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The intercalated smectic A phase

The liquid crystal properties of the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-alkyloxycinnamoate)alkanes

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A novel system of non-symmetric dimers containing 4-*n*-alkyloxy-substituted cinnamic acid and cyanobiphenyl groups has been studied. Two series were prepared: in one the flexible spacer was varied in length while the spacer was fixed. The spacer length has a profound influence on the nematic-isotropic transition temperature of these materials and a large odd-even effect is observed for the series. The terminal chain also plays a significant role in determining the liquid crystal phase behaviour: a smectic A phase is exhibited for the ethyl and propyl homologues, in addition to a nematic phase; this smectic phase vanishes for intermediate chain lengths but then reappears for the nonyl and decyl members of the series. X-ray diffraction has revealed the structure of the smectic A phase for the ethyl homologue to be intercalated, whereas that for the decyl compound is interdigitated. The existence of the intercalated smectic A phase has previously been explained in terms of a charge-transfer interaction between unlike mesogenic groups. However, for the non-symmetric liquid crystal dimers described here this specific interaction appears unlikely and we discuss, therefore, other possible mechanisms for the formation of intercalated smectic phases.

1. Introduction

Liquid crystal dimers have now become well established, not only because of fundamental interest in them, but also because they can be used as models of thermotropic, semi-flexible main chain liquid crystalline polymers [1]. Symmetric liquid crystal dimers are well-known [2] and are composed of two mesogenic groups linked together by a flexible spacer. More recently structural variants known as non-symmetric liquid crystal dimers have been reported [3] where now two different mesogenic groups are linked by a flexible spacer. Of these the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-alkylanilinebenzylidene-4'-oxy)alkanes are particularly interesting as certain homologues exhibit novel intercalated smectic phases [4]. The incidence of the intercalated smectic phases was shown to be controlled by the relative lengths of the spacer and terminal chain. If this terminal chain could be accommodated in the space between the layers, which is determined by the spacer length, an intercalated phase resulted, whereas if this was not possible, an interdigitated phase was formed (see figure 1). For some

homologues only a nematic phase was formed, presumably because neither the driving force responsible for the intercalated smectic A or that for the interdigitated smectic A was dominant. The interdigitated smectic A phase results from an interaction between the polar and polarizable cyanobiphenyl groups; an antiparallel correlation of these moieties and the molecular inhomogeneity produced by the long terminal chains leads to the formation of the smectic phase. The intercalated smectic A phase is thought to result [3, 4] from a charge-transfer interaction between neighbouring cyanobiphenyl and Schiff's base units [5]. However, it is possible that electrostatic quadrupolar interactions between groups with quadrupole moments which are opposite in sign could be responsible for favourable interactions between unlike mesogenic groups which would also create an intercalated smectic phase. There is also the possibility that the intercalated smectic phase is driven by an increase in entropy as a result of homogeneous mixing of the mesogenic groups rather than their segregation into different regions of the phase.

To explore these possibilities, we have synthesized two series of non-symmetric liquid crystal dimers, where now the Schiff's base unit is replaced by the 4-*n*-alkyloxycinnamoate group. In this way we have not only produced

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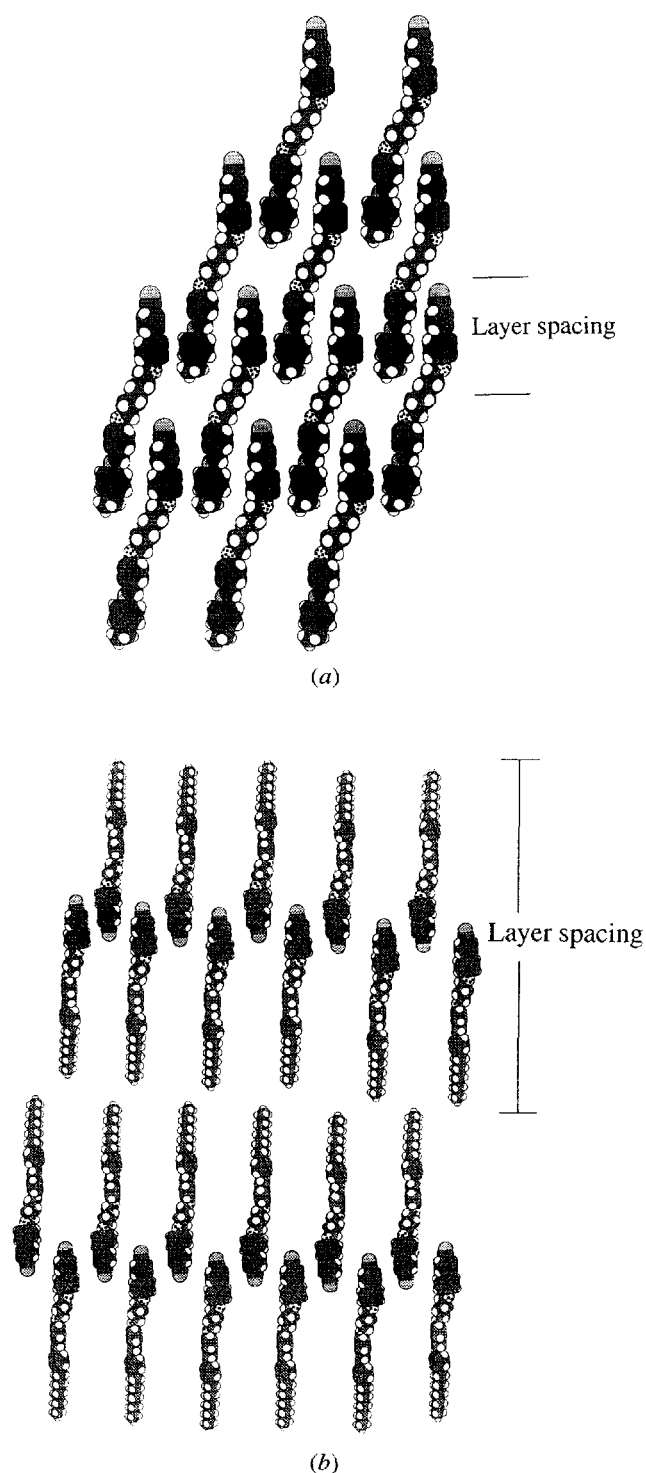


