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On the structure of binary mixtures of non-symmetric liquid crystal dimers: the α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-alkylanilinebenzylidene-4′-oxy) alkanes

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Liquid crystal dimers, in which two mesogenic groups are linked by a flexible spacer, exhibit a rich smectic polymorphism for both symmetric and non-symmetric dimers which differ in the nature of the mesogenic groups. For example, smectic phases having monolayer, interdigitated and intercalated structures have been discovered. We have extended our studies of such systems to binary mixtures in an attempt to understand the origin of the different phase structures at the molecular level. The dimers studied include non-symmetric systems differing in the parity of the spacer and in the length of the terminal chains; for comparison we have also studied a mixture of symmetric dimers differing solely in the parity of the spacer. We have constructed the phase diagrams for the various mixtures and found that for certain systems the smectic phases exhibited by either one or both components can be destroyed. To investigate the local structure of the nematic phase for mixtures in which a smectic A phase is eliminated from the phase diagram we have determined their orientational order using NMR and ESR spectroscopy. To provide more direct information on the local structure an X-ray diffraction study was undertaken on certain of the mixtures.

1. Introduction

The fascinating behaviour of liquid crystal dimers, in which two mesogenic groups are linked by a flexible spacer, is usually associated with the major dependence of the properties at the nematic–isotropic transition on the parity, as well as the length of the spacer [1]. However, the smectic phase behaviour of the dimers has been found to be equally intriguing. For example, certain non-symmetric dimers in which different mesogenic groups are linked together are found to form interdigitated phases in which the smectic periodicity is about 1·8 times the molecular length and intercalated smectic phases in which the periodicity is approximately half the molecular length. A structure proposed for the intercalated smectic phase is sketched in figure 1: in this the different groups are taken to be arranged more or less uniformly within the layers, while the spacers link, at random, mesogenic groups within different layers. The nature of the smectic phase formed is found to depend on the relative lengths of the spacer and of the terminal chain. The non-symmetric dimers, α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-alkylanilinebenzylidene-4′-oxy) alkanes (denoted as CBO*n*O.*m* where *n* is the spacer length and *m* that of the terminal chain), give an intercalated smectic A phase for $n=6$ when *m* is between 0 and 6, although the stability decreases with increasing *m*; then for *m* equal to 7, 8 and 9 no smectic phase appears [2]. The explanation for the destruction of the smectic A phase is that the terminal chain is too long, in comparison with the spacer length, to be accommodated in the space between the two linked mesogenic groups, but not long enough to stabilize an interdigitated smectic A phase. It is thought that the intercalated smectic A phase, $\mathrm{SmA_c}$, results from favourable interactions between different mesogenic groups which stabilize a layer structure in which the mesogenic groups are uniformly distributed. The spacers are then introduced randomly into the structure so that they link mesogenic groups in different layers, giving a structure which is presumably entropically favoured. In view of this rationalization of the structure for the intercalated smectic A phase, the observation of such a smectic A phase for symmetric dimers, the α,ω-bis(4-butyloxybiphenyl-4′-carbonyloxy) alkanes, is especially intriguing [3]. Now the layer structure may result from the molecular inhomogeneity, as for monomeric mesogens, and the random distribution of the chains is again

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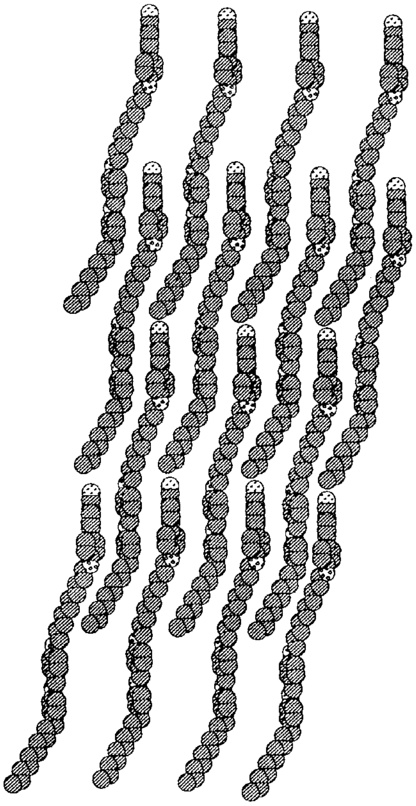

Figure 1. A caricature of the molecular organization in the intercalated smectic A phase of a non-symmetric dimer.

stabilized entropically. Given this explanation it is difficult to see why the occurrence of intercalated smectic phases is not more widespread; in fact several groups of symmetric dimers are known to form monolayer smectic phases [4].

