Liquid Crystals

Smectic mesophase properties of dimeric compounds. 1. Dimeric compounds based on the mesogenic azobenzene unit

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Smectic mesophase properties of dimeric compounds. 1. Dimeric compounds based on the mesogenic azobenzene unit

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We have studied the mesophase behaviour and structure of certain dimeric compounds, the α,ω-bis(4-n-alkoxyazobenzene-4'-carbonyloxy)alkanes, in which two azobenzene moieties with alkoxy tails are linked by a polymethylene spacer. The effect of the length of the $(CH_2)_n$ spacer was examined by preparing four series of the dimers in which the carbon number of the spacer, n, is varied from 3 to 9 while the carbon number of the terminal chain, m, is held constant at either 2, 4, 8 or 12. A marked odd–even effect typical of main chain polymers was observed, such that the transition parameters and mesophase structures strongly depend on the odd–even parity of the carbon number of the spacer. The effect of the alkyl tail length was also examined in six series of the dimers with the other combination in which n is held constant at either 4, 5, 6, 7, 8 or 9. For the dimers with even n, a short alkyl tail tends to produce a nematic phase. Increase in the length stabilizes a smectic A phase, but a further increase again induces the nematic phase. In contrast, the dimers with odd n invariably formed a smectic C_A phase irrespective of the terminal tail length. These effects of the spacer and terminal chain lengths are discussed in relation to the molecular shapes which are imposed in a liquid crystalline field.

1. Introduction

We have so far reported the thermotropic mesophase properties and structures of the main chain BB-n polyesters that can be constructed by an alternate arrangement of the mesogenic p,p'-bibenzoate unit and the flexible spacer with carbon number n [1–6]:
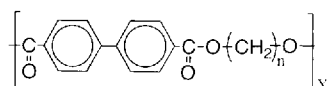

This BB-n homologous series ($n = 3$–9) forms smectic mesophases, whose isotropization temperatures and entropies exhibit an even–odd oscillation with the number of intervening methylene units, n. The even–odd oscillation was also observed in the type of smectic phase. In BB-n with even n, a smectic A phase is found in which the axes of both the polymer chain and the mesogenic group lie perpendicular to the layers. In contrast, the smectic phase of BB-n with odd n was identified as a new type of smectic phase, smectic C_A [1, 2]. In this phase, the tilt direction of the mesogenic groups is the same in every second neighbouring layer, but opposite in two neighbouring layers (refer to figure 6 of [1]).

The formation of such a distinct S_{C_A} structure, as well as the odd–even appearance of the smectic structures have

been explained as resulting from a coupling of the polymeric and the mesogenic effects whereby the spatial arrangement of mesogenic groups within a polymer molecule is strongly confined by the conformation of the intervening alkylene spacers and so is different depending on the odd–even parity of the spacer carbon number [2, 6, 7]. The preferred chain conformations in the even- and odd-membered BB-n are illustrated in figures 1 (a) and (b), respectively. The polymers with odd n tend to assume the conformation with two successive mesogenic groups tilted towards each other, while the mesogenic groups of a polymer with even n lie parallel to each other.