Figure 1. A schematic representation of the structure of (a) the intercalated and (b) the interdigitated smectic A phase [4].

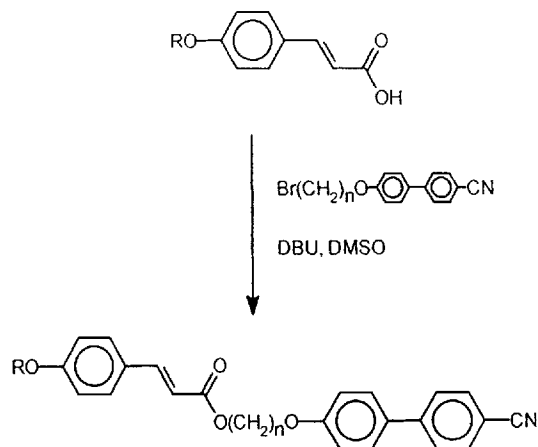
compounds structurally similar to those in [4], but also sufficiently different to further our understanding of the interaction between the two unlike mesogenic units in non-symmetric liquid crystal dimers. The smaller cinnamate moiety was chosen as the likelihood of any significant charge-transfer interactions with cyanobiphenyl is small; none the less the charge distribution within the two groups should be sufficiently different to change the electrostatic quadrupole moment. Furthermore, it is also of interest to us to explore the liquid crystal properties of dimers containing the cinnamate moiety. Based on a report of smectic B phase behaviour for the symmetric dimers, the α,ω -bis(4-methoxycinnamate)polyoxyethylenes [6], we decided to join a 4-methoxycinnamate moiety to cyanobiphenyl through a flexible spacer. Thus one of the series of non-symmetric dimers considered also allows us to probe the mesogenicity of the cinnamate moiety itself.

Here we describe the synthesis and characterization of two series of non-symmetric liquid crystal dimers the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-methoxycinnamate)alkanes and the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-alkyloxycinnamate)heptanes; these are denoted by the mnemonics CBO_nCO_1 and CBO_7CO_m , respectively, where n is the number of methylene units in the flexible alkyl spacer, C is cinnamate, m is the length of the terminal alkyl chain and CB is cyanobiphenyl.

2. Experimental

The synthetic step to the CBO_nCO_1 s is shown in the scheme and in this section we give the synthetic details for CBO_7CO_2 as an example. The synthesis of the 4- n -alkyloxycinnamic acids and the α -bromo- ω -(4-cyanobiphenyl-4'-yloxy)alkanes are described in [7] and [8], respectively. 4-Methoxycinnamic acid is commercially available from Lancaster Synthesis and was used without further purification. All intermediates were structurally characterized by IR (Perkin-Elmer 1600 series FTIR spectrometer) and ^1H NMR spectroscopy (Bruker 300 MHz Fourier transform NMR spectrometer). Final products were also characterized by high field ^1H NMR spectroscopy (Bruker AM 360 MHz NMR spectrometer) and mass spectroscopy (VG 70-250); their purity was controlled by thin layer chromatography. The optical textures of the liquid crystal phases were investigated using an Olympus BH-2 optical microscope coupled to a TMS90 Linkam hot stage. A Perkin-Elmer DSC7 differential scanning calorimeter was used to determine the thermal behaviour at the phase transitions. The smectic layer spacings were measured by X-ray diffraction. A Guinier camera fitted with a bent quartz monochromator (R. Huber, Germany) was used; the monochromator was adjusted to isolate $\text{CuK}\alpha$ radiation ($\lambda = 1.5405 \text{ \AA}$). The X-rays were produced by a GX20 rotating anode generator

fitted with a 0.1 mm focusing cup (Marconi Avionics, England). The intensities of the X-ray diffraction patterns were measured using a Mark IIIc microdensitometer (Joyce-Loebl, England).



The synthetic step to the CBO_nCO₁s.

