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The liquid crystal properties of symmetric and non-symmetric dimers based on the azobenzene mesogenic group

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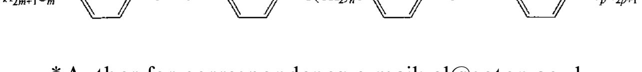
A novel system of symmetric and non-symmetric dimers containing azobenzene groups has been synthesized and studied in an attempt to understand further the molecular origins of the intercalated smectic phases. For the non-symmetric dimers, the lack of symmetry was derived solely from the differences in length of the two terminal alkyl chains. Both the spacer and terminal chain lengths were varied. The spacer length was found to exert a profound influence on the clearing temperatures of these materials and a large odd–even effect was observed for the series. The smectic A phase stability was observed to increase with the terminal chain length, yet decrease with increasing spacer length. X-ray diffraction has revealed the structure of the smectic A phase of both the symmetric and non-symmetric azobenzene dimers to be of the monolayer type and not intercalated. The existence of the intercalated phase has previously been explained in terms of either a charge-transfer interaction, or by an electrostatic quadrupolar interaction. However, it has been thought that it may also be the result of an excluded volume or space filling constraint. For the non-symmetric liquid crystal dimers described here, a charge-transfer interaction should be minimal, as should the stabilization from the quadrupolar interaction between the two mesogens. However, it appears that some sort of specific interaction is required to stabilize the intercalated structure.

1. Introduction

Since the discovery of liquid crystal dimers [1], and the subsequent interest in these materials [2], many dimeric systems have been reported. Liquid crystal dimers are of interest because they can act as models for main group liquid crystalline polymers that allow the study of the flexibility and properties of different mesogenic groups. Thus dimeric liquid crystals retain the crucial structural components of many thermotropic main group polymers, namely a flexible spacer linking two mesogenic groups, yet they are easier to study and are amenable to a more straightforward interpretation. Furthermore, as a distinct class of compounds with unusual properties and potential for application, dimeric liquid crystals are of interest in their own right.

Many studies of symmetric dimers have been reported. For example, the symmetric Schiff's base dimers prepared by Date *et al.* [3], namely the α,ω-bis(4-alkylaniline-benzylidene-4′-oxy)alkanes; these dimers were found to exhibit a rich smectic polymorphism.



An X-ray diffraction study of these compounds showed that the molecules are arranged in monolayers in the smectic phases [3], see figure 1 (*a*); i.e. a microphase separation into three regions—terminal chains, mesogenic groups and flexible alkyl spacers—has occurred. If the formation of the layers was considered from a purely steric viewpoint, it could well be imagined that symmetric dimers may assemble into an intercalated structure where the terminal chains and spacer overlap, see figure 1 (*b*). However, the results for the symmetric Schiff's base dimers showed that for smectic behaviour to be observed the terminal chain length must be greater than half the spacer length [3]. This suggests that the terminal chain-spacer interaction is an unfavourable one. If the spacer is considered to be part of the overall mesogenic centre, such that the mesogen–spacer–mesogen sequence is thought of as a central unit, then the observed phase behaviour parallels the effect of increasing the size of the core in monomeric systems which leads to the reduction of smectic tendencies [4]. That is, increasing the spacer length for a given terminal chain length serves to increase the mesogen–mesogen interactions thus diluting the influence of the smectic-promoting terminal chains.

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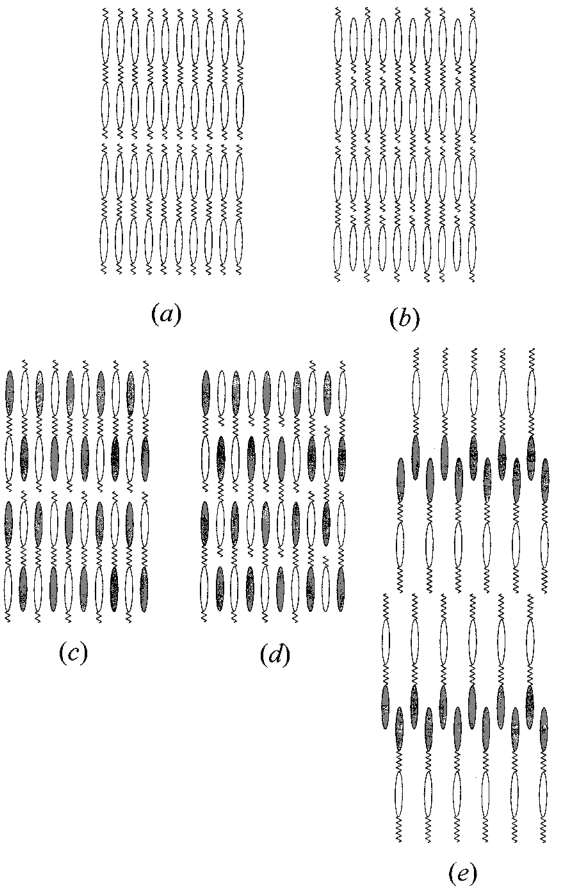
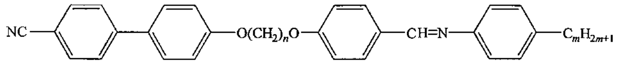


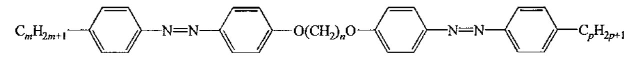
Figure 1. Schematic representation of the structure of (*a*) the monolayer, (*b*) the intercalated smectic A phases for symmetric dimers; and (*c*) the monolayer, (*d*) the intercalated and (*e*) the interdigitated smectic A phases for non-symmetric dimers.

However, exceptions to this rule exist. Such an exception is shown by the non-symmetric dimers α-(4-alkylanilinebenzylidene-4′-oxy)-ω-(4-cyanobiphenyl-4′-yloxy)alkanes, where now two different mesogenic groups are linked through a flexible spacer [5, 6].

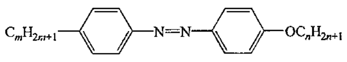


Contrary to expectations, the smectic behaviour exhibits an unusual dependence on the relative terminal chain and spacer lengths. If the terminal chain length was such that it could easily fit into the gap allowed by the spacer, then an intercalated smectic phase is formed, see figure 1 (*d*). However, if the terminal chain was longer, the molecules adopted an antiparallel, interdigitated arrangement, shown in figure 1 (*e*), presumably driven by an electrostatic interaction between the polar cyano and polarizable phenyl groups, the smectic phase resulting from the molecular inhomogeneity caused by the long terminal chains, as for monomers. The intercalated smectic phase arrangement was originally postulated [5, 6] to be stabilized by a favourable charge-transfer interaction between the cyanobiphenyl and Schiff's base groups. However, a more recent study [7] of the non-symmetric dimers formed by linking the cyanobiphenyl mesogen to a cinnamoate moiety through a flexible spacer, has cast doubt on this explanation. The cinnamoate moiety was chosen because the likelihood of any significant charge transfer interaction with the cyanobiphenyl groups is small. It was found that where the terminal chain and spacer lengths were compatible, an intercalated smectic A phase was formed. In this instance, it was suggested that in addition the intercalated smectic phase may be stabilized by an electrostatic quadrupolar interaction between unlike mesogenic groups with quadrupole moments having opposite signs. It was also suggested that the intercalated smectic phase formation is driven by an increase in entropy as a result of homogeneous mixing of the mesogenic groups, rather than their segregation into different spatial regions.