These studies were then extended to the dimeric compounds, di-BB-n [5],
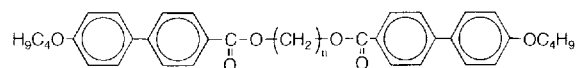
which can be regarded as model compounds of the BB-n polymers. Similar even–odd effects to the polymers have been observed on the transition behaviour and smectic structure of the dimers. This close similarity can be easily understood by considering the conformational constraint mentioned above, since in the dimeric compounds two mesogenic biphenyl groups within a molecule are linked to each other by the flexible alkylene spacer [8]. On the other hand, it should be noted that the dimeric compounds are essentially different from the polymers with respect to
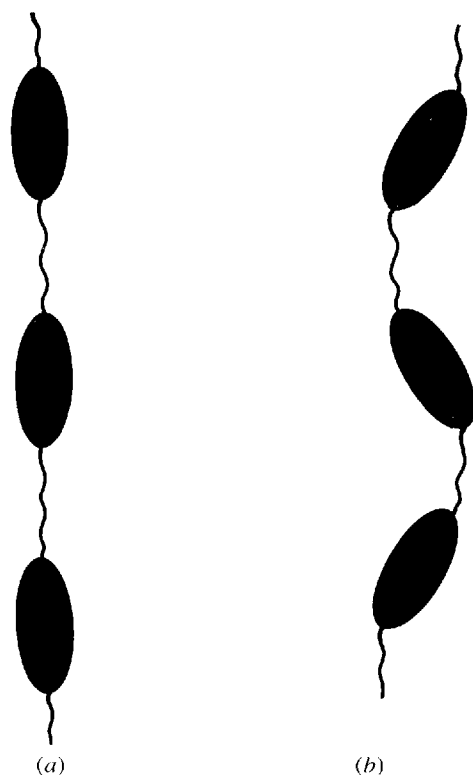
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Figure 1. The conformations of (*a*) the even-membered and (*b*) the odd-membered BB-*n* polymer molecules which are imposed in the smectic liquid crystalline field.

the molecular length or the number density of the molecular ends. In the polymeric system, the confined orientation correlation of the mesogenic groups is maintained along a whole polymer chain, while in the dimeric system it persists only over two mesogenic groups within a single molecule. In order to give a more detailed picture of the smectic layered structure in the dimeric system, we therefore have to understand how the alkyl tail and the spacer groups are being accommodated into a smectic layer. In the dimeric di-BB-*n*, the smectic layer spacing has been observed to be half the molecular length [5]. This means that each molecule is not working as a separate unit, but rather that each mesogenic biphenyl group participates to form the basic layer with a random mixing of the alkyl tail and spacer groups. Such a mixing of two groups may be reasonable since they are not significantly different in length.

A simple question now arises as to how the smectic layer structure is constructed by dimeric compounds when the length of the alkyl tail is remarkably different from that of the alkylene spacer. If the two aliphatic groups are still randomly mixed with each other, the smectic layer structure would be significantly damaged or destabilized. On the other hand, if the molecules tend strongly to form the smectic phase, segregation of the two groups may

occur because of steric incompatibility of the two components [9]. In an attempt to clarify this structural aspect, we have prepared a homologous series of the dimeric compounds, α,ω-bis(4-alkoxyazobenzene-4'-carbonyloxy)alkanes with a variety of tail and spacer groups of different lengths,

$$H_{2m+}C_mO-\bigcirc-N=N-\bigcirc-\underset{O}{\overset{O}{C}}-O+CH_2+_nO-\underset{O}{\overset{O}{C}}-\bigcirc-N=N-\bigcirc-OC_mH_{2m+1}$$
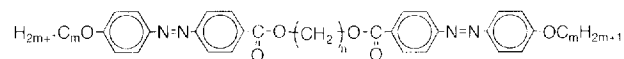
These compounds are abbreviated here as *m*OAz*n*AzO*m* where *m* (= 2, 4, 8 and 12) and *n* (= 3–9) indicate the carbon numbers of the alkyl tails and the spacer, respectively. The transition behaviours and mesophase structures have been studied by differential scanning calorimetry, optical microscopy and X-ray methods, and are described as functions of *m* and *n*.

2. Experimental

2.1. *Materials*

The *m*OAz*n*AzO*m* compounds were synthesized according to the scheme. Each procedure is described in detail below.
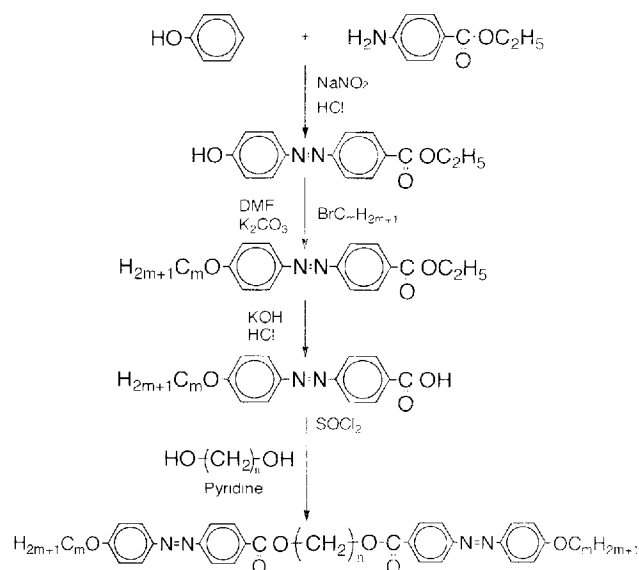
Ethyl 4-hydroxyazobenzoate was prepared by coupling diazotized ethyl 4-aminobenzoate with phenol and purified by recrystallization from ethanol/water.