2.1. Synthesis of α -(4'-cyanobiphenyl-4'-yloxy)- ω -(4-ethoxycinnamoate)heptane

4-Ethoxycinnamic acid (0.53 g; 2.76×10^{-3} mol) was dissolved in 30 ml of anhydrous dimethyl sulphoxide in a 50 ml conical flask. DBU (1,8-diazabicyclo[4.3.0]undec-7-ene) (0.46 g; 3.04×10^{-3} mol) was added and the mixture stirred on a water bath at 30°C for 30 min. α -Bromo- ω -(4-cyanobiphenyl-4'-yloxy)heptane (0.93 g; 2.51×10^{-3} mol) was added and the mixture left to stir for 5 h. The mixture was then poured into water and organic materials extracted with diethylether. The extracts were washed with saturated sodium carbonate solution to remove the excess of 4-ethoxycinnamic acid and were then evaporated to give a white solid. This was recrystallized twice from methanol to yield white crystals which were dried *in vacuo*. Yield 0.77 g (64 per cent). IR (NaCl disc, film): ν/cm^{-1} 1632 (C=C), 1705 (C=O), 2222 (C \equiv N). ^1H NMR (CDCl₃): δ/ppm 1.3–2.0 (m, 13 H), 3.9–4.3 (m, 6 H), 6.2–6.4 (d, 1 H, $J = 16$ Hz), 6.8–7.1 (m, 4 H), 7.4–7.8 (m, 9 H). MS (EI) 175 (C₂H₅OPhCH=CH.C=O, 100 per cent), 483 (M⁺, 15 per cent).

3. Results and discussion

3.1. The CBO_nCO₁ series

In this series of compounds the number of methylene units, n , in the alkyl spacer was varied between 3 and 12. Except for $n = 7$, all of the homologues in the series have monotropic nematic phases. The nematic phase was characterized by two and four point singularities in the optical texture which flashed when stressed mechanically. The spacer is found to have a significant effect on the transition temperatures, enthalpies and entropies as we can

Table 1. Transition temperatures, enthalpies and entropies for the CBO_nCO₁ series.

n	$T/^\circ\text{C}$		$\Delta H/\text{kJ mol}^{-1}$		$\Delta S/\text{R}$	
	†C-N C-I	N-I	†C-N C-I	N-I	†C-N C-I	N-I
3	157	(149)	51.1	(4.7)	14.3	(1.4)
4	128	‡(52)	51.6		15.5	
5	147	(134)	45.7	(4.2)	13.1	(1.2)
6	115	‡(71)	58.9		18.3	
7	†122	128	†36.2	5.9	†11.0	1.8
8	101	(83)	47.6	(5.8)	15.3	§
9	122	(110)	52.2	(6.1)	15.9	(1.9)
10	88	(82)	44.4	(0.9)	15.2	(0.3)
11	125	(103)	56.9	(6.1)	17.2	(2.0)
12	82	(81)	47.5	(1.0)	16.1	(0.3)

‡ Observed only by polarizing microscopy by supercooling isolated droplets.

§ Not possible to measure by DSC.

Parentheses indicate a monotropic transition.

see from the values listed in table 1. For this series of compounds we should remember that an odd number of methylene units in the spacer leads to a molecular shape which, in the all-*trans* conformation, allows the cinnamate moiety to lie approximately parallel to the cyanobiphenyl group, so the –CO.O– and –O– linking units must be included when determining the parity of the total spacer length. Since these units contribute an odd number of atoms to the spacer, we expect to see an enhancement of liquid crystal behaviour for spacers composed of an odd number of methylene units relative to the even membered homologues. Figure 2 shows the effect of the number of methylene units in the alkyl spacer, n , on the transition temperatures of the CBO_nCO₁s. For the $n = 3$ –6 homologues there is a dramatic odd–even effect

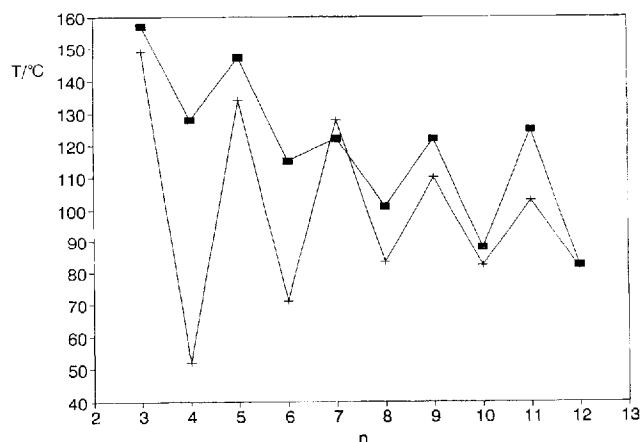


Figure 2. The dependence of the transition temperatures for the CBO_nCO₁ series, C-I (■), N-I (+), on the number of methylene units, n , in the flexible alkyl spacer.