However, the intercalated phase may also form as a result of excluded volume or space filling constaints. In order to explore this possibility, we have attempted to prepare an intercalated phase structure where the charge-transfer interaction was minimized, as was the difference in the quadrupole moments of the two mesogens. We have therefore synthesized non-symmetric dimers in which the lack of symmetry derives solely from differences in the terminal alkyl chain lengths, thereby prohibiting any specific interactions between the mesogenic groups. These materials are the α-(4′-alkylazobenzene-4-oxy)-ω-(4′-alkylazobenzene-4-oxy)alkanes.

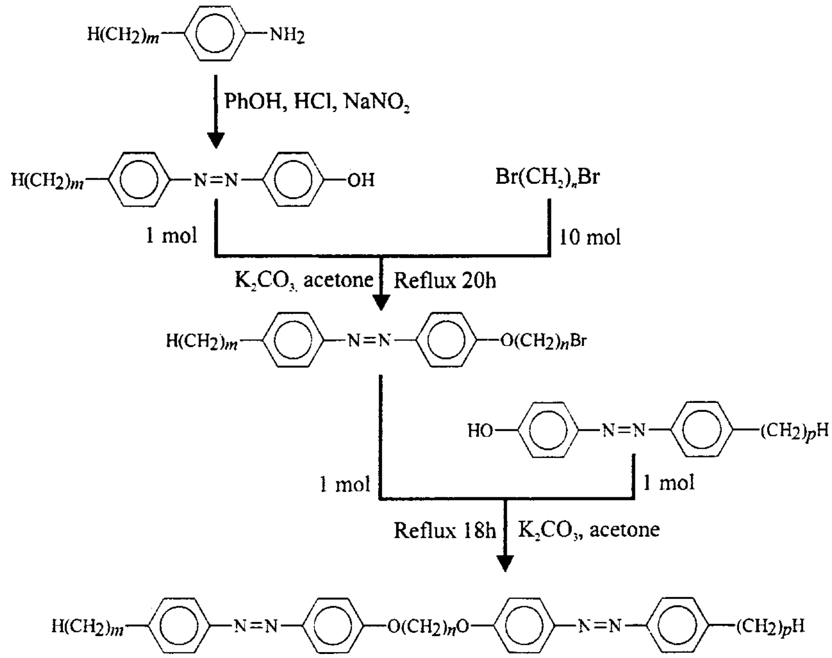


They are denoted by the mnemonic *m*AO*n*OA*p* where A indicates the azobenzene moiety, O an oxygen atom, *m* and *p* are the lengths of the terminal chains and *n* is the length of the alkyl spacer. The nature of the structure of these materials meant that in synthesizing homologous series of non-symmetric dimers, symmetric dimers were also available. The liquid crystalline properties of these symmetric azobenzene dimers are also discussed. The monomeric analogues of the dimers are the 4-alkoxy-4′-alkylazobenzenes, and are referred to as *n*OA*m* where *n* represents the length of the terminal alkoxy chain and *m* that of the terminal alkyl chain.



2. Experimental

The *m*AO*n*OA*p* dimers were prepared according to the reaction scheme. The synthetic route used in the preparation of these non-symmetric dimers involved



Scheme.

three steps: (i) the coupling reaction of phenol with the diazotized 4-alkylaniline to produce the 4-alkyl-4′-hydroxyazobenzenes; (ii) the subsequent reaction of these with a tenfold excess of an α,ω-dibromoalkane to produce the 4-alkyl-4′-(ω-bromoalkyloxy)azobenzenes (the tenfold excess of the dibromide ensured that the main product of the reaction was the singly substituted species); (iii) the reaction of these products with a different 4-alkyl-4′-hydroxyazobenzene yielded the dimers.

The detailed synthetic procedure is illustrated using α-(4′-hexylazobenzene-4-oxy)-ω-(4′-propylazobenzene-4-oxy)hexane as an example. The 4-alkylanilines were obtained commercially and were redistilled immediately before use. All intermediates and final products were structurally characterized by high field proton NMR spectroscopy (Bruker AM 360 MHz NMR spectrometer), thin layer chromatography and elemental analysis. 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 measure the thermal behaviour at the phase transitions. The smectic layer spacings were determined by X-ray diffraction. A Guinier camera fitted with a bent quartz monochromator (R. Huber, Germany) was used; the monochromator was adjusted to isolate CuK$_\alpha$ radiation ($\lambda = 1.5405$ Å). 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, Gateshead, England).

2.1. *Synthesis of 4-hydroxy-4′-propylazobenzene*

4-Propylaniline (0.072 mol, 9.72 g) was dissolved in 6M hydrochloric acid (52 ml) with warming. The solution was then cooled in ice causing crystallization of some of the 4-propylaniline hydrochloride. Whilst maintaining the reaction temperature between 0 and 5°C, a cold solution of sodium nitrite (0.107 mol, 7.38 g) in water (16 ml) was added to give a solution of the diazonium salt. This solution was added to a cold solution of phenol (0.070 mol, 6.58 g) in sodium hydroxide (7M, 50 ml), carefully maintaining the same temperature limits, and the resulting mixture acidified with concentrated hydrochloric acid. The product was filtered and washed until the washings were neutral to litmus. After air drying, the product was washed with petroleum ether (b.p. 40–60 or 60–80°C) yielding the 4-hydroxy-4′-propylazobenzene. Yield 68% (yields ranging from 64 to 72% for the series). ^{1}H NMR (CDCl$_3$, δ), 0.9–1.1 (t, 3H), 1.5–1.6 (sx, 2H), 2.6–2.7 ppm (t, 2H), 6.8–7.2 (m, 8H). MS: 240 (M$^+$).

2.2. *Synthesis of 4-ω-bromohexyloxy-4′-propylazobenzene*

Into a 500 ml single-necked round-bottomed flask were placed 1,6-dibromohexane (0.4 mol, 97.5 g), potassium carbonate (0.29 mol, 40.1 g) and 160 ml acetone. 4-Hydroxy-4′-propylazobenzene (0.04 mol, 9.6 g) was then added and the mixture stirred for 20 h under reflux conditions. The solution was hot filtered to remove the potassium bromide and excess of potassium carbonate. The acetone was partially removed to induce crystallization of the product which was then filtered and recrystallized several times from ethanol. (The excess of dibromide was recovered by distillation under reduced pressure for re-use.) Yield 71% (yields ranged from 64 to 71% for the series). ^{1}H NMR ($CDCl_3$, δ), 1.0 (t, 3H), 1.4–1.6 (m, 4H), 1.6–1.8 (sx, 2H), 1.8–1.9 (qn, 2H), 1.9–2.0 (qn, 2H), 2.6–2.8 (t, 2H), 3.4–3.5 (t, 2H), 4.0–4.1 ppm (t, 2H), 6.8–7.2 (m, 8H). MS: 402 (M^+). Elemental analysis: calculated for $C_{21}H_{27}N_2OBr$, C 60.72, H 9.40, N 6.75; found, C 60.66, H 9.29, N 6.73%.

