, the layer spacing increasing slightly as the temperature approaches both T_{AN_R} and

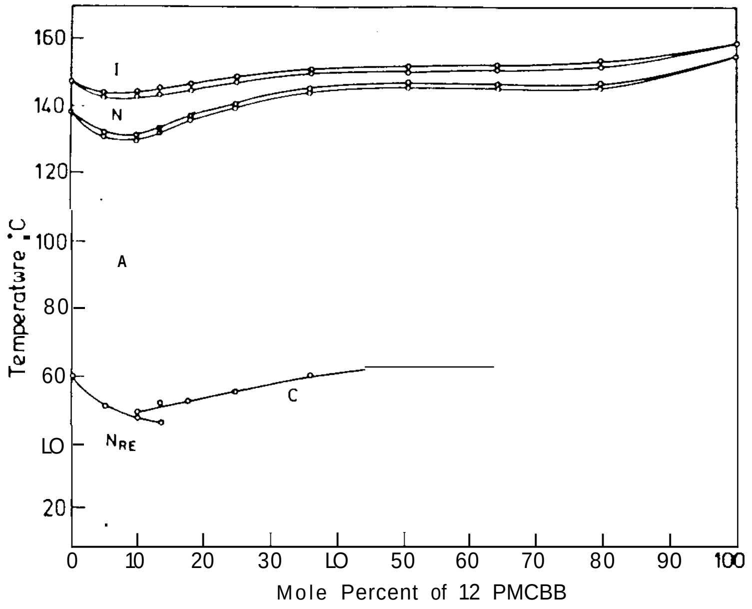

Fig.3. Phase diagram of the mixtures of 12 CPMBB and 12 PMCBB.

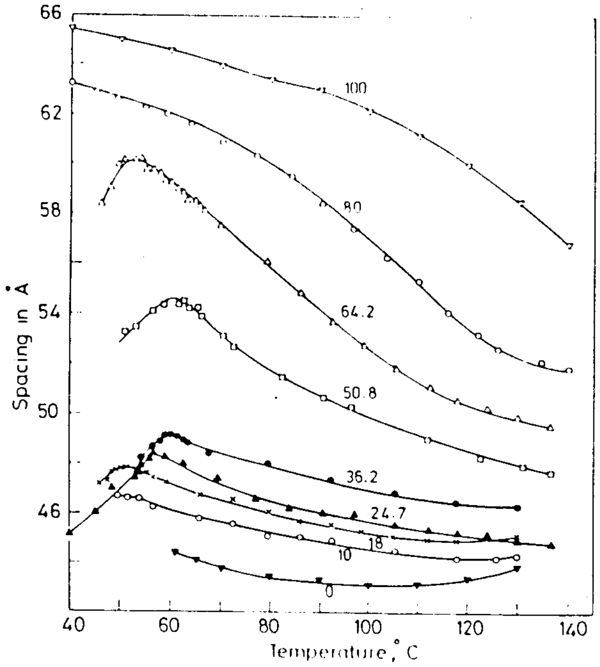

Fig.4. Temperature variation of the smectic layer spacing in mixtures of 12 CPMBB and 12 PMCBB. The number against each curve indicates the mole percent of 12 PMCBB in the mixture.

T_{AN}. 12 PMCBB shows a substantial increase in the layer spacing as the temperature is lowered. Further, a slope change in the curve indicates a possible A-A transition. Curiously, the mixture with 80% of 12 PMCBB shows an even larger increase in layer spacing over a similar temperature range (Fig. 4). In the case of the mixture with 65% of 12 PMCBB also, the layer spacing expands substantially on cooling the sample, the rate of expansion increasing as the temperature is lowered, unlike in the case of mixtures with larger proportion of 12 PMCBB. Further, in the former case the layer spacing goes through a well defined maximum at about 52.5°C and then starts decreasing with further lowering of temperature, indicating that the AC transition has taken place. A similar trend is noted for mixtures with 50, 36, 24.7 and 18 per cent of 12 PMCBB. The layer spacing generally decreases as the proportion of 12 PMCBB in the mixture is lowered, except for a cross over between the 24.7 and 18% mixtures close to T_{AN}. However, the peak values show a monotonically decreasing trend.

The Xray diffraction photographs show a clear cut broadening of the Bragg spots on going from the smectic A to the C phase. The second order reflection is strong for mixtures containing 80% and 65% of 12 PMCBB at low temperatures, both in the A and C phases. But for mixtures with lesser percentages of 12 PMCBB the second order reflection is not observed even at lower temperatures.