One way in which the forces responsible for the intercalated smectic phases can be explored is by studying the phase behaviour of binary mixtures of the dimers. This has the advantage that the nature of the interactions can be changed continuously from one extreme to the other in a way which is not possible in the study of single compounds. Some investigations of mixtures have already been undertaken using the symmetric counterparts of the non-symmetric CBO*n*O.*m* dimers, that is CBO8OCB and 2.O8O.2 [5]. These pure dimers do not form smectic phases [4, 6], but the equimolar mixtures do form a smectic A phase which has an intercalated structure. This seems to support the view that the specific interactions between the unlike mesogenic groups are responsible for the formation of the smectic phase. We have now extended such studies to include binary mixtures of non-symmetric dimers, and the systems which we have investigated are the following. Dimers CBO*n*O.*m*, in which the spacer of one has an odd number of methylene groups and the other has an even number (these were CBO11O.6 and CBO10O.6, both of which form intercalated smectic phases), and for comparison CBO7O.10 and CBO6O.10, which form interdigitated smectic phases, together with the symmetric dimers 5.O7O.5 with 5.O8O.5, since both of these form monolayer smectic phases. These particular mixtures are also of interest because, although the dimers with odd spacers form smectic C phases, those with even spacers do not. We should, therefore, be able to explore how the introduction of even dimers destabilizes the tilted smectic phase. These three mixtures have components in which the spacers are different but the terminal chains have the same length. We have reversed this and studied a mixture in which the spacers are the same and the terminal chains have different lengths. This was CBO12O.10 mixed with CBO12O.2, both of which form intercalated smectic phases. In the other two mixtures both the spacer and terminal chain lengths of the components are different. For one, the components were CBO12O.10 and CBO8O.2, both of which form intercalated smectic phases, although it is significant that the mixed system CBO8O.10 does not form a smectic phase. For the other mixture, CBO5O.10 and CBO12O.10, one component forms an intercalated smectic phase and the other an interdigitated smectic phase so that it is of some interest to see the effect on the mixture of these totally different phase structures.

The layout of our paper is the following. In § 2 we describe the determination of the phase diagrams using a combination of DSC and optical microscopy. We have also used NMR and ESR spectroscopy to determine the orientational order of the nematic phases in some of the binary mixtures. The results are of interest in their own right, but can also be used to provide some indication of the local structure which may mimic that of the subsequent smectic phase. A more direct route to the local structure is provided by X-ray diffraction and we describe our experiments using this technique in § 3. Our conclusions are given in § 4.

2. Experimental

2.1. *Synthesis*

The synthetic routes for the CBO*n*O.*m* and *m*.O*n*O.*m* compounds have been described elsewhere [2, 4, 5] and these methods were followed here. The purity of the dimers was checked by proton NMR spectroscopy and the transition temperatures determined by DSC and optical microscopy; these were found to be in good agreement (±1°C) with those from previous studies [4, 5]. Samples of the non-symmetric dimers were also prepared with deuterons in the Schiff's base group. This was achieved by first deuteriating the relevant alkylaniline *ortho* to the amine group using a procedure given by Zimmermann [7] and then proceeding with the dimer synthesis as for the protonated material. The degree of deuteriation of the non-symmetric dimers was checked by proton NMR and found typically to be about 90%. The phases formed and the transition temperatures are given in table 1.

2.2. *Sample preparation*

When preparing mixtures of liquid crystals two main methods can be employed. The first involves dissolving the two components in a common solvent and then allowing the solvent to evaporate. This is, however, unsuitable for the CBO*n*O.*m* compounds as no common solvent is available. We therefore employed the method which involved taking the samples into the isotropic phase and mixing them mechanically. For both methods, however, the problem exists that on crystallization the two components may again phase-separate. For the CBO*n*O.*m* compounds, therefore, before each measurement the binary mixtures were again taken into the isotropic phase.

2.3. *Experimental techniques*

The transitional enthalpies and associated transitional entropies were determined using a Perkin Elmer DC7 differential scanning calorimeter controlled by an Opus PCII computer. A cooling rate of 10°C min^{-1} was used throughout on samples containing 5–10 mg of material. The optical textures were examined using an Olympus BH2 polarizing microscope equipped with a Linkam THM-600 heating stage.

The X-ray powder diffraction studies were carried out using a Guinier camera fitted with a bent quartz monochromator which was adjusted to isolate the $\mathrm{CuK}_{\alpha 1}$ radiation. The sample tubes were mounted in a metal heating block, with the temperature control provided by a modified Eurotherm VTU. The quartz Lindemann sample tubes were between 2 and 1 mm in diameter. The film was moved at a rate of either 0·03 or 0·06 mm min^{-1} depending on the liquid crystal range; a temperature change rate of between 10 and 20°C h^{-1} was employed.

The electron spin resonance experiments were performed using an ECS 106 Bruker ESR spectrometer. The temperature of the sample was regulated using a temperature control unit based on a Eurotherm B-VT 2000 VTU. The paramagnetic spin probe 3β-DOXYL-5α-cholestane was used, as previous studies have shown it to mimic the orientational order of the mesogenic groups of the CBO*n*O.*m* [8]. The spin probe was added to the liquid crystal in the minimum proportion necessary to eliminate induced chiral behaviour resulting from the chirality of the probe, as well as to reduce the influence of the probe on the transition temperatures. Both constraints were easy to achieve, however, because of the high sensitivity of the ESR technique; typically the concentration of the spin probe was about 1×10^{-4} M. The solution of the spin probe in the liquid crystal was degassed (using a freeze–thaw cycle under vacuum) first to reduce oxygen-induced line-broadening and secondly to minimize the thermal decomposition of the spin probe.

The NMR experiments were performed using a Bruker MSL 200 NMR spectrometer. The samples were prepared in 5 mm NMR tubes and were approximately 200 mg in weight. The spectrometer was fitted with a Eurotherm-based temperature controller allowing temperature studies up to approximately 190°C. An orientational order parameter for the dimers was calculated from the dipolar and quadrupolar splittings by taking the biaxiality in the Saupe ordering matrix to be zero. For a complete description of the NMR and ESR experiments and their analysis see references [9, 10].