2.3. *Synthesis of α-(4′-hexylazobenzene-4-oxy)-ω-(4′-propylazobenzene-4-oxy)hexane*

4-Hexyl-4′-hydroxyazobenzene (0.0013 mol, 0.37 g) and 4-propyl-4′-bromohexyloxyazobenzene (0.0013 mol, 0.54 g) were dissolved in 25 ml of acetone. Potassium carbonate (0.013 mol, 1.80 g) was added and the mixture stirred for 18–20 h under reflux conditions. The mixture was hot filtered and the residue washed through with a little hot acetone. The acetone was removed and the product recrystallized several times from ethyl acetate. Yield 69% (yields ranged from 58 to 71% for the series). ^{1}H NMR ($CDCl_3$, δ), 0.9–1.1 (t, 6H), 1.1–1.8 (m, 18H), 2.6–2.8 (t, 4H), 4.0–4.2 (t, 4H), 6.8–7.2 (m, 8H), 7.4–7.8 (m, 8H). MS: 604 (M^+). Elemental analysis: calculated for $C_{39}H_{48}N_4O_2$, C 77.48, H 7.95, N 9.27; found, C 77.43, H 7.84, N 9.25%.

3. Results and discussion

3.1. *Phase assignments*

Nematic phases were assigned from their schlieren optical texture containing both types of point singularities, which flashed when subjected to mechanical stress, combined with the high mobility of the phase. On cooling some of the compounds, the schlieren texture changed to give coexisting regions of focal-conic fan and homeotropic textures. The presence of focal-conic fans implied a layered structure, while the homeotropic alignment indicated an orthogonal arrangement of the director with respect to the layer planes. In consequence, this lower temperature phase was assigned as a smectic A phase.

3.2. *The symmetric dimers*

3.2.1. *The dependence of the transitional properties on the length of the alkyl spacer: the 5AOnOA5 series*

The transition temperatures of the 5AO*n*OA5 series are given in table 1; all members of the series up to and including ten methylene units in the flexible alkyl spacer exhibit smectic behaviour. The dependence of the transition temperatures on the number of methylene units, *n*, in the flexible alkyl spacer is shown in figure 2. All the members of the series exhibit enantiotropic mesophases with the exception of the $n = 3$ dimer. The $n = 3$ and 10 dimers form monotropic smectic A phases.

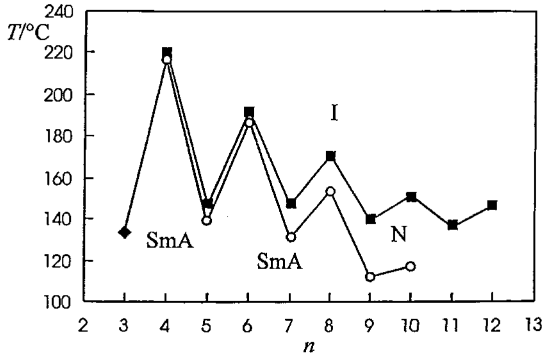
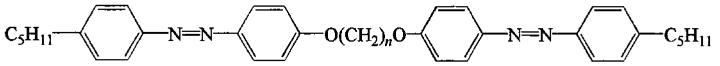


Figure 2. The dependence of the transition temperatures on the number of methylene units, *n*, in the alkyl spacer for the 5AO*n*OA5 series. The N–I transition is indicated by ■, the SmA–I transition by ◆, and the SmA–N transition by ○. The melting points have been omitted for clarity.

Table 1. Transition temperatures and entropies [in square brackets] for the 5AO*n*OA5 series.



	Transition temperatures/°C [$\Delta S/R$]						
n	Cr		SmA		N		I
3	•	154[17.7]	(•	133[1.33])[a]			•
4	•	118[9.1]	•	218[0.64]	•	220[2.11]	•
5	•	115[10.9]	•	139[0.49]	•	147[0.48]	•
6	•	146[9.6]	•	187[0.43]	•	192[2.07]	•
7	•	118[12.1]	•	131[0.16]	•	147[0.85]	•
8	•	120[15.4]	•	154[0.13]	•	171[2.05]	•
9	•	104[12.5]	•	112[0.10]	•	139[0.81]	•
10	•	127[20.6]	(•	117[0.05])[a]	•	151[2.23]	•
11	•	114[18.8]			•	136[0.98]	•
12	•	123[20.0]			•	146[2.37]	•

[a] Parentheses () denote a monotropic transition.

There is a pronounced odd–even effect in the clearing and SmA–N transition temperatures in which the even members have the greater values, and as expected this alternation attenuates with increasing spacer length. The early members of the 5AO*n*OA5 series exhibit smectic A–isotropic ($n = 3$) and smectic A–nematic ($n = 4$–10) phase transitions, whereas the higher members ($n = 11$ and 12) are purely nematogenic. This observation is not in accord with the general result that increasing the length of an alkyl chain promotes smectic behaviour in low molar mass mesogens [4] (although in this case we are comparing spacer length with terminal chain length) and that increasing the spacer length in semi-flexible main chain polymers also promotes smectic behaviour. This intriguing aspect will be discussed later.

A comparison of the phase behaviour of the dimers with the analogous monomers is noteworthy. As expected, the dimers possess higher melting and clearing temperatures resulting from the enhanced length and hence anisotropy, as well as an assumed increase in the orientational order (of the even membered dimers) compared with their monomeric analogues, resulting from the reduction in the degree of freedom of the mesogens arising from the central linking group. However, the monomers are purely nematogenic [8], whereas the analogous dimers exhibit smectic and nematic behaviour. In this context, the corresponding monomer is taken as exactly *half* the dimer, i.e. as if the dimer were cut in two at the centre of the linking chain. For example, the transition temperatures for 5AO8OA5 are Cr 120°C SmA 154°C N 171°C I, and for the corresponding monomer, 5AO4, are Cr 66°C N 86°C I. This is contrary to the previously held view [2] that smectic behaviour is lost on passing from the monomer to the dimeric analogue, but agrees with the findings of Date *et al.* [3], who argued that there is no apparent reason for dimers to be less smectogenic than the corresponding monomer, because smectic behaviour is thought to be a consequence of molecular inhomogeneity, i.e. the smectic phase formation is driven by the preference of the different regions of the molecules (the terminal chains, spacer and mesogenic moieties) to separate.

The entropy changes associated with the liquid crystal transitions for the 5AO*n*OA5 series are also given in table 1. Figure 3 shows the dependence of the entropy changes associated with the smectic A–nematic/isotropic and nematic–isotropic phase transitions on the number of methylene units, *n*, in the flexible alkyl spacer; a dramatic odd–even effect is revealed for transitions into the isotropic phase, which does not attenuate on increasing *n*. The nematic–isotropic transition entropies for the even members are in most instances several times larger than those of the odd members. The underlying trend in the clearing entropies for the 5AO*n*OA5 series is a slightly increasing one with increasing *n*, as is the case for monomers. It is interesting to note the absence of an alternation for the smectic A–nematic transition, in agreement with observations by Le Masurier and Luckhurst for non-symmetric dimers [9].