A mixture of ethyl 4-hydroxyazobenzoate (7·4 mmol), anhydrous potassium carbonate (10 mmol) and *n*-alkyl bromide (8·0 mmol) in *N,N*-dimethylformamide (50 ml) was heated with stirring for 16 h. The cooled reaction mixture was then poured into water (300 ml). The resulting precipitate was filtered off and washed with water. The crude product was recrystallized from ethanol.

Ethyl 4-*n*-alkoxyazobenzoate was then hydrolysed to produce 4-*n*-alkoxyazobenzene-4'-carboxylic acid by adding a 10 wt% solution of potassium hydroxide in

70 per cent ethanol and boiling for 6 h. The reaction mixture was acidified by adding concentrated HCl and the precipitate was filtered off. The products were then recrystallized from DMSO/EtOH.

The 4-alkoxyazobenzene-4'-carboxylic acid (2·0 g) was heated under reflux with thionyl chloride (40 ml), until no further evolution of HCl was observed. The excess of thionyl chloride was removed by distillation under reduced pressure and the acid chloride was collected. The acid chloride (0·005 mol) was dissolved in anhydrous pyridine (30 ml). To this solution, the alkane diol (0·002 mol) previously dissolved in pyridine (30 ml) was added. The solution was boiled for 24 h and then poured into a dilute solution of HCl. The dimeric compound, a solid precipitate, was filtered off, purified by column chromatography (silica gel; chloroform as eluent), and finally recrystallized twice from chloroform/ethanol. All the synthesized compounds gave proton NMR spectra (recorded on a JEOL FX90Q spectrometer), which were consistent with their formulae.

2.2. Methods

The calorimetric behaviour was investigated using a Perkin–Elmer DSC-II calorimeter at a scanning rate of $10°C \, min^{-1}$. The textures of the mesophases were studied using a polarizing microscope (Olympus BH-2) equipped with a Mettler FP-80 hot stage. X-ray diffraction photographs were taken at different temperatures and using Ni-filtered CuK_α radiation. The temperature was measured and regulated within an accuracy of $0·2°C$ by using a Mettler FP-80 heater. The film to specimen distance was determined by calibration with silicon powder.

3. Results

The transition behaviours were elucidated by the DSC thermograms. The thermodynamic DSC data are summarized in tables 1, 2, 3, and 4 for 2OAznAzO2, 4OAznAzO4, 8OAznAzO8 and 12OAznAZO12, respectively. Almost all specimens with $n = 3$ to 9 and $m = 2$ to 12 exhibit mesophases. The same tables also list the types of mesophase, the identification of which is described in detail below.

3.1. Identification of the mesophases

In this study, we observed three types of mesophase—nematic, smectic A and smectic C_A. These phases can be easily distinguished from each other and are readily identified by their microscopic textures as described below.