3. Results and discussion

The following sections give the detailed results from the experiments conducted on the dimer binary

Table 1. Transition temperatures for the non-symmetric α-(4-cyanobiphenyl-4′-yloxy)-ω-(4-alkylanilinebenzylidene-4′-oxy) alkanes, and the symmetric α,ω-bis(4-alkylanilinebenzylidene)4′-oxylalkanes used in this study.

Compound	T_{Cr}/°C	$T_{\mathrm{J_cSmI_c}}$/°C	$T_{\mathrm{SmI_cSmC_c}}$/°C	$T_{\mathrm{SmC_cSmA_c}}$/°C # $T_{\mathrm{SmC_dSmA_d}}$/°C * $T_{\mathrm{B_cSmA_c}}$/°C	$T_{\mathrm{SmA_cN}}$/°C # $T_{\mathrm{SmA_dN}}$/°C * T_{SmAN}/°C	T_{NI}/°C
CBO8O.2	112			(100)	151#	177
CBO12O.2	116			(114)	159#	168
CBO10.O6	168			(111)#	165#	168
CBO11O.6	147	(60)	(86)	112#	138#	147
CBO5O.10	101			(87)*	106*	137
CBO6O.10	118			(107)*	155*	180
CBO7O.10	114			(87)*	(90)*	138
CBO12O.10	117				146#	148
5.O7O.5	115				119	135
5.O8O.5	131				146	167

mixtures. The phase behaviour is described for the CBO11O.6/CBO10O.6, CBO7O.10/CBO6O.10, 5.O8O.5/5.O7O.5, CBO12O.10/CBO12O.2, CBO12O.10/CBO8O.2 and CBO12O.10/CBO5O.10 mixtures. This is followed by results from the magnetic resonance and X-ray experiments which were used to probe the orientational order and local molecular structure, respectively.

3.1. *Phase behaviour*

3.1.1. *Binary mixtures of CBO11O.6 and CBO10O.6*

The CBO11O.6/CBO10O.6 binary mixtures were studied to investigate the dependence of the stability of the intercalated smectic phases on the parity of the spacer. With this choice of dimer, the effective parity of the spacer can be varied in the mixtures without significant changes in the overall molecular length and the distance between unlike mesogenic groups in a single molecule. Figure 2 shows the phase diagram for the CBO11O.6/CBO10O.6 mixtures. The N–I and SmA_c–N transition temperatures are observed to be completely linear in composition, but, the SmC_c phase is stable only for concentrations of CBO10O.6 of less than 18 mole %. It is the only smectic phase, for all of the mixtures which we have studied, for which the transition temperatures are not linear in composition. The miscibility of the intercalated smectic A phases formed by odd and even spacer dimers is difficult to understand both in terms of the intercalated structure of the phase and the significantly different molecular structures of the components. Thus the even dimer has an essentially linear structure with the two mesogenic groups parallel, whereas for the odd dimer the groups are inclined to each other giving a bent structure. The way in which these molecules with their quite different molecular shapes can be accommodated within an intercalated layer structure is not easy to visualize and yet the linear dependence of the smectic A–nematic transition temperature on composition suggests that this packing is readily achieved. Pure CBO11O.6 exhibits a SmI_c–SmC_c transition, whereas pure CBO10O.6 has a B_c–SmA_c transition; it seems reasonable, therefore to assume that mixtures rich in CBO11O.6 should form an intercalated smectic I phase, whereas those rich in CBO10O.6 should form an intercalated B. This implies that there should be a concentration dependent SmI_c–B_c transition, analogous to that found for the intercalated smectic C and smectic A phases, or possibly a narrow miscibility gap between the intercalated smectic I and B phases—although we were not able to detect either from the optical textures. An indication of the alteration in the nature of the phase is provided by the composition dependence of the entropy change at the SmI_c–SmC_c and B_c–SmA_c transitions. These are shown in figure 3, where we can see that the transitional entropy passes through a maximum; in contrast the entropy changes at the nematic–isotropic and intercalated smectic A–nematic transition are linear in composition. The rapid growth in $\Delta S/R$ occurs at a concentration when the mixture exhibits an intercalated smectic C phase and it seems reasonable to assume that such mixtures also form an intercalated smectic I phase. It would appear, therefore, that the bent molecular structure of the odd dimer is essential for the formation of a tilted smectic phase and that once its concentration falls below about 80 mole % an orthogonal smectic phase is formed. The transitions into the intercalated smectic I and crystal B phases are also linear in composition which again shows, somewhat surprisingly, that the layer structures are able to accommodate molecules with quite different geometries.

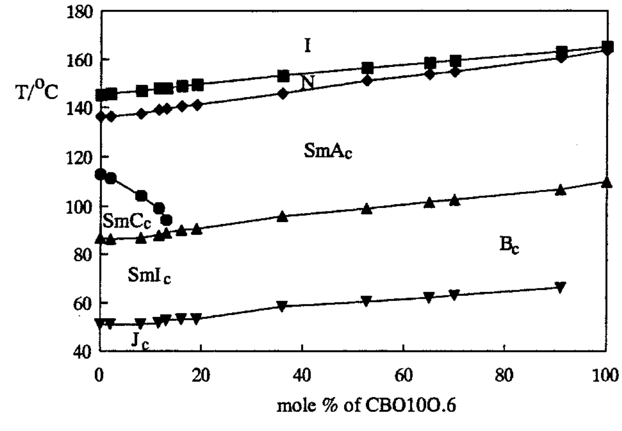

Figure 2. Phase diagram for the binary mixture of CBO11O.6 (intercalated smectic) and CBO10O.6 (intercalated smectic).