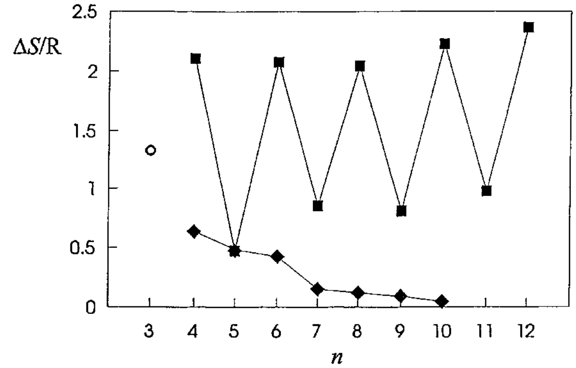


Figure 3. The dependence of the transition entropies on the number of methylene units, *n*, in the alkyl spacer for the 5AO*n*OA5 series. The N–I transition is indicated by ■, the SmA–N transition ◆, and the SmA–I transition by ○.

Figure 4 shows a comparison of the clearing temperatures of the symmetric azo dimers, 5AO*n*OA5, with the analogous Schiff's base dimers, 5SBO*n*OSB5 [3]. Not surprisingly, the two series exhibit similar clearing temperatures, mirroring the likeness of the mesogenic groups. The phase stabilities of the azo dimers are slightly higher however, and this is attributed to a difference in the angle between the planes of the benzene rings influenced by the linking group. For the azo linkage, the benzene rings are planar [10], whereas for the Schiff's base link, the angle between the planes of the benzene rings is 40–45° [10]. Purely smectic behaviour does persist for longer in the Schiff's base dimer series, up to $n = 5$, whereas the $n = 3$ azo dimer is the only homologue to possess a smectic A–isotropic transition.

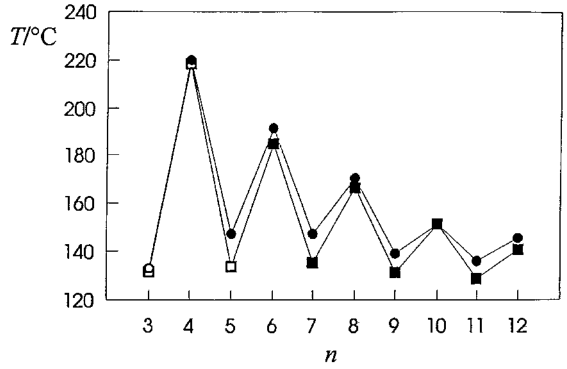


Figure 4. The dependence of the transition entropies on the number of methylene units, *n*, in the alkyl spacer for the 5AO*n*OA5 (●, ○) and 5SBO*n*OSB5 (■, □) series. Filled symbols represent nematic–isotropic transitions and open symbols denote smectic–isotropic transitions.

Furthermore, the Schiff's base dimers exhibit smectic A and smectic B phases as well as the nematic phase, whereas the azo-linked dimers exhibit only smectic A and nematic phases.

The 5AO*n*OA5 series acts as an archetypal example of a homologous series of dimeric liquid crystals with a very large alternation in both the nematic–isotropic transition temperatures and entropies with the length of the flexible spacer. This has been rationalized in terms of the conformations which the flexible spacer adopts [11]. For the even spacer, there is a greater number of conformations which preserve the parallelism of the two mesogenic groups than there is for the odd spacer. The elongated conformers are favoured in the nematic environment and furthermore, the energy barrier between bent and linear conformers for the even spacer dimer is small and thus the increased orientational order introduced by the liquid crystallinity promotes conformational order, which in turn increases the orientational order. For the odd spacer dimer, the conformational energy barrier to the more linear molecules (where the molecule would have to bend rather like a hairpin) is so high that the conformational distribution does not change on cooling into the nematic phase and so the dimer behaves like the monomer. The transition entropy is then rather small whereas the entropy change at the nematic–isotropic transition for the even spacer dimer is much greater because the variation in the conformational distribution indirectly enhances the orientational order.

3.2.2. *The dependence of the transitional properties on the length of the terminal alkyl chains: the mAO6OAm series*

Table 2 lists the transition temperatures for the *m*AO6OA*m* symmetric dimers for *m* = 0–6. This variation in length of the terminal chains was investigated because we were interested in the smectic phase behaviour of the dimers where the terminal chains were such that they could in principle overlap the spacer in a smectic phase arrangement and so give an intercalated SmA phase. The dependence of the transition temperatures on the number of carbon atoms, *m*, in the terminal alkyl chains is shown in figure 5. The first member of the series ($m=0$) is not liquid crystalline. Subsequent increases in the lengths of the terminal alkyl chains stabilize enantiotropic liquid crystal phases for all the remaining homologues. For this series, the spacer contains an even number of linking units and as such it would be expected to possess a greater number of conformations in which the parallelism of the mesogenic groups is preserved, than for the corresponding odd spacer series. This is reflected in the earlier appearance of liquid crystalline behaviour for the *m*AO6OA*m* series (at $m = 1$, whereas for the *m*AO5OA*m* series, liquid crystallinity is not observed until *m* is 2 [12]). Furthermore, the melting points and clearing temperatures are approximately 50°C higher for the even spaced *m*AO6OA*m* dimers than for the corresponding *m*AO5OA*m* series [12]. The clearing temperatures exhibit

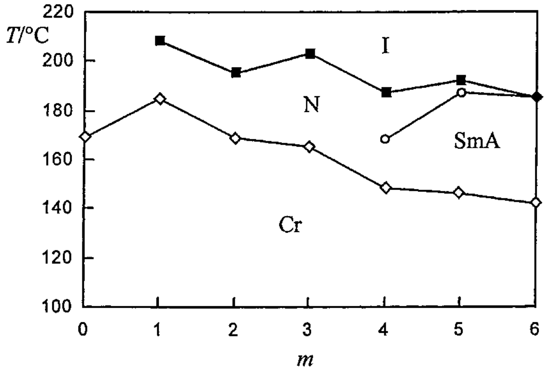
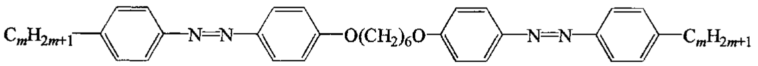


Figure 5. The dependence of the transition temperatures on the number of carbon atoms, *m*, in the terminal alkyl chains for the *m*AO6OA*m* series. The N–I transition is indicated by ■, the SmA–N transition by ○, the SmA–I transition by ◆, and the Cr–SmA/N/I transition by (◇).

Table 2. Transition temperatures and entropies [in square brackets] for the *m*AO6OA*m* series.



	Transition temperatures/°C [$\Delta S/R$]						
m	Cr		SmA		N		I
0	•	169[20.0]					•
1	•	185[14.0]			•	208[1.74]	•
2	•	169[10.7]			•	195[1.37]	•
3	•	165[10.3]			•	203[1.85]	•
4	•	148[8.9]	•	168[0.16]	•	187[1.54]	•
5	•	146[9.6]	•	187[0.39]	•	192[2.11]	•
6	•	142[13.9]	•	185[3.88]			•

a small, but marked, alternation which attenuates on increasing *m*. The clearing temperatures for homologues with an odd number of carbon atoms in the terminal alkyl chain lie on a curve above the corresponding values for the even members, reflecting the enhanced length-to-breadth ratio for the odd terminal chain. This behaviour is typical of a homologous series of conventional monomeric mesogens possessing high clearing points [13].

