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## Induction of Smectic C Phase in Binary Mixtures of Compounds with Cyano End Groups

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We have studied binary mixtures of 4-cyanophenyl-3'-methyl-4'(4''-*n*-dodecylbenzo-yloxy)benzoate (12 CPMBB) and 4-*n*-dodecylphenyl-3'-methyl-4'(4''-cyanobenzo-yloxy)benzoate (12 PMCBB). The former compound exhibits nematic, smectic A and reentrant nematic phases and the latter one nematic and smectic A phases with a possible  $A_A-A_2$  transition. Over a fairly wide composition range, the mixtures exhibit an induced smectic C phase on cooling the sample from the A phase. The phase diagram, and the temperature variations of the layer spacings for some specific compositions are reported. The possible origin of the C phase is also discussed.

### INTRODUCTION

Mesomorphic compounds with the strongly polar cyano end group exhibit a variety of interesting phenomena. Neighbouring molecules of such compounds tend to align with an antiparallel configuration<sup>1,2</sup> to minimize the mutual interaction energy. Generally this leads to the formation of bilayers, with an interdigitation of parts of neighbouring molecules.<sup>3,4</sup> The bilayer spacing depends on 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 (Figure 1a) 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

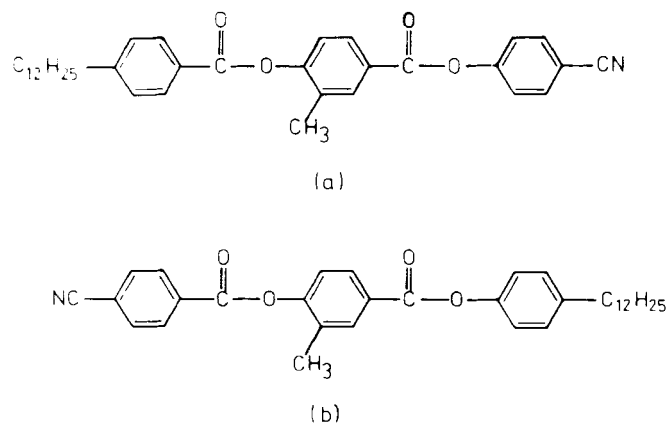


FIGURE 1 Structural formulae of (a) 4-cyanophenyl-3'-methyl-4''-(4'-*n*-dodecylbenzoxyloxy)benzoate (12 CPMBB), (b) 4-*n*-dodecylphenyl-3'-methyl-4''-(4'-cyanobenzoxyloxy)benzoate (12 PMCBB).

smectic A phase.<sup>5</sup> Further, X-ray studies<sup>6</sup> (see Figure 4) reveal that the bilayer spacing  $d \approx 1.3 l$  where  $l$  is the molecular length as calculated using Dreiding models. If we now interchange the two end groups, the resulting 12 PMCBB (Figure 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 ( $\approx 1.7 l$  at the lowest temperature of measurement) which decreases rapidly as the temperature is raised in the A phase.<sup>7</sup> Further, the layer spacing vs. temperature diagram exhibits a slope change indicative of a possible  $A_d$ - $A_2$  transition (see Figure 4).

A physical model to account for these observations was proposed in Ref. 7. While neighbouring 12 CPMBB molecules would prefer to have an 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 (see Figure 5).

In this paper, we report our studies on mixtures of 12 CPMBB with 12 PMCBB. 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 synthesis are reported elsewhere.<sup>5,8</sup> The mixtures were made

by weighing definite proportions of the two 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 X-ray studies were made on samples taken in Lindemann capillary tubes. Copper  $K\alpha$  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-constantan thermocouple.

## RESULTS AND DISCUSSION

Many of the mixtures exhibit striped focal conic domains and the schlieren texture characteristic of the C phase when the sample is cooled from the A phase (Figure 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.