3.1.2. *Binary mixtures of CBO7O.10 and CBO6O.10*

In order to compare the binary mixtures of intercalated phases formed by odd and even spacer dimers

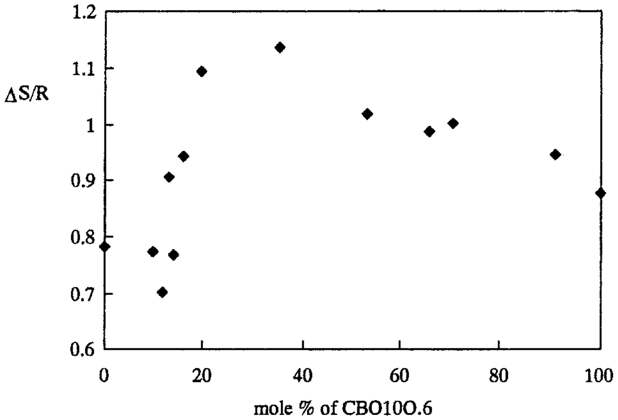

Figure 3. Variation in the molar entropy change, $\Delta S/R$, for the transitions into the crystal B or smectic I phase with the mole % of CBO10O.6 (intercalated smectic) in a mixture with CBO11O.6 (intercalated smectic).

with those of interdigitated phases also formed by odd and even spacer dimers, mixtures of CBO7O.10 and CBO6O.10 were studied. Figure 4 shows the complete phase diagram for the binary mixture of CBO7O.10 and CBO6O.10. The form of the phase diagram is identical to that found for the intercalated dimers, with both the N–I and SmA$_d$–N transition temperatures being linear in composition. The smectic C phase is again destroyed by the addition of the even spacer dimer as we have found for the intercalated dimers. This, therefore, supports the view that the presence of an odd spacer is crucial to the formation of a smectic C phase for both interdigitated and intercalated structures. The addition of only 20 mole % of the even spacer dimer has the effect, in both cases, of destroying the smectic C phase. The molar entropy change for the N–I transition is, as for the intercalated dimers, linear in concentration suggesting ideal mixing [11]. The molar entropies of the SmA$_d$–N transitions were too small to be determined accurately.

3.1.3. *Binary mixtures of 5.O7O.5 and 5.O8O.5*

For the sake of completeness binary mixtures of two dimers with odd and even spacers forming monolayer smectic A phases were investigated, namely the two symmetric Schiff's base dimers 5.O7O.5 and 5.O8O.5; their phase diagram is shown in figure 5. Again both the N–I and SmA–N transition temperatures are seen to be linear in concentration, as is the molar entropy change for the N–I transition. Therefore, for intercalated, interdigitated and monolayer smectic A phases formed by dimers, the fact that the parities of the component dimers are different, has no effect on the stability of the smectic A phase, is somewhat surprising. In addition the difference in parity of the two components has no influence on the formation of the nematic phase, which is also unexpected.

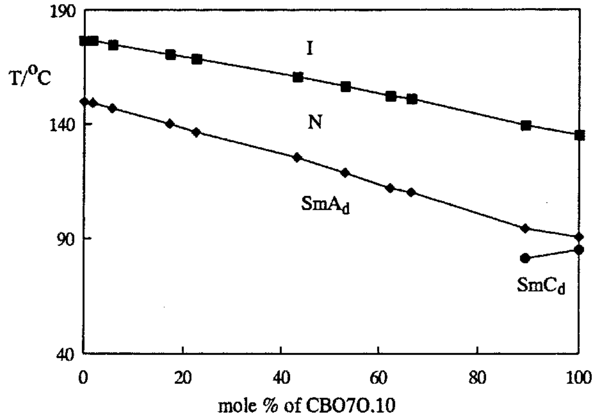

Figure 4. Phase diagram for the binary mixture of CBO7O.10 (interdigitated smectic) and CBO6O.10 (interdigitated smectic).

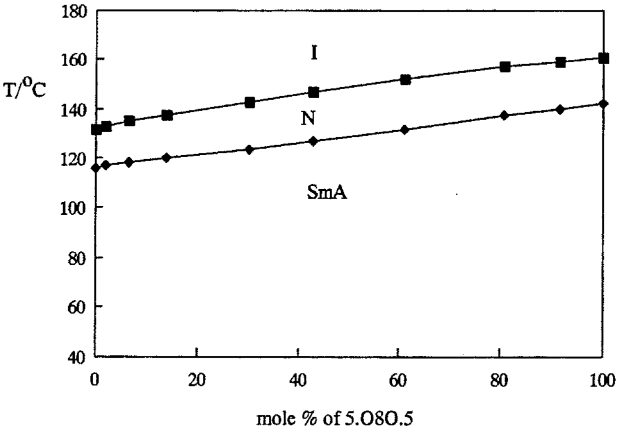

Figure 5. Phase diagram for the binary mixture of 5.O8O.5 (monolayer smectic) and 5.O7O.5 (monolayer smectic).