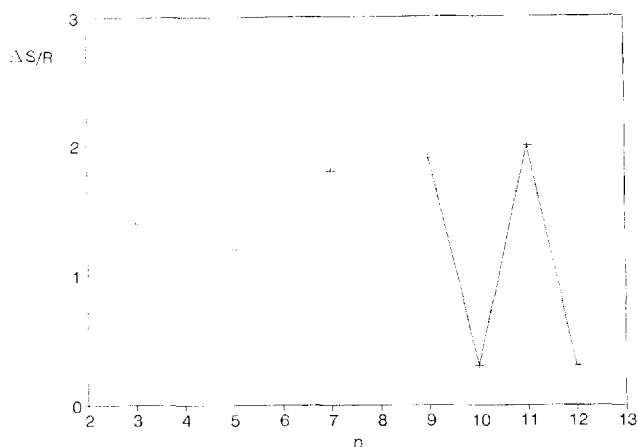


Figure 3. The dependence of the entropy change at the nematic-isotropic transition for the CBO_nCO_1 series on the number of methylene units, n , in the flexible alkyl spacer.

for the nematic-isotropic transition temperatures; indeed these temperatures are so low for the $n=4$ and 6 homologues that a nematic phase could only be detected by supercooling isolated, isotropic droplets of the materials. The nematic-isotropic transition temperatures of the even membered homologues lie on a steadily increasing curve, whereas the nematic-isotropic transition temperatures for the odd membered homologues fall as the spacer length increases; these properties are typical of liquid crystal dimers [2-4]. Figure 3 shows the effect of the number of methylene units, n , in the flexible spacer on the nematic-isotropic entropy change. It was not possible to measure this change for the $n=4, 6$ and 8 homologues as crystallization occurred before the transition to the nematic phase could be reached. For the odd membered homologues, we see that the entropy change at the nematic-isotropic transition rises steadily across the series; these high entropy changes ($\Delta S/R$) are typical of dimeric compounds with a total number of atoms in the flexible alkyl spacer which is even. The $n=10$ and 12 homologues have low nematic-isotropic entropy changes which are also typical of dimeric compounds with an odd membered spacer [2]. Comparing the transitional entropies for the $n=9$ to 12 homologues reveals a very large alternation. It is of interest to compare the odd-even effect in the nematic-isotropic transition temperatures for the CBO_nCO_1 series with that found for other liquid crystal dimers both symmetric and non-symmetric. Figure 4 shows such a comparison for the α,ω -bis(4-cyanobiphenyl-4'-yloxy)alkanes (BCBO_n) [9] and the α -(4-cyanobiphenyl-4'-yloxy)- ω -(4-cyanophenyl-4'-yloxy)alkanes (CBO_nOCP) [10], together with those for the CBO_nCO_1 s; here T_{NI} is given as a function of the total number of atoms, p , in the spacer. We see that

the nematic-isotropic transition temperatures for the CBO_nCO_1 s lie well below those of the BCBO_n s and this reflects presumably the greater anisotropy of a cyanobiphenyl group relative to a 4-methoxycinnamate group. However, they compare well to the T_{NIS} of the three homologues of the CBO_nOCP series (particularly when $p=6$ and 8) and hence we can say that the mesogenicities of the 4-methoxycinnamate and cyanophenyl moieties are similar. This, of course, is only true in the absence of any specific interactions between the cinnamate moiety or of cyanophenyl with the cyanobiphenyl group. The mesogenicity of the cinnamate moiety itself appears to be very low. We have confirmed this by synthesizing and characterizing some symmetric dimers consisting of 4- n -alkyloxycinnamate moieties linked together by a flexible spacer—the α,ω -bis(4- n -alkyloxycinnamate)alkanes ($m\text{OC}_n\text{CO}_m$). For example, the $2\text{OC}_8\text{CO}_2$ homologue was not liquid crystalline (C 92°C I) and from mixtures with I-35 (C 29°C N 108°C I, Merck Ltd., Poole, U.K.) was found to have a virtual nematic-isotropic transition temperature of 37°C.

3.2. The CBO_7CO_m series

We chose to study the effect of lengthening the terminal chain on the liquid crystal behaviour for this series in particular, since for the CBO_nCO_1 s, only the $n=7$ homologue is an enantiotropic nematogen. Table 2 lists the transition temperatures, enthalpies and entropies for the CBO_7CO_m s and figure 5 shows the influence of the length of the terminal chain on the transition temperatures. We see that the $m=1-8$ homologues possess a nematic phase which was characterized from its optical texture and that the clearing transition temperatures exhibit a weak

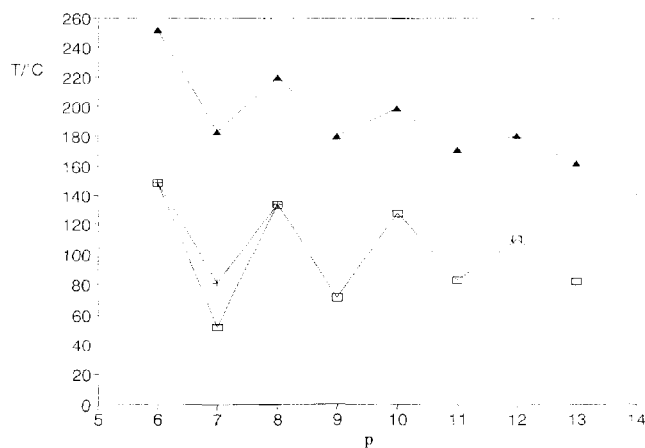


Figure 4. A comparison of the influence of the total length of the flexible alkyl spacer, p , on the nematic-isotropic transition temperature for the BCBO_n s (▲) where p is $n+2$, the CBO_nOCP s (+) where p is also $n+2$, and the CBO_nCO_1 s (□) where p is $n+3$.