Figure 2 shows a typical texture of the nematic phase, as observed for 2OAz6AzO2. The nematic phase can be assigned on the basis of the schlieren texture which flashed when subjected to shearing stress, and was of high mobility.
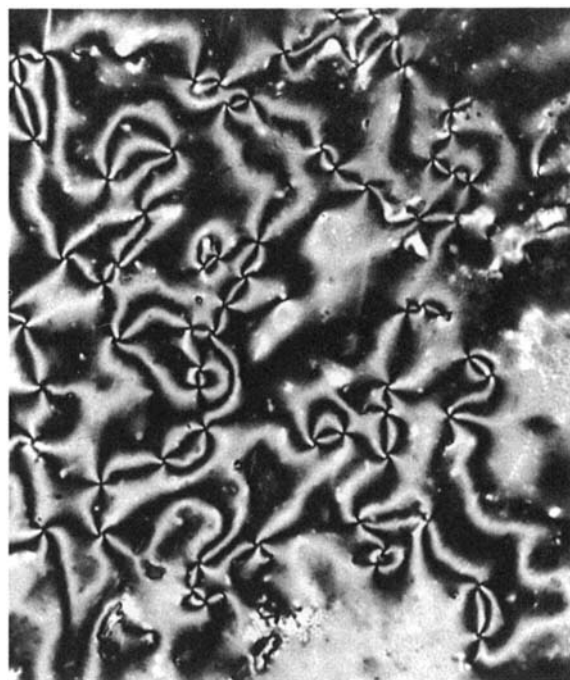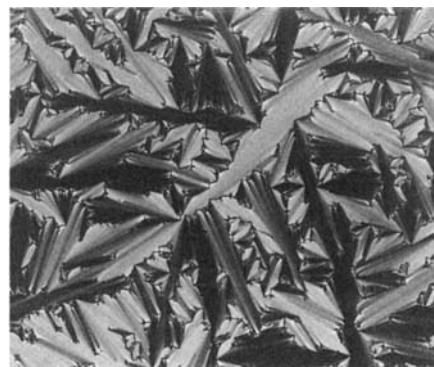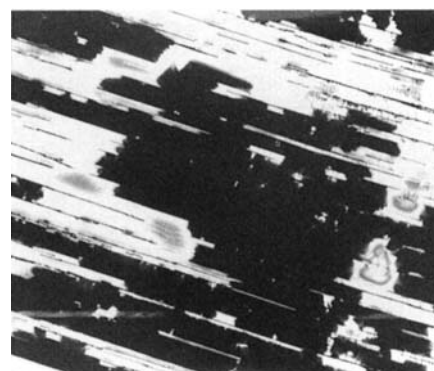

Figure 2. The schlieren texture of the nematic phase of 2OAz6AzO2.



(a)

(b)

Figure 3. (a) The focal-conic fan texture and (b) the partly homeotropic texture of the S_A phase of 8OAz8AzO8.

Figures 3 (*a*) and 3 (*b*) show the microscopic textures of smectic A (S_A) as observed typically for 8OAz8AzO8. First, on cooling the isotropic melt, bâtonnets appear and then coalesce to give the fan-shaped texture (see figure 3 (*a*)). Shearing the specimen between glasses alters the fan-shaped texture to give a texture in which homeotropic regions with no birefringence are observed between
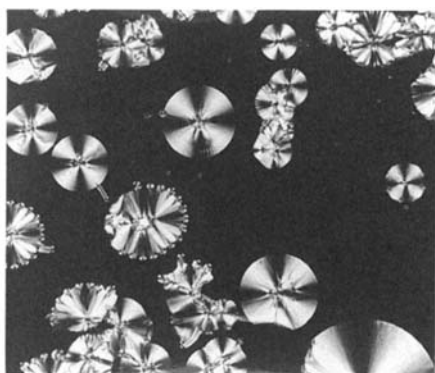
(*a*)
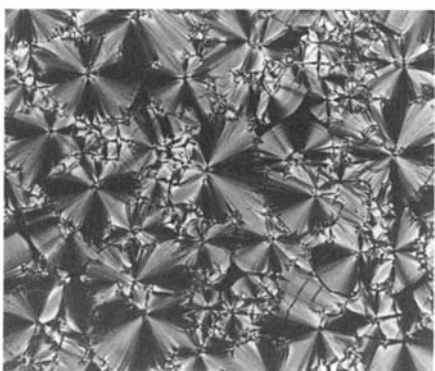
(*b*)
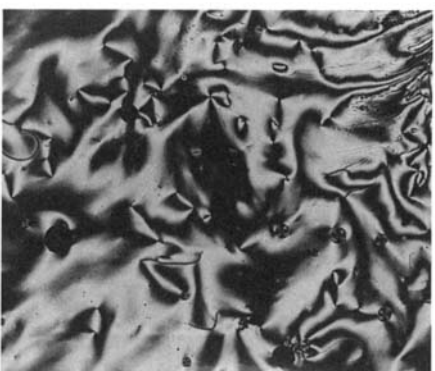
(*c*)