3.1.4. *Binary mixtures of CBO12O.10 and CBO12O.2*

In order to explore the effect of the terminal chain length on the stability of the intercalated smectic phases, mixtures of the CBO12O.10 and CBO12O.2 dimers were studied. The proportion of dimers with long and short chains could, therefore, be varied continuously by increasing the percentage of CBO12O.10 in CBO12O.2. Figure 6 shows the phase diagram for the binary mixture of these dimers and, as we have come to expect, the N–I transition temperature is linear in composition. However, the SmA$_c$–N transition temperature exhibits a slight deviation from linearity corresponding to a moderate reduction in the stability of the smectic A phase. These results are reflected in the molar entropy changes for the N–I and SmA$_c$–N transitions which are shown in figure 7; thus the values for the N–I transition are large, as expected for even dimers, and essentially linear in the composition, indicating ideal mixing behaviour, whereas those for the intercalated smectic A–nematic transition, although small, do exhibit a minimum at approximately

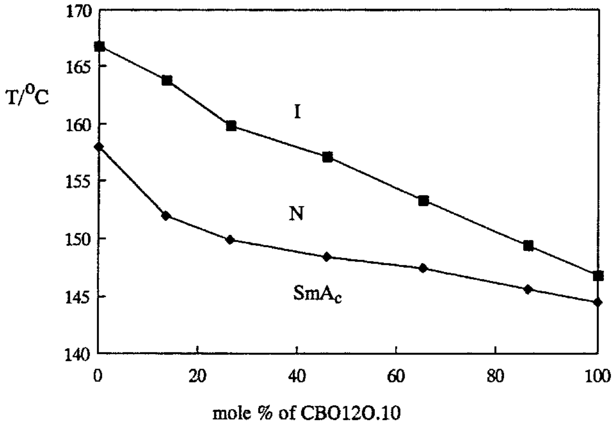

Figure 6. Phase diagram for the binary mixture of CBO12O.10 (intercalated smectic) and CBO12O.2 (intercalated smectic).

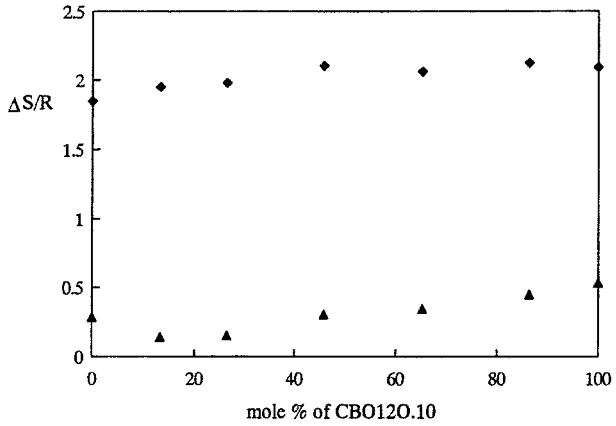

Figure 7. Variation in the molar entropy change, $\Delta S/R$, for the N–I [◆] and SmA_C–N [▲] transitions with the mole % of CBO12O.10 (intercalated smectic) in a mixture with CBO12.O2 (intercalated smectic).

the same composition as that for the smectic A–nematic transition temperature.

To understand this behaviour we first consider the molecular organization in the smectic A phase of the pure components. From the classic structure proposed for the intercalated smectic phases with unlike mesogenic groups adjacent to each other (see figure 1), we would expect that the non-symmetric dimers with the same spacer should have the same smectic periodicity. This does not prove to be the case for the two dimers which we have studied; thus for CBO12O.10 the smectic periodicity is 25·4 Å whereas for CBO12O.2 with the shorter terminal chain it is 20·8 Å. This difference can be interpreted as follows: the terminal decyl chain for CBO12O.10 has a length slightly less than that of the spacer and so the molecules are able to pack with the different mesogenic groups adjacent to each other. In contrast, for CBO12O.2, with its shorter ethyl terminal chain, the mesogenic groups cannot be adjacent without creating voids within the structure, which is undesirable. To avoid this problem the dimers must pack so as to fill the voids and in so doing the smectic periodicity is reduced.

With this background we return to the mixtures. The addition of small amounts of CBO12O.10 to CBO12O.2 will force the structure to become more open in order to accommodate the long decyl chain. This is not easy to achieve and the smectic phase is destabilized. At the other extreme it appears to be easier to add the dimer with the short terminal chain to that with the long chain, presumably because the mesogenic groups can remain in register while allowing the terminal chains to pack into the structure although at the expense of creating some voids.

3.1.5. *Binary mixtures of CBO12O.10 and CBO8O.2*

Mixtures of the CBO12O.10 and CBO8O.2 dimers were studied to explore the effect of mixing dimers with two seemingly incompatible spacer lengths in the sense that the mesogenic groups could not be in register as in a classic intercalated smectic structure (see figure 1). It might be expected, therefore, that such mixtures should not be able to support an intercalated smectic structure formed by the two components. This proves to be the case as the phase diagram in figure 8 clearly shows. Thus although the nematic–isotropic transition temperature is linear in the composition, the stability of the smectic A phase formed by the pure components decreases rapidly with the addition of the other component until it is destroyed for concentrations greater than 20 mole %. Associated with this dramatic change in the phase behaviour is the implication that the local structure of the nematic phase also changes with composition. At low concentrations of either component it should be intercalated whereas it might be expected to become normal for compositions at which the smectic phase is removed from the phase diagram. The two components of the mixture do have significantly different lengths because of different terminal chains. However, our results given in the previous section for CBO12O.10 and CBO12O.2, in which the spacers have the same length, but the molecules are different in length, show that this is not the case, for the smectic phase is not destroyed on forming these mixtures. The interpretation of these observations is that it is indeed the difference in the spacer lengths which causes the destruction of the smectic phase, but we cannot eliminate the possibility that the difference between the length of the terminal chain for CBO12O.10 and the spacer of CBO8O.2 also plays a role. In strong support of this is the observation that CBO8O.10 is purely nematic whereas CBO8O.6, with its slightly shorter terminal chain, has