Table 2. The transition temperatures, enthalpies and entropies for the CBO7CO_m series.

m	T/°C			ΔH/kJ mol ⁻¹			ΔS/R		
	†C-I		†S _A -I	†C-I		†S _A -I	†C-I		†S _A -I
	‡C-S _A C-N	S _A -N	N-I	‡C-S _A C-N	S _A -N	N-I	‡C-S _A C-N	S _A -N	N-I
1	122		128	36.2		5.9	11.0		1.8
2	118	(101)	125	49.1	(1.5)	6.8	15.1	(0.48)	2.1
3	†126	(101)	(117)	†40.9	(2.7)	(6.3)	†12.3	(0.86)	2.0
4	†118		(116)	†39.2		(6.7)	†12.1		2.1
5	104		114	46.4		5.6	14.8		1.8
6	96		114	51.1		5.8	16.6		1.8
7	90		110	45.8		5.6	15.2		1.8
8	95		111	55.3		6.1	18.1		1.9
9	‡80		†107	‡43.7		†8.3	‡14.9		†2.6
10	‡91		†108	‡50.9		†7.4	‡16.8		†2.3

Parentheses indicate a monotropic transition.

odd-even effect across the series. As expected, the melting points gradually decrease as the terminal chain is lengthened. More importantly, some members of the CBO7CO_ms also possess a smectic A phase. The incidence of the smectic A phase for this series has an interesting dependence on the length of the terminal chain: the *m* = 2 and 3 homologues exhibit a monotropic smectic A phase in addition to a nematic phase, whereas the *m* = 9 and 10 homologues only possess an enantiotropic smectic A phase. In each case the smectic A phase was characterized by the coexistence of the focal-conic fan and homeotropic textures [11], although the optical texture of the smectic A phase for the *m* = 9 and 10 homologues had a tendency to exhibit predominantly a homeotropic texture. The failure of compounds with intermediate chain lengths to form smectic A phases suggests that its occurrence is frustrated by two competing driving forces

which are different for homologues with short and long terminal chains. Figure 6 shows the effect of the terminal chain length, *m*, on the smectic A–nematic and clearing entropies of transition. The nematic–isotropic entropy change, for which there is no real odd–even effect, has values typical for dimeric liquid crystals with an even spacer. The larger smectic A–nematic entropy of transition for CBO7CO₃ relative to that for CBO7CO₂ is consistent with the shorter nematic range of the former and is in qualitative agreement with the predictions of McMillan's theory [12].

The disappearance and then reappearance of smectic A behaviour for the CBO7CO_ms is reminiscent of the unusual phase behaviour found for the α-(4-cyanobiphenyl-4'-yloxy)-ω-(4-alkylanilinebenzylidene-4'-oxy)alkanes (CBO_nO_m) [3, 4]. We might expect, therefore, that the shorter homologues would exhibit

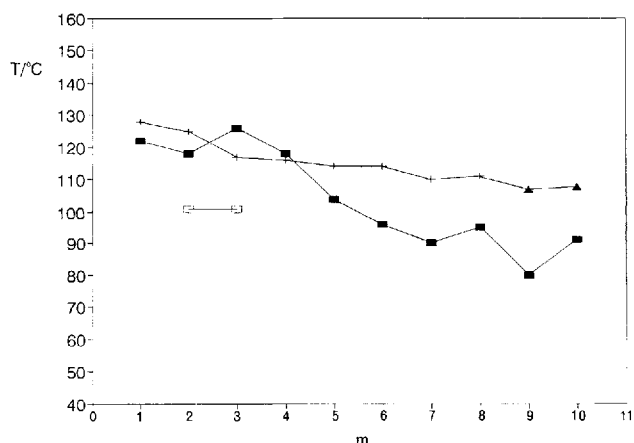


Figure 5. The dependence of the transition temperatures for the CBO7CO_ms. C-I (■), S_A-N (□), N-I (+), S_A-I (▲) on the number of carbon atoms, *m*, in the terminal alkyl chain.

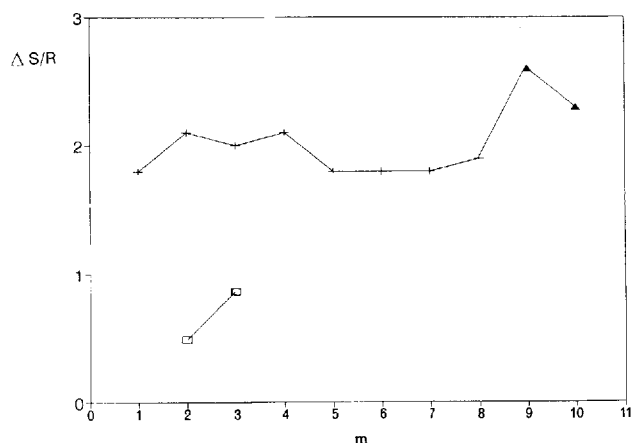


Figure 6. The dependence of the entropies of transition for the CBO7CO_ms. N-I (+), S_A-N (□), S_A-I (▲) on the number of carbon atoms, *m*, in the terminal alkyl chain.