As *m* increases so also does the smectic A phase stability at the expense of the nematic phase range such that the $m = 6$ homologue is purely smectogenic. The *m*AO6OA*m* series exhibits very slightly higher transition temperatures than the analogous Schiff's base dimers [3], reflecting the difference in the planarity of the rings discussed earlier. As with the observations based on varying the spacer length in § 3.2.1, whereas the azo-linked dimer liquid crystal phases are thermally more stable, the Schiff's base linkage generates more varied smectic behaviour. For example, the *m*AO6OA*m* dimers where $m = 4$–6 form a smectic A phase whereas the corresponding *m*SBO6OSB*m* dimers exhibit a greater smectic polymorphism (SmB and SmF as well as SmA phases).

It has been suggested that the smectic tendencies of monomers are lost when coupled to form the dimer [2]. However, if we consider the monomeric analogue of 6AO6OA6 to be 6AO3 [8], then the opposite is in fact true—6AO3 is purely nematic whereas 6AO6OA6 exhibits a smectic A phase. In this case, and in comparisons for the other dimers for which the monomer data are available, coupling of the monomer to form a dimer leads to an enhancement of the smectic tendencies.

Table 2 also lists the entropies associated with the liquid crystal transitions for the *m*AO6OA*m* symmetric dimers for $m = 0$–6. The dependence of the transition entropies on the number of carbon atoms, *m*, in the terminal alkyl chains is shown in figure 6. A small odd–even effect is observed in the nematic–isotropic transition entropies, with the values for the odd terminal chain homologues lying above the corresponding data for the even members. The alternation is clearly much smaller than for a homologous series based on increasing the spacer length, primarily because the molecular shape does not change dramatically with the parity of the terminal chain.

3.3. *The non-symmetric dimers*

3.3.1. *The dependence of the transitional properties on the length of the terminal chains: the mAO6OAp series*

The transition temperatures and entropies for the *m*AO6OA*p* series are given in table 3. Figures 7 (*a*–*g*) show the dependence of the transition temperatures on the number of carbon atoms, *m*, in one of the terminal alkyl chains. The melting points of the various series do not appear to show any common trends when compared with each other as the following observations show. The melting points for the *m*AO6OA0 series exhibit an alternation in a similar manner to the clearing temperatures, i.e. the even membered homologue values lie below the curve of the odd *m* members, but this alternation is less pronounced than for T_{NI}.

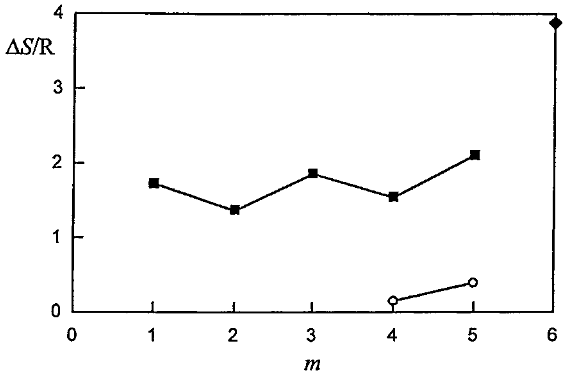


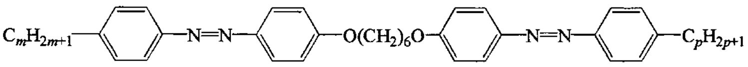
Figure 6. The dependence of the transition entropies on the number of carbon atoms, *m*, in the terminal alkyl chains for the *m*AO6OA*m* series. The N–I transition is indicated by ■, the SmA–N transition by ○, and the SmA–I transition by ◆.

All of the compounds are liquid crystalline with the exception of 0AO6OA0, and all of the liquid crystalline transitions are enantiotropic. In figure 7 (*b*), for the *m*AO6OA1 series, the nematic–isotropic transition temperature is seen to increase markedly on passing from 1AO6OA0 to 1AO6OA1; it is not apparent why the addition of a single methyl group should have such a profound affect on T_{NI} although it has been suggested that this results from a change in the shape of the mesogenic group rather than from its anisotropy [6]. This observation is mirrored in all members of the series, except for the first, 0AO6OA0, which is not liquid crystalline, see figure 7 (*a*).

From the data it can be seen that the homologues corresponding to *m*AO6OA0 lie at least 40°C below the other members of the series. The clearing temperatures show the classic small alternation on ascending each series, and this attenuates with increasing terminal chain length. As anticipated, the members of the series possessing an even number of carbon atoms in the terminal alkyl chain lie on a curve at lower temperatures than for the odd members. The common gradual fall in the clearing temperatures as a homologous series is ascended, typical for high clearing temperature mesogens, is observed.

The only smectic phase exhibited by these materials is the smectic A phase. The earliest homologue, i.e. with the smallest total number of carbon atoms in the terminal chains, to exhibit this smectic phase is 2AO6OA4.

Table 3. Transition temperatures and entropies [in square brackets] for the mAO6OAp series and 4AO7OA4 dimer.



	Transition temperatures/°C [$\Delta S/R$]						
mAO6OAp	Cr		SmA		N		I
0AO6OA0	•	169[20.0]					•
1AO6OA0	•	149[13.5]			•	159[1.20]	•
2AO6OA0	•	142[15.5]			•	153[0.97]	•
3AO6OA0	•	142[15.2]			•	161[1.29]	•
4AO6OA0	•	139[15.1]			•	154[1.20]	•
5AO6OA0	•	140[15.3]			•	158[1.35]	•
6AO6OA0	•	136[15.5]			•	151[1.18]	•
1AO6OA1	•	185[14.0]			•	208[1.74]	•
2AO6OA1	•	156[14.3]			•	201[1.55]	•
3AO6OA1	•	151[13.3]			•	206[1.79]	•
4AO6OA1	•	130[14.6]			•	197[1.60]	•
5AO6OA1	•	133[13.5]			•	198[1.73]	•
6AO6OA1	•	139[13.2]			•	191[1.58]	•
2AO6OA2	•	169[10.7]			•	195[1.37]	•
3AO6OA2	•	158[9.9]			•	200[1.61]	•
4AO6OA2	•	140[9.0]	•	143[0.00]	•	192[1.51]	•
5AO6OA2	•	120[11.6]	•	159[0.06]	•	193[1.65]	•
6AO6OA2	•	130[10.8]	•	165[0.09]	•	183[1.58]	•
3AO6OA3	•	165[10.3]			•	203[1.85]	•
4AO6OA3	•	154[9.8]	•	161[0.08]	•	196[1.71]	•
5AO6OA3	•	136[8.5]	•	174[0.00]	•	197[1.86]	•
6AO6OA3	•	125[11.4]	•	179[0.21]	•	191[1.73]	•
4AO6OA4	•	148[8.9]	•	168[0.16]	•	187[1.54]	•
5AO6OA4	•	141[8.9]	•	180[0.29]	•	191[1.86]	•
6AO6OA4	•	126[12.0]	•	182[0.50]	•	185[1.88]	•
5AO6OA5	•	146[9.6]	•	187[0.39]	•	192[2.11]	•
6AO6OA5	•	137[13.6]	•	188[3.35]			•
6AO6OA6	•	142[13.9]	•	185[3.88]			•
4AO7OA4	•	111[12.4]	•	121[0]	•	142[0.47]	•

Throughout the series, as anticipated, the smectic phase stability increases on increasing one or both terminal alkyl lengths; thus the 6AO6OA5 and 6AO6OA6 dimers possess smectic A–isotropic transitions.