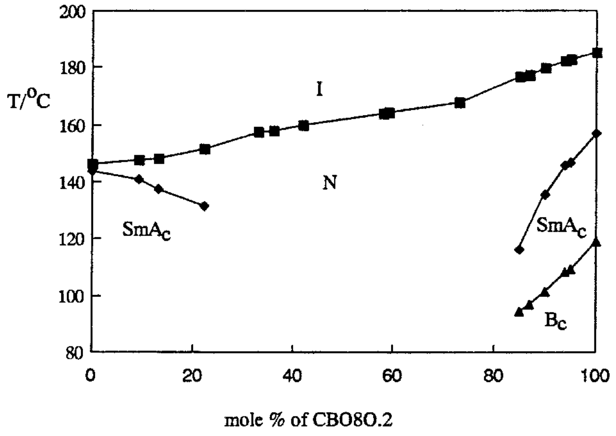

Figure 8. Phase diagram for the binary mixture of CBO12O.10 (intercalated smectic) and CBO8O2 (intercalated smectic).

an intercalated smectic A phase [5]. The fact that the two components form smectic A phases with dramatically different periodicities, and hence incommensurate lengths, seems to be the likely reason why the smectic phase is destroyed in the mixtures. This difference in the smectic structure for the two components clearly results from the difference in the spacer length with respect to the terminal chain [2].

3.1.6. *Binary mixtures of CBO5O.10 and CBO12O.10*

Finally, the miscibility of dimers forming intercalated and interdigitated smectic phases was investigated by studying mixtures of CBO12O.10 (intercalated) and CBO5O.10 (interdigitated). Analogous studies have also been described with similar findings [12]. Figure 9 shows the phase diagram for the CBO12O.10/CBO5O.10 system. The nematic–isotropic transition temperature and molar entropy are linear in concentration as is now seen to be the norm for mixtures of dimers. In addition, as for the CBO12O.10/CBO8O.2 mixtures, the intercalated and interdigitated smectic phases are destroyed by the addition of more than 20 mole % of unlike dimer. The fact that the two components form smectic A phases with dramatically different periodicities and hence incommensurate lengths seems to be the most likely reason for the smectic phase to be destroyed in the mixtures. This difference in the smectic structure for the two components clearly results from the difference in the spacer length with respect to the terminal chain [2, 6]. The possibility exists of observing nematic phases with different local structures across the phase diagram, this time of the form interdigitated, conventional and intercalated. These structural changes and those expected for the nematic phase of the CBO12O.10/CBO8O.2 binary mixtures could, perhaps, be observed in the orientational order and the local molecular separations in the phase. We have, therefore, investigated the nematic phases of the CBO12O.10/CBO8O.2 and CBO12O.10/CBO5O.10 mixtures using ESR and NMR spectroscopy, together with X-ray powder diffraction.

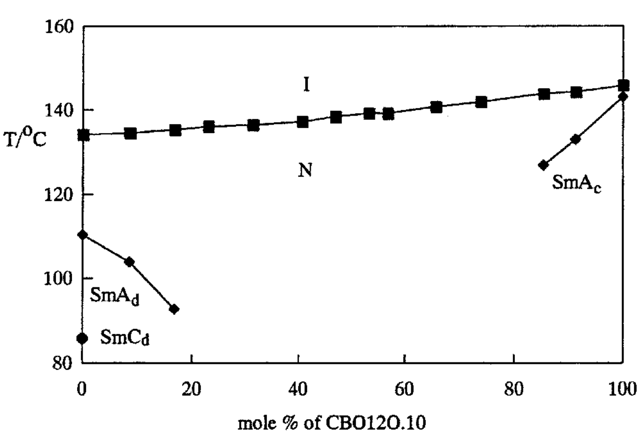

Figure 9. Phase diagram for the binary mixture of CBO5O.10 (interdigitated smectic) and CBO12O.10 (intercalated smectic).

3.2. *Magnetic resonance experiments*

3.2.1. ^{2}*H NMR spectroscopy for CBO12O.10/CBO8O.2*

Within the nematic phase preceding an intercalated smectic phase a local intercalated structure has been observed [5]. Therefore, for the CBO12O.10/CBO8O.2 mixtures there is the possibility that the local structure of the nematic phase should change with concentration. In the nematic phase preceding the SmA$_c$ phases of pure CBO12O.10 there will be a degree of intercalation. As CBO8O.2 is added the intercalated smectic phases are removed and it is probable, therefore, that the intercalated character of the preceding nematic is also destroyed. As we had mentioned earlier, we might expect a variation of the local structure of the nematic phase, across the phase diagram, of the form—intercalated, conventional, intercalated. A nematic phase possessing a locally intercalated structure would, perhaps, be anticipated to have a higher degree of orientational order, than its conventional counterpart (due to the restrictions which the intercalated structure might impose on the allowed conformations). The orientational order was, therefore, studied across the phase diagram using ^{2}H NMR. The orientational order parameter for the *para*-axis of the aniline ring of the mesogenic group was determined by comparing the dipolar and quadrupolar splittings, associated with the two equivalent deuterons, and taking the biaxiality in the Saupe ordering matrix to be zero [10].