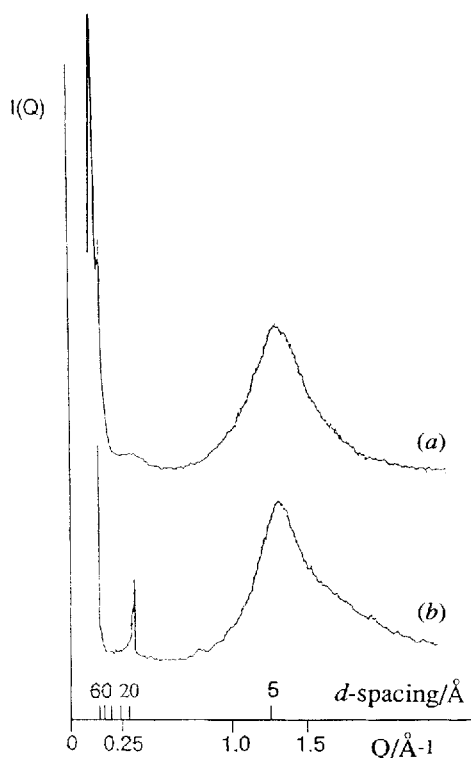


Figure 7. The intensity profile of the X-ray diffraction pattern for the smectic A phase of (a) CBO7CO10 at 100°C and (b) CBO7CO2 at 98°C .

intercalated phases while the higher homologues would form interdigitated smectic A phases. To investigate this intriguing possibility, we have measured the X-ray diffraction patterns of two homologues of the CBO7CO m s ($m = 2$ and 10); the intensity profiles for these diffraction patterns are shown in figure 7. In addition to the wide angle peak corresponding to a nearest neighbour separation of 4.4 \AA , the pattern for the smectic A phase of the $m = 10$ homologue (see figure 7(a)) contains a small angle reflection corresponding to a periodicity of 62.5 \AA (the all-*trans* molecular length is 44 \AA as measured from a CPK molecular model). This suggests that the smectic A phase has an interdigitated structure which is to be expected from the presence of a cyanobiphenyl group. However, the ratio of the periodicity to the molecular length is only 1.4, which is somewhat smaller than that found for the CBO n O m s where the corresponding ratio is 1.8. This implies an unusual structure at the centre of the layer with the cyanobiphenyl group of one dimer overlapping the alkyl spacer of its neighbour and not another cyanobiphenyl group as is usually found; we shall return to the possible structure of this interdigitated phase shortly. The X-ray diffraction experiments performed on CBO7CO2 did show the smectic A phase to be intercalated, as the small angle reflection gave a smectic periodicity of 16.6 \AA (the

all-*trans* molecular length is estimated to be 35 \AA from a CPK molecular model). This dramatic change in the periodicity is clearly shown by the profile of the diffraction pattern given in figure 7(b); this also reveals that the nearest neighbour separation is unchanged at 4.4 \AA . The discovery of an intercalated smectic A phase for this non-symmetric dimer is of considerable interest, for it is hard to imagine a charge transfer interaction between a cinnamate moiety, which is not a good electron donor, and a cyanobiphenyl group which is an electron acceptor.

This leads us to consider other mechanisms for the formation of the intercalated phase. For example, it might be explained simply in terms of an entropy gain resulting from the homogeneous mixing of the mesogenic groups, although this would be reinforced by electrostatic quadrupolar interactions between mesogenic groups with quadrupole moments which are opposite in sign. To see this more clearly, consider a smectic phase formed by an equimolar mixture of two monomeric species corresponding to the mesogenic groups in the non-symmetric dimer; the entropy of the system would be most favourable when, on average, one species was surrounded by the other species (see figure 8). Such an arrangement would be further stabilized if the interaction between the unlike species was greater than the mean of the interaction between like species. This would certainly be the case for molecules with quadrupole moments of opposite sign held parallel to each other. To arrive at the analogous smectic structure for the non-symmetric dimers it is necessary to link pairs of unlike mesogenic groups in adjacent layers with a flexible spacer. Again entropic reasons alone would suggest that the most favourable arrangement would be one in which the spacer connects pairs of neighbouring unlike mesogenic groups more or less randomly throughout the structure, thus giving the intercalated smectic A phase (see figure 8(b)). The formation of such a structure would, however, be inhibited if connecting the mesogenic groups resulted in the creation of a significant volume fraction of voids. In this case a monolayer smectic A phase would be formed, as we have sketched in figure 8(a),