The dependence of the entropy changes associated with the clearing transitions on the number of carbon atoms, m, in one of the terminal alkyl chains, for the mAO6OA6 series is shown in figure 8 and is typical of the other series. A small alternation in the clearing transition entropies is observed which attenuates rapidly on increasing m, where the values for the odd m members lie on a curve above the even m homologues, in contrast to the spacer behaviour. The values for the smectic A–nematic/isotropic and nematic–isotropic transitions are in general accord with those observed for the symmetric Schiff's base dimers [3].

3.3.2. *The dependence of the transitional properties on the length of the flexible spacer*

The transition temperatures for the 2AOnOA6 non-symmetric dimers are given in table 4. The dependence of the transition temperatures on the number of methylene units, n, in the flexible alkyl spacer is shown in figure 9. All members of this series are liquid crystalline, exhibiting nematic behaviour. Both the melting points and the nematic–isotropic transition temperatures show a very pronounced odd–even effect in which the even members have the higher values; this alternation in the nematic–isotropic transition temperatures attenuates with increasing spacer length as we have come to expect. In addition to the nematic behaviour, the $n = 4$–9 homologues possess a smectic A phase. The smectic A–nematic transition temperatures also exhibit a large odd–even

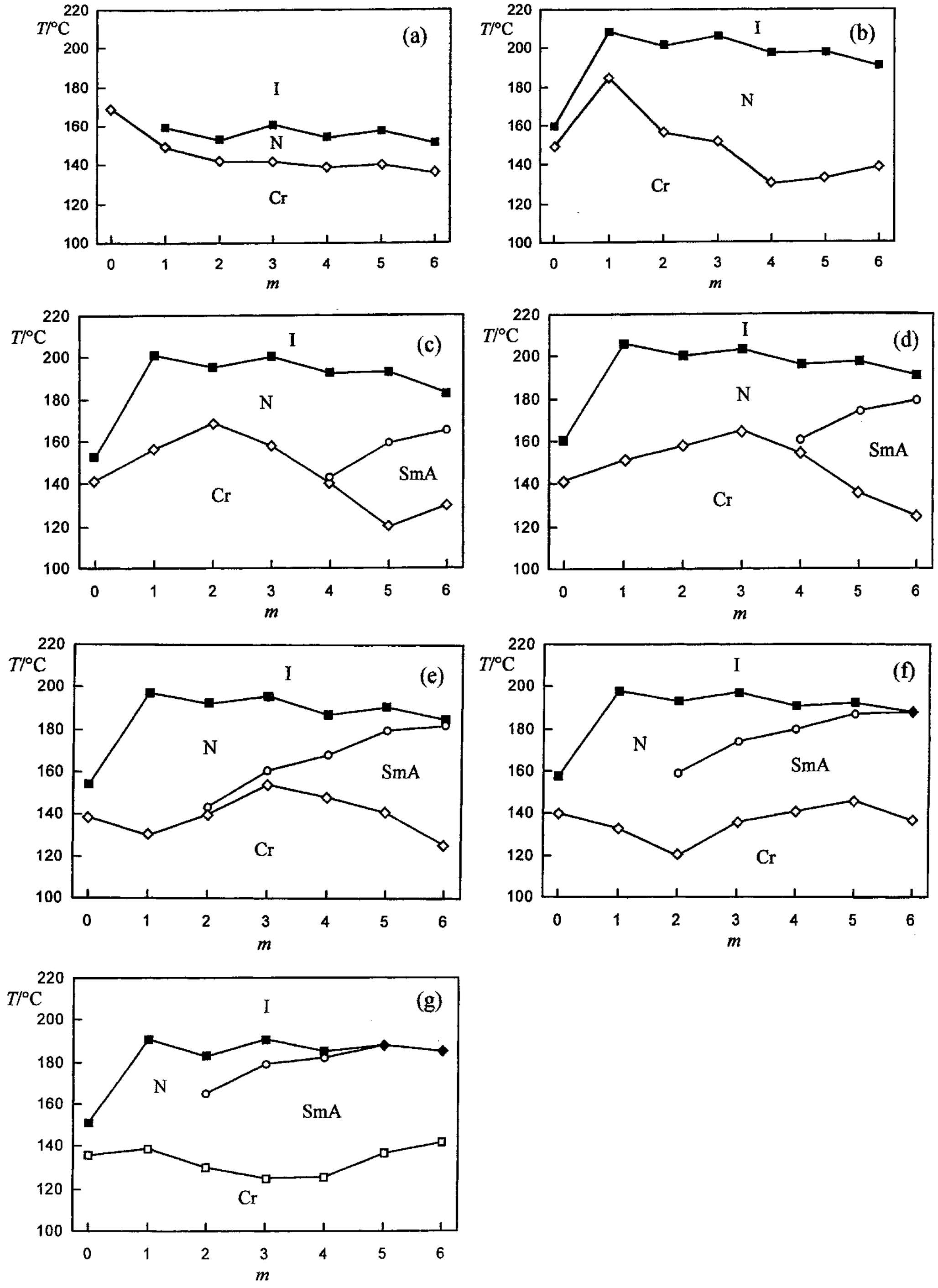
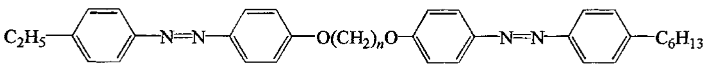


Figure 7. The dependence of the transition temperatures on the number of carbon atoms, *m*, in the terminal alkyl chains for the *m*AO6OA*p* non-symmetric dimers where (*a*) $p = 0$, (*b*) $p = 1$, (*c*) $p = 2$, (*d*) $p = 3$, (*e*) $p = 4$, (*f*) $p = 5$, (*g*) $p = 6$. The N–I transition is indicated by ■, the SmA–N transition by ○, the SmA–I transition by ◆, and the Cr–SmA/N transition by either ◇ or □.

effect; however, the smectic A phase stability steadily decreases until smectic behaviour is extinguished in the compounds with spacer lengths of $n = 10$ and greater.

Table 4 also lists the entropy changes associated with the liquid crystalline transitions; the dependence of these entropy changes on the number of methylene units, *n*, in the alkyl spacer is shown in figure 10. A profound odd–even effect is revealed which does not attenuate on increasing *n*. The entropies for the even members are several times greater than the corresponding values for the

Table 4. Transition temperatures and entropies [in square brackets] for the 2AO*n*OA6 series.



	Transition temperatures/°C [$\Delta S/R$]						
m	Cr		SmA		N		I
4	•	132	•	186[0.50]	•	190[1.50]	•
5	•	114	•	122[0.17]	•	139[0.29]	•
6	•	130	•	165[0.09]	•	183[1.58]	•
7	•	115	(•	108[0.04])^a	•	135[0.48]	•
8	•	130	•	134[0.11]	•	170[1.72]	•
9	•	111	•	122[0.34]	•	128[0.65]	•
10	•	129			•	154[1.83]	•
11	•	107			•	132[0.71]	•
12	•	123			•	144[1.95]	•

[a] Parentheses () denote a monotropic transition.