We have calculated the 'expected' values of layer spacings of the mixtures using those of the two pure compounds at the temperature corresponding to the peak in each case. The calculated value agrees with the measured value only for the 50% mixture. On the other hand, the calculated value is higher (lower) than the experimental value for mixtures with lower (higher) percentage of 12 PMCBB. Obviously mutual interactions between 12 CPMBB and 12 PMCBB molecules are important in the mixtures. We could visualise the formation of 12 CPMBB-12 PMCBB pairs with an antiparallel alignment. The energy of such a pair arises from (1) the strong anisotropic dispersion force between the aromatic parts of the molecules which favours a maximum overlap between the cores and (2) the interactions between the cyano and ester dipole moments of the two molecules which may be either attractive or repulsive. As we have mentioned earlier, two 12 CPMBB molecules would favour a complete overlap of the aromatic cores as in Fig. 5(a), while two 12 PMCBB molecules would favour an overlap only near the polar end groups as in Fig.5(b). The latter structure is fragile, since the interaction

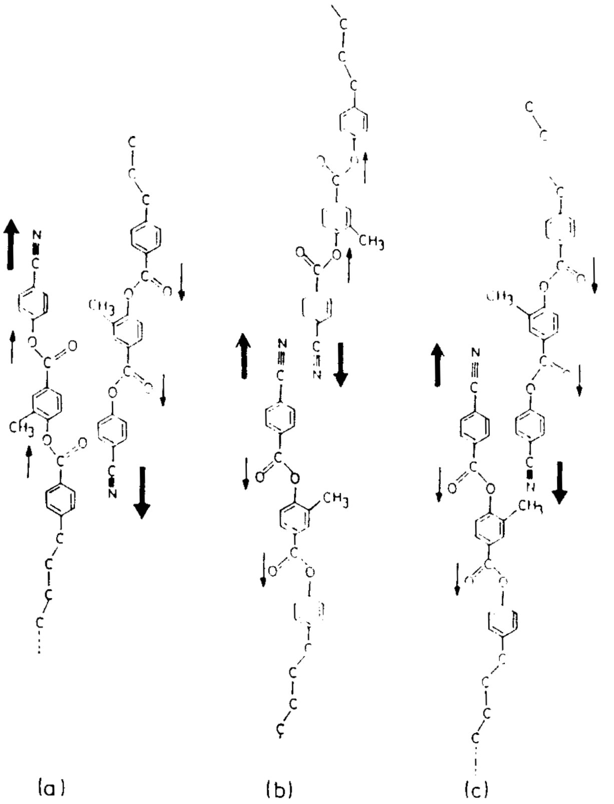

Fig.5. Schematic diagram of the proposed arrangement of (a) a pair of 12 CPMBB molecules, (b) a pair of 12 PMCBB molecules and (c) a 12 CPMBB molecule and a 12 PMCBB molecule.

holding the pair together is confined to one end of the molecule. Thus it can easily break up giving rise to the large thermal contraction of the layer spacing (Fig. 4). A simple estimate shows that if there is a complete overlap of the aromatic cores of a pair of 12 PMCBB and 12 CPMBB molecules, the net dipolar interaction is weakly positive. Probably the energy minimum occurs for a partial overlap of the cores as in Fig.5(c). This would lead to a bilayer thickness which is intermediate between those of 12 CPMBB and 12 PMCBB pairs. This structure could account for the deviations between the calculated and measured values of the layer spacings of the mixtures. Further, this structure should also be relatively fragile and the break up of the structure would contribute to the large temperature variation of the layer spacing of the mixtures.

We also notice from Fig. 5(c) that while the dipolar interaction between the cyano group of the 12 PMCBB molecule and one of the ester groups of the 12 CPMBB molecule is attractive, that between the cyano group of the 12 CPMBB molecule and an ester group of the 12 PMCBB molecule is repulsive. It is thus likely that such a structure would be splayed, with the two molecules not being exactly antiparallel to each other. This may in turn be partly responsible for the occurrence of the smectic C phase over a considerable composition range of the mixtures. As the temperature is lowered, the number of pairs of molecules with the structure of Fig. **5(c)** should increase, contributing firstly to the layer expansion, and as the number reaches some critical value, to the tilted structure characteristic of the C **phase.As** the temperature is lowered in the C phase, **it** is very likely that the number of pairs of 12 **PMCBB - 12 CPMBB** as well as two 12 **PMCBB** molecules continues to increase. Hence we have not tried to calculate the **tilt** angles from the measured layer spacings.

It is worthwhile noting that in some earlier work where binary mixtures of cyano compounds one of which exhibits the C phase have been studied, the latter phase does not extend over a wide composition range of the mixtures [9].

In conclusion, mutual dipolar interaction between the 12 **CPMBB** and **12 PMCBB** molecules appears to be responsible for the induction of the tilted smectic C phase.

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