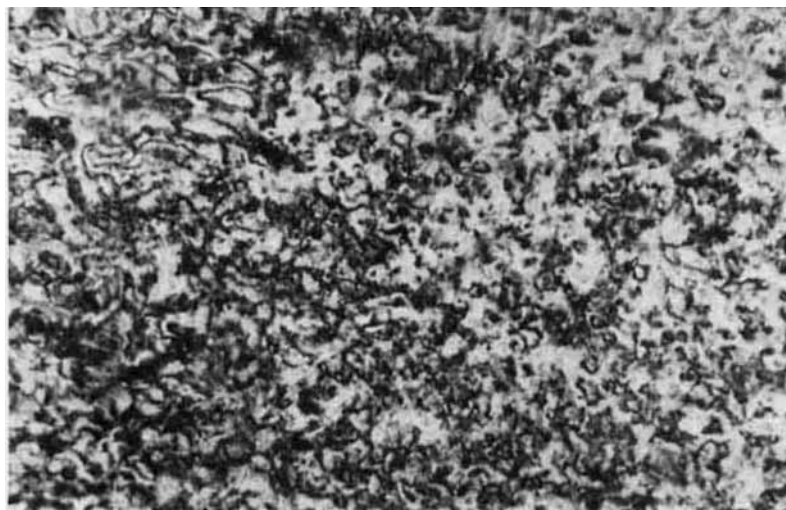


FIGURE 2 The schlieren texture of the smectic C phase of the 50% mixture of 12 CPMBB and 12 PMCB.

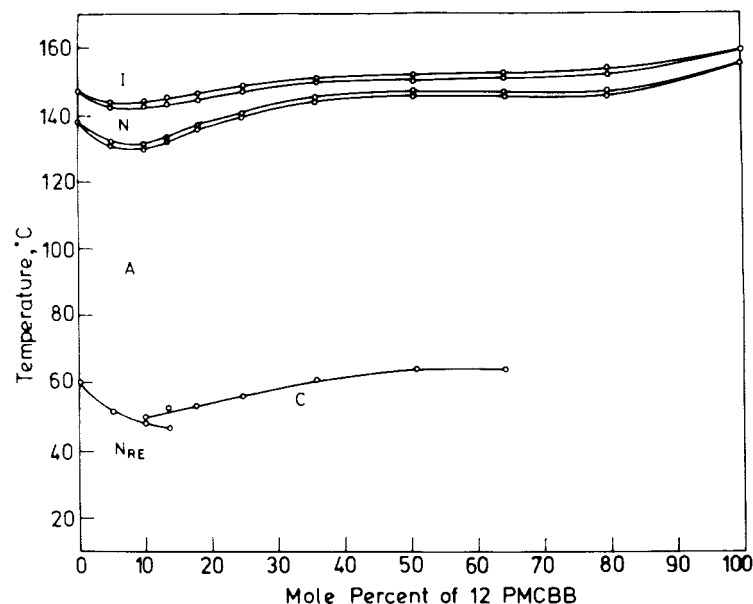


FIGURE 3 Phase diagram of the mixtures of 12 CPMBB and 12 PMCBB.

The phase diagram of the mixtures is shown in Figure 3. All the transition temperatures correspond to those recorded while cooling the sample. It is seen that mixtures with  $\sim 10\%$  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 ( $T_{AN_R}$ ) decreases as 12 PMCBB is added to this compound, and the mixture with  $\sim 10\%$  of 12 PMCBB exhibits the sequence A-C- $N_R$  as it is cooled. Beyond  $\sim 15\%$  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  $\sim 55\%$  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  $\sim 80^\circ\text{C}$  above that temperature.

The temperature variations of the layer spacings of 12 CPMBB (taken from Ref. 6), 12 PMCBB (taken from Ref. 7) and a few mixtures are shown in Figure 4. 12 CPMBB shows a broad minimum in the curve, the layer spacing increasing slightly as the temperature

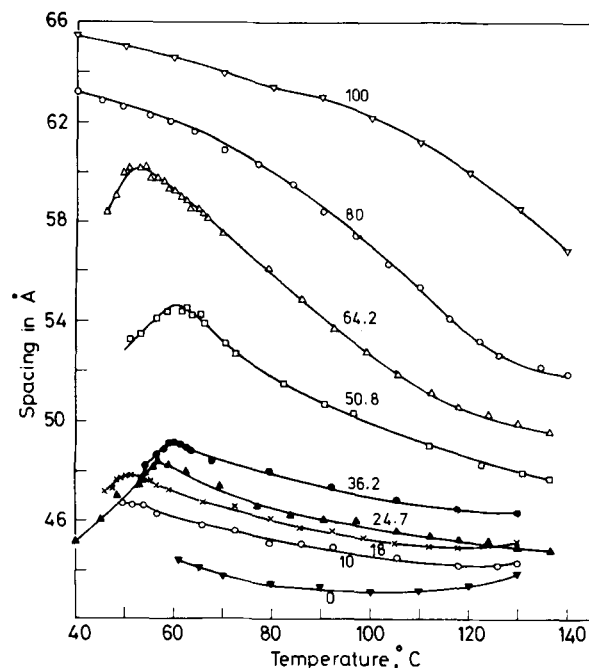


FIGURE 4 Temperature variation of the layer spacing in mixtures of 12 CPMBB and 12 PMCB. The number against each curve indicates the per cent of 12 PMCB in the mixture.