Figure 10 shows the order parameter, S_{zz}, obtained in this way for increasing concentrations of CBO12O.10-d$_2$ in CBO8O.2-d$_2$. The most obvious result is that the

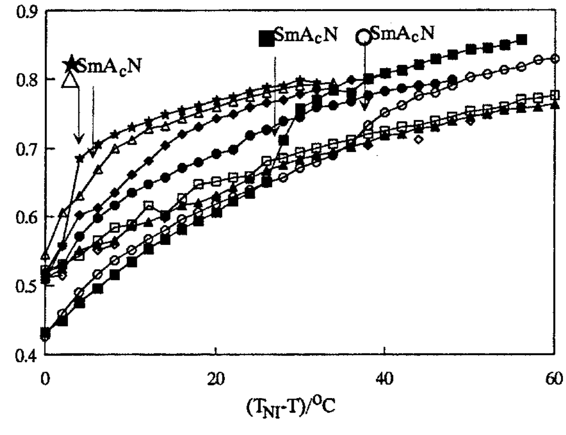

Figure 10. Dependence of the orientational order parameter, S_{zz}, on the shifted temperature for differing mole % of CBO8O.2 (intercalated smectic) in CBO12O.10 (intercalated smectic); ★(0%), △(11·2%), ◆(17.4%), ●(26%), □(47·5%), ▲(63%), ◇(79%), ○(92·0%), ■(100%).

order parameter at the nematic–isotropic transition adopts one of either two values ~0·52 or ~0·43. For pure CBO8O.2-d$_2$ and the mixture with 92·5 mole % of CBO8O.2-d$_2$, the value is ~0·43. With a decrease in the amount of CBO8O.2-d$_2$ to only 79 mole %, the order parameter at the N–I transition increases to ~0·52. It remains at this level for all of the other mixtures up to pure CBO12O.10-d$_2$. The 79 mole % of CBO8O.2-d$_2$ corresponds to the concentration where the mixtures no longer form intercalated smectic phases and only possess a nematic phase, at least until the mixture freezes. The mixtures with 79, 63 and 47·5 mole % of CBO8O.2-d$_2$ possess only nematic phases. If the S_{zz} plots for these three are compared with the 100 and 92·5 mole % mixture, it can be seen that the increase in the orientational order with increasing shifted temperature is greater for the mixtures possessing smectic phases. The difference at the N–I transition is ~0·11, but by a shifted temperature of 25°C the difference has become negligible. This could be consistent with the 100 and 92·5 mole % mixtures possessing nematic phases with a locally intercalated structure and so increased orientational order. The results seem to indicate, therefore, two changes in the local nematic structure, from a nematic with an intercalated structure to a conventional nematic, at a concentration of between 26 and 47 mole %, and 92·5 and 79 mole % of CBO8O.2-d$_2$.

If now the orientational order is compared in the smectic phases, it is clear that with an addition of CBO12O.10-d$_2$ to pure CBO8O.2-d$_2$ or vice versa the orientational order within the smectic phases decreases. This suggests a breakdown in the intercalated structure of the smectic phases and so a decrease in their orientational order. An alternative conclusion could, however, be that for pure CBO8O.2-d$_2$ and the 92·5 mole % CBO8O.2-d$_2$ mixture the nematic phases possess a local intercalated structure dominated by the CBO8O.2-d$_2$ dimer. Their orientational order at the N–I transition will be lower because of the shorter spacer length. However, as the concentration of CBO12O.10-d$_2$ is increased, the nematic phases are dominated by the intercalating CBO12O.10-d$_2$ structures. The orientational order at the N–I transition would, therefore, be larger because of the longer spacer [1]. The steeper gradient of S_{zz} against shifted temperature for the nematic range of the CBO8O.2-d$_2$ and the 92·5 mole % mixture is, therefore, only a result of the initially high values of the order parameters.

3.2.2. *ESR spectroscopy for the CBO5O.10/CBO12O.10 mixtures*

With the nematic phase exhibited by the CBO12O.10/CBO5O.10 mixture, the possibility also exists of observing a variation in the local structure across the phase diagram, this time of the form—interdigitated, conventional, intercalated. The degree of orientational order in a liquid crystal can be explored using ESR spectroscopy and a paramagnetic spin probe dissolved in the liquid crystal host. This method has the advantage that there is no need for partial deuteriation of the liquid crystal materials under investigation, and for the CBO*n*O.*m* dimers a cholestane spin probe has been shown to mimic the orientational order of the dimers [8]. To investigate the possibility of a structural variation across the phase diagram, the orientational order parameter, $\langle P_2\rangle$, was measured for the long axis of a cholestane spin probe dissolved in the binary mixtures. Figure 11 shows $\langle P_2\rangle$ as a function of the shifted temperature for increasing concentrations of CBO12O.10 in CBO5O.10. For the pure dimers there is a dramatic difference in $\langle P_2\rangle$ measured at the N–I transition of ~0·3, with CBO12O.10 having a value of ~0·6 and CBO5O.10 having the lower value of ~0·3; this reflects the dramatic odd–even effect characteristic of the behaviour at the nematic–isotropic transition of dimers [1]. For the mixtures, $\langle P_2\rangle$ measured at the N–I transition appears to be linear in composition as we can see from the results in figure 12. The behaviour of the order parameter of the spin probe gives no indication, therefore, of a structural variation across the phase diagram, a result in keeping with the composition dependence of the transitional entropy. However, the more likely explanation is that the change from a nematic with a local intercalated structure, to a nematic with a local interdigitated structure, involves no major variation in the orientational order.