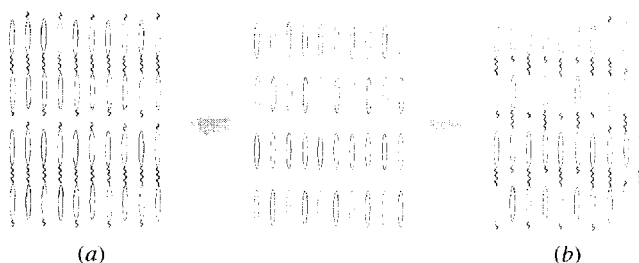


Figure 8. Caricatures illustrating the formation by non-symmetric dimers of (a) monolayer and (b) intercalated smectic A phases from a smectic A structure composed of an equimolar mixture of mesogenic monomers.

although other interactions might intervene to modify this monolayer structure. Thus for the dimers with a cyanobiphenyl group, dipolar interactions result in the creation of an interdigitated structure. In order to avoid the formation of the monolayer structure and create an intercalated smectic structure, it would seem to be necessary for the spacer and the terminal chain to have comparable lengths. However, just how comparable the lengths of the spacer and terminal chains should be proves to be a delicate issue. For example, whereas the cyanobiphenyl–Schiff's base dimers CBO12O.10, CBO11O.10 and CBO10O.10 all form intercalated smectic A phases, the next two members of the series CBO9O.10 and CBO8O.10 are purely nematogenic and the following members with spacer lengths of seven to three exhibit interdigitated smectic A phases [4]. On the basis of this evidence, it would seem that the spacer length should be at least two atoms longer than the terminal chain. Alternatively the vacancies could be filled to a certain extent by moving the liquid crystal dimers with respect to each other, although in so-doing the translational order characteristic of the smectic phase will be lowered and the overlap between unlike mesogenic groups would be reduced. If neither mechanism can fill voids, then a monolayer smectic phase would result and this would certainly be stabilized by long terminal chains which enhance microphase separation.

We shall now consider how our results for the CBO7CO m series and those of Attard *et al.* [4], for the CBO n O. m series fit in with these ideas concerning the formation of intercalated and interdigitated smectic A phases. The homologue CBO7CO10 might, according to the model, have been expected to form an intercalated phase, since the spacer is comparable in length to the terminal chain. However, even including the ester group as part of the spacer gives nine atoms, which is shorter than the terminal chain with eleven atoms. Our experience with the cyanobiphenyl–Schiff's base dimers [4] would suggest therefore, that CBO7CO10 should not exhibit an intercalated smectic phase, but rather an interdigitated smectic A; this is indeed the case. For CBO7CO2, the terminal alkyl chain is significantly shorter than the flexible spacer and so, according to the model, it would be difficult to fill the voids generated in an intercalated smectic A phase and yet such a phase is favoured by this mesogen. Indeed, the cyanobiphenyl–Schiff's base non-symmetric dimers (the CBO n O. m s) [4] exhibit equally anomalous behaviour. For example, CBO12O.2 would not be expected to form an intercalated smectic A phase, because the terminal chain is significantly shorter than the flexible spacer and yet it does.

The problem for the intercalated smectic A phases formed from non-symmetric dimers with spacer and terminal chains which differ significantly in length is to see

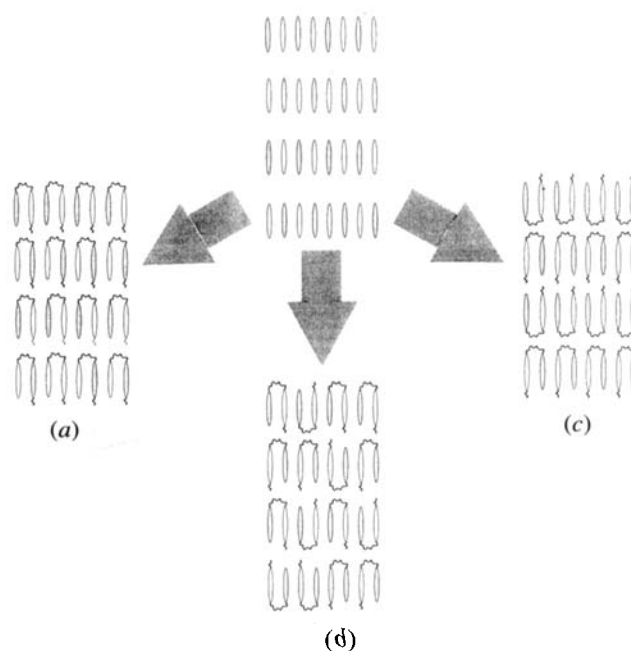


Figure 9. Caricatures illustrating the formation of (a) and (b) intercalated and (c) bilayer smectic A phases from a smectic A structure of an equimolar mixture of mesogenic monomers.

how the resultant voids inherent in the system, sketched in figure 8(b), can be filled. One possible, although extreme, solution to this problem can be seen by returning to the hypothetical smectic A phase formed by an equimolar mixture of mesogenic monomers (see figures 8 and 9). Now, when we come to form the non-symmetric dimers instead of linking together different mesogens in adjacent layers with the flexible spacer we connect together different mesogens in the same layer. Clearly the connection of mesogenic groups in identical smectic layers can only be achieved by deforming the chain, possibly through the introduction of *gauche* links; presumably the energetic cost of the creation of such hairpin or horseshoe-like structures could be regained from the favourable interaction between unlike mesogenic groups. Three ways in which the intralayer links might be formed are sketched in figure 9 and it is apparent from these that such structures require long spacers and short terminal chains, as observed experimentally. In structures (a) and (b), the periodicity is equal to half the molecular length as required for an intercalated structure, although if this is the structure, then the term *intercalated* will not be appropriate; however, until the structure has been identified definitively it seems reasonable to persist with this term. Structure (a) links mesogenic groups coherently with the spacers for one layer being on the same side of the layer. A phase with this structure would be ferroelectric unless domains within the structure with opposite orientations