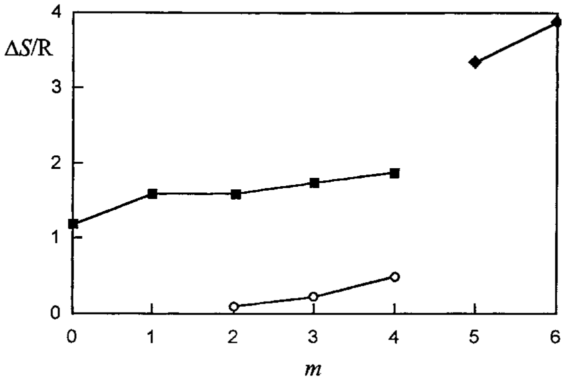


Figure 8. The dependence of the transition entropies on the number of carbon atoms, *m*, in the terminal alkyl chains for the *m*AO6OA6 non-symmetric dimers. The N–I transition is indicated by ■, the SmA–N transition by ○, and the SmA–I transition by ◆.

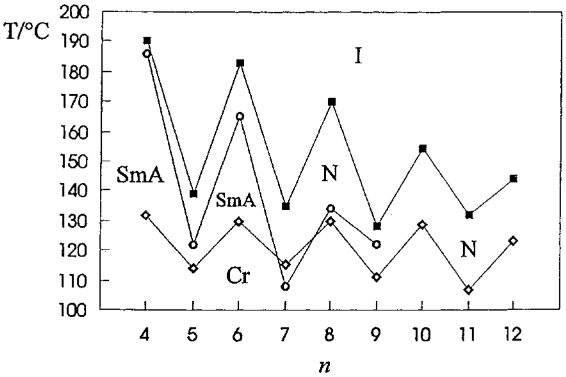


Figure 9. The dependence of the transition temperatures on the number of carbon atoms, *n*, in the alkyl spacer for the 2AO*n*OA6 series. The N–I transition is indicated by ■, the SmA–N transition by ○, and the Cr–N/SmA transition by (◇).

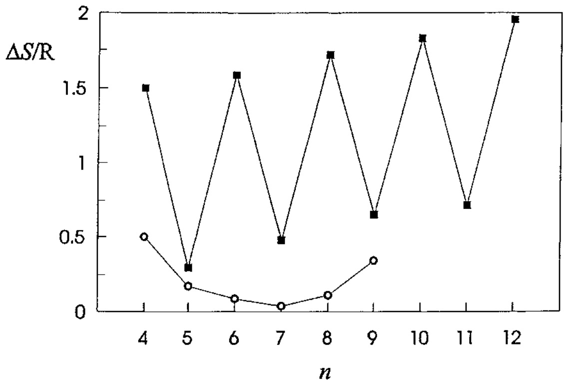


Figure 10. The dependence of the transition entropies on the number of carbon atoms, *n*, in the alkyl spacer for the 2AO*n*OA6 series. The N–I transition is indicated by ■ and the SmA–N transition by ○.

odd dimers, and mirror the behaviour of the symmetric azobenzene dimers reported in § 3.2.

3.4. *The smectic A–nematic transition*

The smectic A–nematic transitions were found to be first order in all cases, for both the symmetric and non-symmetric dimers, with the exception of the 4AO7OA4 dimer. The DSC peak for the 4AO7OA4 dimer was too small to observe, indicating a continuous transition. The SmA–N transition was, however, clearly visible by polarized optical microscopy. The values of the entropy changes associated with this transition varied significantly—from approximately zero to 0.7—with the spacer length. To understand this variation, the smectic A–nematic transition entropy is plotted against the McMillan parameter, $T_{\mathrm{SmAN}}/T_{\mathrm{NI}}$, in figure 11. It can be seen that the magnitude of the transitional entropy

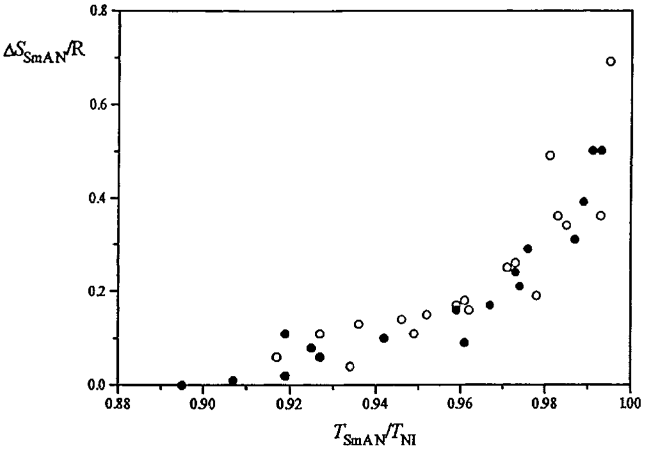


Figure 11. The dependence of $\Delta S_{SmAN}/R$ on T_{SmAN}/T_{NI} for the azobenzene dimers; open circles represent dimers with an even membered spacer and filled circles denote dimers possessing an odd membered spacer.

decreases as the nematic range increases, and is consistent with the McMillan theory [14]. The tricritical point at which the transition becomes second order is at T_{SmAN}/T_{NI} of approximately 0.9. The McMillan theory was originally developed for rigid molecules with cylindrical symmetry. However, the $\Delta S_{SmAN}/R$ values for the dimers weaken in much the same way as is observed for conventional mesogens. It is interesting to note that the values for the odd and even spacers appear to behave in essentially the same way, in contrast to the nematic–isotropic transition for these materials. This behaviour is mirrored by the analogous Schiff's base dimers [3] although it contrasts with results obtained for non-symmetric dimers where the odd members appear to have stronger transitions after allowance is made for the length of the nematic phase [9].

3.5. *The smectic behaviour of dimers*

In the series of non-symmetric azobenzene dimers studied here, we have found that the smectic phase stability increases with increasing terminal alkyl chain length, and conversely decreases with increasing spacer length. This behaviour is in accord with that of the symmetric azobenzene dimers, and with the symmetric Schiff's base dimers reported by Date *et al.* [3]. This is in marked contrast to the liquid crystalline properties of the non-symmetric CBO*n*OSB*m* dimers that we were attempting to mimic (CBO*n*OSB*m* denotes the cyanobiphenyl/Schiff's base non-symmetric dimers). For the CBO6OSB*m* dimers, increasing the terminal chain length leads to a decreased smectic phase stability such that for intermediate chain lengths, i.e. where the spacer and terminal chains are of similar size, smectic behaviour is extinguished. Smectic phases are then observed as the terminal chain is lengthened further. The two smectic phases for early ($m = 0$–6) and late ($m = 10$) members of the CBO6OSB*m* series were found to have intercalated and interdigitated structures, respectively. Furthermore, increasing the spacer length of the CBO*n*OSB*m* dimers resulted in steadily increasing smectic phase stability and smectic polymorphism. It was found that when the spacer length was such that the terminal chain could comfortably be accommodated alongside the spacer of an adjoining molecule, an intercalated smectic structure was formed. In addition, the smectic A–nematic transitions of the CBO*n*OSB*m* dimers did not vary in accord with the predictions of the McMillan theory [14]; for example, T_{SmAN}/T_{NI} for the CBO6OSB10 dimer is closer to unity than for the smaller terminal chain homologues, yet the entropy change is significantly smaller. In comparison therefore, the smectic phase properties of the non-symmetric azobenzene dimers are quite different from those of the cyanobiphenyl/Schiff's base dimers, and so we would not expect them necessarily to have the same intercalated structure. We can assume that the driving force for the formation of the intercalated smectic phase is absent in the azobenzene non-symmetric dimers. (The nature of the intercalated structure is discussed in the next section.)