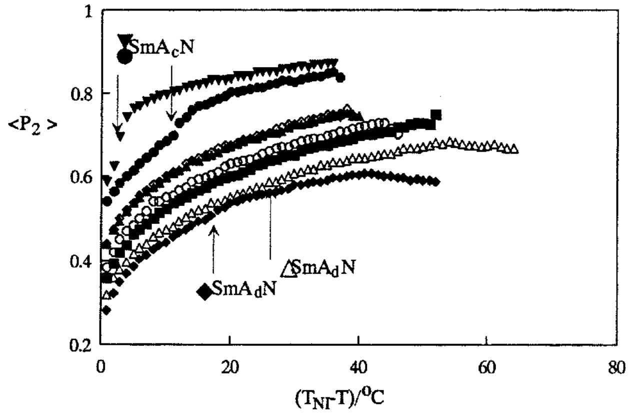

Figure 11. Variation in the orientational order parameter, $\langle P_2\rangle$, for the cholestane spin probe dissolved in various mixtures of CBO12O.10 (intercalated smectic) in CBO5O.10 (interdigitated smectic), with the shifted temperature. ( ) Mole percentage of CBO12O.10; ◆(0%), △(10%), ■(31%), ○(40%), ▲(58%), ◇(64%), ●(90%), ▼(100%).

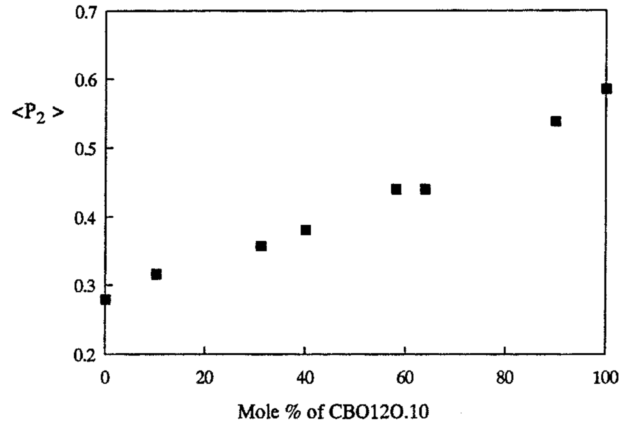

Figure 12. Order parameter of the cholestane spin probe, $\langle P_2 \rangle$, at the N–I transition, as a function of the molar concentration of CBO12O.10 (intercalated smectic) in its mixture with CBO5O.10 (interdigitated smectic).

3.3. *X-ray diffraction studies for CBO12O.10/CBO8O.2*

A more direct measurement of the local structure in a nematic phase is provided by X-ray diffraction which gives the separation between neighbouring molecules; of particular interest to us is the separation between mesogenic units along the director. This distance is the analogue of the smectic periodicity and so would be expected to vary from a value of half the molecular length, when the local intercalated structure dominates, to a value equal to the molecular length in a conventional nematic. The mesogenic separations along the director measured in the nematic phase, for each of the pure dimers and the mixtures studied, are listed in table 2. It is clear that for 20 mole % of CBO8O.2 and 93·7 mole % of CBO8O.2 the mesogenic separations are, within experimental error (±0·5 Å), the same as for the pure CBO12O.10 and CBO8O.2, respectively. For the mixture with 35·8 mole % of CBO8O.2, the separation has an intermediate value between that for the two pure compounds, suggesting that the nematic phase still has a local structure that is closer to that for CBO12O.10 than for CBO8O.2. This confirms our explanation of the order parameter measurements indicating a nematic phase dominated by the CBO12O.10 intercalated structure, up until a concentration of CBO8O.2 of more than ~79 mole %. This is probably due to the ability of the CBO12O.10 spacer length to accommodate the terminal chain of CBO8O.2 within the intercalated structure.

Table 2. Mesogenic separations measured by X-ray diffraction for the nematic phases of CBO12O.10 (intercalated smectic), CBO8O.2 (intercalated smectic) and their mixtures.

Mole % CBO12O.10	Mole % CBO8O.2	Mesogenic separation in the nematic phase
100	0	25·5 Å
80	20	25·0 Å
64·2	35·8	23·0 Å
6·7	93·7	18·5 Å
0	100	18·5 Å

4. Conclusions

A range of binary mixtures of intercalating, interdigitating and monolayer forming dimers have been studied. The results indicate that the miscibility of the nematic and smectic A phases of these three forms of dimer are independent of the parity of the flexible spacer. The stability of the intercalated smectic A phase is, however, dependent on the compatibility of the spacer and terminal chain lengths (i.e. the ability of the spacer length to accommodate the terminal chain), and also perhaps the compatibility of the mesogenic–mesogenic distance which is determined by the spacer length alone. In addition the intercalated and interdigitated smectic C phases have been shown to be unstable to the addition of more than 20 mole % of even spacer dimer.

For mixtures with seemingly incompatible spacer and terminal chain lengths, the stability of the smectic phases is greatly reduced, although X-ray powder diffraction and magnetic resonance studies indicate that the nematic phase still possesses a local intercalated structure, for all compositions. For the CBO12O.10/CBO8O.2 mixtures the structure of the nematic phase was dominated by that of the CBO12O.10 dimer, probably because of the ability of the molecules of CBO8O.2 to accommodate themselves in the CBO12O.10 intercalated structure, but with the reverse not being the case.

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