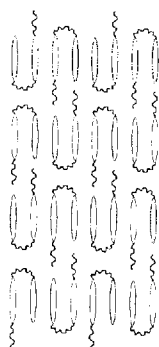


Figure 10. A caricature of a possible organization within the intercalated smectic A phase of a non-symmetric dimer with a long terminal chain comparable in length to the spacer. The dimer adopts a horseshoe conformation as a result of the favourable interaction between unlike mesogenic groups.

averaged out the ferroelectric property. In structure (b) the arrangement of the spacers linking different mesogenic groups within the same layer is more or less random on either side of the layer. This structure would seem more likely on entropic grounds and would also give a non-ferroelectric phase. Structure (c) has a periodicity equal to the molecular length and so is not an intercalated smectic A phase. On entropic grounds, it seems unlikely although favourable interactions between the terminal alkyl chains could lead to its stabilization.

If the horseshoe conformation of the spacer is stabilized by specific interactions between the two different mesogenic groups, it is to be expected that this arrangement might also occur for the other smectic phases formed by the non-symmetric dimers. For example, when the terminal chain is long, but only just shorter than the spacer, then an intercalated smectic phase may also form as we found for the cyanobiphenyl–Schiff's base dimers [4]. It proves to be possible with some ingenuity to pack such dimers in their horseshoe conformations into an arrangement in which the periodicity is equal to half the molecular length as we have found for the intercalated phase. The proposed molecular organization within such an intercalated smectic A phase is sketched in figure 10. It is also tempting to explore the possibility of packing such horseshoe conformations of the non-symmetric dimers with long terminal chains to give an interdigitated smectic A phase as exhibited by CBO7CO10. In fact this can be achieved as the sketch in figure 11 clearly demonstrates for a cyanobiphenyl–Schiff's base dimer; in fact this is a straightforward extension of the structure in figure 9(c) to dimers with longer terminal chains. The bilayer structure has a periodicity which is less than twice the molecular length because the molecule is folded as a result of the favourable interaction of the unlike mesogenic groups.

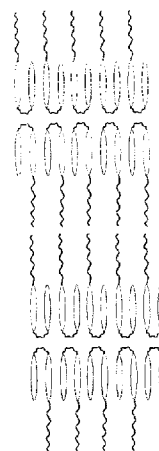


Figure 11. A caricature of the possible organization of non-symmetric dimers, in their horseshoe conformation, within an interdigitated smectic A phase.

4. Conclusions

We have presented the liquid crystal properties of two series of non-symmetric dimers composed of the 4-*n*-alkyl-oxycinnamate and cyanobiphenyl groups. The length and parity of the flexible alkyl spacer has a major effect on the nematic–isotropic transition temperatures for the CBO n CO1s such that a large odd–even effect is exhibited by the series; this is also apparent in the entropy change at the nematic–isotropic transition. Except for the $n = 7$ homologue, the CBO n CO1s exhibit monotropic nematic phases. We have investigated the liquid crystal properties of the CBO7CO m s and have discovered an unusual smectic behaviour as the series is traversed: smectic A phases are only exhibited by the $m = 2, 3, 9$ and 10 homologues. X-ray diffraction experiments performed on the smectic A phases of the ethyl and decyl members of the series revealed their phase structures to be intercalated and interdigitated, respectively. This intriguing behaviour can be understood in terms of an average uniform mixing of the unlike monomeric mesogenic groups caused partly by entropic forces and possibly by specific, favourable interactions between the different groups. Such interactions may be quadrupolar in origin and not the charge transfer interaction originally proposed for the intercalated phases formed by non-symmetric dimers with cyanobiphenyl and Schiff's base groups [3]. The linking of these groups by the spacer to give an interdigitated structure may then result from the long terminal chain which drives microphase separation. If this constraint is removed by having much shorter terminal chains, then the mesogenic groups can be connected to give an intercalated phase in which the translational disorder may help to remove voids in the structure. However, when the difference in length between the spacer and terminal chains is large, as it is for certain of the cyanobiphenyl–

Schiff's base non-symmetric dimers, it is difficult to see how the voids in the structure resulting from this difference can be filled. This difficulty would vanish if the flexible spacer connects different mesogenic groups in the same rather than adjacent smectic layers. This would require the dimers to adopt an energetically unfavourable horseshoe conformation of the spacer, although a favourable interaction between unlike mesogenic groups might compensate for this. It also seems possible to pack dimers with long terminal chains when they adopt this horseshoe conformation into interdigitated as well as intercalated smectic A phases. Whether this is the correct explanation for any or all of these structures must await the results of further experiments, possibly using neutron scattering of protonated/deuteriated mixtures

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