approaches both  $T_{AN}$  and  $T_{ANR}$ . 12 PMCB 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 PMCB shows an even larger increase in the layer spacing over a similar temperature range (Figure 4). In the case of the mixture with 65% of 12 PMCB 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 higher proportion of 12 PMCB. Further, in the former case the layer spacing goes through a well defined maximum at  $\sim 52.5^\circ\text{C}$  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 PMCB. The layer spacing generally decreases as the proportion of 12 PMCB 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 X-ray 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 PMCBP at low temperatures, both in the A and C phases. But for mixtures with lesser percentages of 12 PMCBP the second order reflection is not observed even at lower temperatures.

We have calculated the 'expected' values of the 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 PMCBP. Obviously mutual interactions between 12 CPMBP and 12 PMCBP molecules are important in the mixtures. We could visualise the formation of 12 CPMBP—12 PMCBP pairs with an antiparallel alignment. The energy of such a pair arises from (i) the strong anisotropic dispersion force between the aromatic parts of the molecules which favours a maximum overlap between the cores and (ii) the interactions between the cyano and ester dipole moments of the two molecules which may be either attractive or repulsive. As we mentioned earlier, two 12 CPMBP molecules would favour a complete overlap of the aromatic cores as in Figure 5(a), while two 12 PMCBP molecules would favour an overlap only near the polar end groups as in Figure 5(b). The latter structure is fragile, since the interaction 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 (Figure 4). A simple estimate shows that if there is a complete overlap of the aromatic cores of a pair of 12 CPMBP and 12 PMCBP molecules, the net dipolar interaction is weakly positive. Probably the energy minimum occurs for a partial overlap of the cores as in Figure 5(c). This would lead to a bilayer thickness which is intermediate between those of 12 CPMBP and 12 PMCBP 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 Figure 5(c) that while the dipolar interaction between the cyano group of the 12 PMCBP molecule and one of the ester groups of the 12 CPMBP molecule is attractive, that between the cyano group of the 12 CPMBP molecule and an ester group of the 12 PMCBP molecule is repulsive. It is thus likely that such a structure would be splayed, with the two molecules not being exactly antiparal-

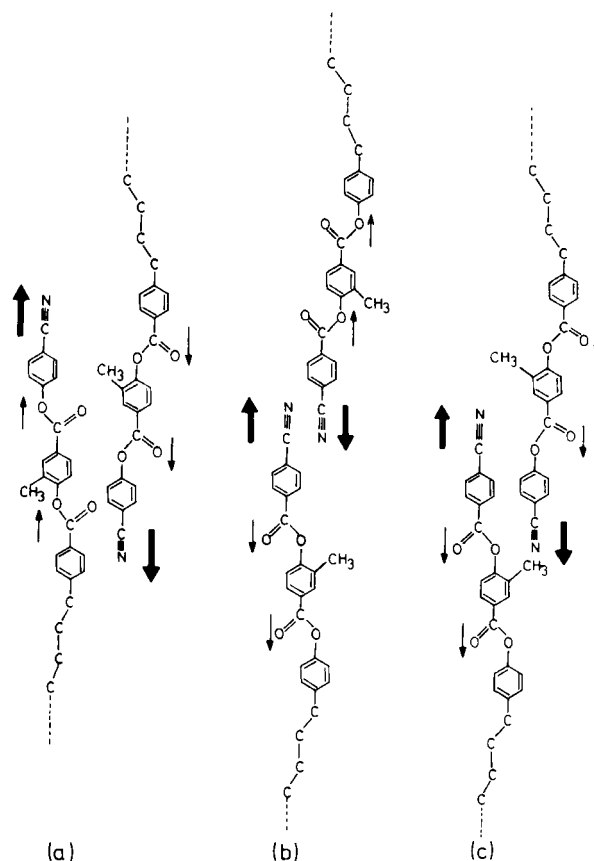


FIGURE 5 Schematic diagram of the proposed arrangement of (a) a pair of 12 CPMBB molecules, (b) a pair of 12 PMCBP molecules and (c) a 12 CPMBB molecule and a 12 PMCBP molecule.

lel 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 Figure 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 CPMBB—12 PMCBP as well as two 12 PMCBP molecules continue 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.<sup>9</sup>

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. Other physical studies on this and a few other mixtures showing similar phase diagrams are underway.

### Acknowledgment

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