A selection of the symmetric and non-symmetric azobenzene dimers were studied by X-ray diffraction. The densitometric scan of the powder diffraction pattern for the smectic A phase of the 2AO6OA4 dimer is shown in figure 12, and is typical of the remaining dimers studied. In the wide angle a broad peak centred at 4.5 Å is present. In the small angle region, only the first order Bragg peak is observed corresponding to the (0 0 1) planes. The layer spacing determined from the first order reflection is 39.9 Å, which is approximately equal to the estimated all-*trans* molecular length (from a CPK molecular model) of 40.3 Å. Table 5 gives the smectic A periodicity, *d*, and the estimated all-*trans* molecular length, *l*, for the *m*AO*n*OA*p* dimers studied. These values show that the smectic A phase has a monolayer structure, as shown in figure 1(*a*), and so the mesogenic groups,

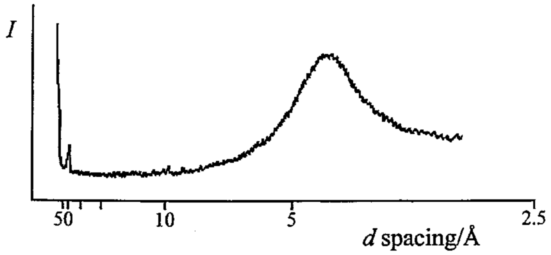


Figure 12. The intensity profile of the powder X-ray diffraction pattern of the smectic A phase exhibited by 2AO6OA4 ($T = 142$°C).

Table 5. The smectic A periodicity, d, and the estimated all-*trans* molecular length, l, for the mAOnOAp non-symmetric dimers.

Compound	d/Å	l/Å	d/l
2AO6OA4	39.9	40.3	0.99
2AO6OA5	40.0	40.7	0.98
3AO8OA5	40.2	41.0	0.98
2AO9OA6	45.2	45.7	0.99

Table 6. The transition temperatures for the 4AO8OA4, 5AO10OA5 and 6AO12OA6 dimers.

	Transition temperatures/°C						
	Cr		SmA		N		I
4AO8OA4	•	125	•	130	•	161	•
5AO10OA5	•	127	(•	117)[a]	•	151	•
6AO12OA6	•	120	•	122	•	132	•

[a] Parentheses () denote a monotropic transition.

terminal chains and spacers can be thought of as constituting a microphase, analogous to the symmetric Schiff's base dimers [3]. If the intercalated smectic phase shown in figure 1 (*b*) had formed it could easily be distinguished from the monolayer structure in that the smectic layer periodicity would have corresponded to approximately half the estimated all-*trans* molecular length. For the monolayer and intercalated arrangements, the mesogen–mesogen interactions are the same; this suggests that for the azobenzene dimers, the terminal alkyl chain–spacer interaction is unfavourable, and so a further interaction would be required to stabilize the intercalated structure. The driving force is not simply an excluded volume, that is a space filling constraint.

Date *et al.* [3] noted that for the symmetric Schiff's base dimers, mSBOnOSBm, the terminal chains would have to be less than half the spacer length for a potential intercalated smectic phase structure to form. However, from the extensive series of Schiff's base dimers which they prepared, an empirical rule emerged that for smectic behaviour to be observed, the terminal chain had to be *greater* than half the spacer length, i.e., $m > n/2$, with no exceptions being found. A similar observation was found for the symmetric azo dimers presented here—for all the observed smectic phases the terminal chain was longer than half the spacer length. However, to test this rule further, three more symmetric azo dimers were synthesized, namely 4AO8OA4, 5AO10OA5 and 6AO12OA6. For these three compounds, the spacer lengths are 10, 12 and 14, and the terminal chain lengths 4, 5 and 6, respectively. The transition temperatures for these three compounds are given in table 6. All three possess smectic A phases below long range nematic phases, in contrast to the rule proposed by Date *et al.* [3]. It would appear that when the terminal chains are shorter than the flexible spacer length, the tendency to form smectic phases is not extinguished but is greatly reduced.

3.6. *A comparison with the symmetric ester linked dimers of Watanabe et al.*

It is of further interest to compare our results with those for the dimers reported by Watanabe *et al.* [15]. They synthesized symmetric dimers, connecting two 4-butyloxybiphenyl mesogens to a flexible alkyl spacer via ester links—the α,ω-bis(4′-butyloxybiphenyl-4-carbonyloxy)alkanes. The mnemonic given to this series is 4OBE.*n*.EBO4, where O denotes an oxygen atom, B is biphenyl, E denotes the ester group, the dot indicating that the ester group originates at the aromatic group, and *n* indicates the number of methylene units in the flexible alkyl spacer; in this study *n* was varied between 4 and 9.

A fascinating odd–even effect was observed in the properties and structures of the dimers. An alternation in the melting and clearing temperatures, and an attenuation in the mesophase temperature ranges, as the spacer length is increased was observed and is typical of analogous dimeric systems [3, 5, 16]. The phases exhibit an even more pronounced dependence on the nature of the alkyl spacer—even membered homologues form the smectic A phase, whereas the odd membered homologues form the smectic C phase. (None of these was found to possess a nematic phase.) Furthermore, an X-ray diffraction study of the smectic A and C phases of the dimers revealed that the small angle reflections corresponded to layer periodicities of approximately half the estimated all-*trans* molecular lengths. This would indicate that the smectic A and C phases of the *symmetric* 4OBE.*n*.EBO4 series are of the intercalated type, whereas, on the basis of our azobenzene dimer results, it would be expected that these dimers would form a monolayer smectic phase. It is not immediately apparent why the switch from an ether to an ester linkage should have such an effect on the smectic phase structure.

4. Conclusions

Several series of symmetric and non-symmetric azobenzene dimers have been prepared. The lack of symmetry in the non-symmetric dimers was based solely on differences in the terminal alkyl chain lengths. The compounds were found to exhibit nematic and smectic A phases. The smectic A phase stability was observed to increase with increasing terminal chain length, yet decrease with increasing spacer length, mirroring the behaviour of the symmetric Schiff's base dimers of Date *et al.* [3]. However, whereas the symmetric Schiff's base dimers formed several smectic modifications, the azobenzene dimers were found only to exhibit the smectic A phase. A comparison was made between the non-symmetric azobenzene dimers and the non-symmetric CBO*n*OSB*m* series [5, 6], and the phase behaviours were found to be very different. The smectic phase stability of the CBO*n*OSB*m* dimers was reported to increase with the spacer length, decrease and then reappear on increasing the terminal chain length for a given spacer. This unusual smectic behaviour was the result of intercalated and interdigitated molecular arrangements in the smectic phases. The X-ray diffraction study of the symmetric and non-symmetric azobenzene dimers revealed that the smectic A phases were of the monolayer type, suggesting that some specific interaction is required between different mesogenic groups to stabilize the intercalated structure. Finally, the azobenzene dimers were compared with the symmetric ester-linked dimers of Watanabe *et al.* [15], revealing a fascinating difference. It was noted that on the switch from ether linkages to ester linkages, the smectic phases gave ratios of the layer periodicity to the molecular length of approximately 0.5, and thus are to be assumed intercalated.

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