Figure 4. (*a*) The spherulitic domains and (*b*) the fan-shaped texture of the S_{C_A} of 8OAz7AzO8 obtained from the isotropic melt. (*c*) The schlieren texture was prepared by shearing the specimen between glasses.

crossed polarizers (see figure 3 (*b*)). These optical textures are typical of a S_A phase. The supplementary evidence for the S_A phase is given by the X-ray diffraction profile. The X-ray pattern for the uniaxially oriented specimen indicates the sharp reflection and the outer broad reflection which have an angular displacement of 90° relative to each other as has been observed in di-BB-*n* (refer to figure 6 (*a*) of [5]). This angular displacement directly indicates the S_A structure in which the molecules lie perpendicular to the layers.

In figures 4 (*a*), 4 (*b*) and 4 (*c*) are shown the textures which were typically observed for the smectic C_A (S_{C_A}) of 8OAz7AzO8. On cooling the isotropic melt, spherulitic domains containing well-aligned focal-conic groups are developed initially (see figure 4 (*a*)) and subsequently coalesce to give the fan-shaped texture (see figure 4 (*b*)). Simply pressing the specimen between glasses promotes a homeotropic alignment *of the layers*. In this specimen, a strong birefringence can be observed with distinct schlierens which show singularities of $s = \frac{1}{2}$ as well as $s = 1$ (see figure 4 (*c*)). The oriented X-ray pattern taken for this specimen shows that the inner reflection is located on the meridian, similarly to that in the S_A phase, but the outer broad reflections are split by about 25° above and below the equator (refer to figure 6 (*b*) of [5]). These features are characteristic of the S_{C_A} phase as elucidated in previous reports [1,2,4–6].

3.2. *Influence of the spacer length*

First, we consider the effect of the spacer length on the mesophase behaviour and structure. This can be examined by considering four series, 2OAz*n*AzO2, 4OAz*n*AzO4, 8OAz*n*AzO8 and 12OAz*n*AzO12, in each of which the terminal chain length, *m*, is held constant at either 2, 4, 8 and 12 and the spacer length, *n*, is varied from 3 to 9.

Table 1 lists the thermodynamic data for the 2OAz*n*AzO2 series. In figure 5 (*a*), the transition temperatures and the type of mesophase are given as a function of *n*. For the even-membered materials with *n* = 4, 6 and 8, the nematic phase is observed, while in the odd-series only 2OAz5AzO2 exhibits the S_{C_A} phase and the two other specimens with *n* = 7 and 9 form no mesophase.

All the materials in the 4OAz*n*AzO4 series form mesophases as indicated in table 2 and figure 5 (*b*). The even-membered materials exhibit both N and S_A phases, while the odd-members show the S_{C_A} phase.

The 8OAz*n*AzO8 series shows a similar phase behaviour to that of series 4OAz*n*AzO4 (see table 3 and figure 5 (*c*)).

Mesophases were observed for all the materials in the 12OAz*n*AzO12 series (see table 4 and figure 5 (*d*)). The materials with even *n* form the nematic phase, while the materials with odd *n* form the S_{C_A} phase. The behaviour is thus similar to that observed in series 2OAz*n*AzO2.

Table 1. Characterization of 2OAznAzO2 compounds.

n	Cr	Transition temperature/°C (enthalpy/kJ mol⁻¹) [entropy/J mol⁻¹ K⁻¹]†	S_CA	N		I	d_{obsd}‡/Å	d_{calcd}§/Å
4	•	168·1 (47·7)[108]	—	•	220·8 (7·1)[14·4]	•	—	34·9
5	•	103·9 (18·8)[49·9]	•	—	124·3 (12·5)[31·5]	•	17·7	32·7
6	•	132·4 (47·7)[118]	—	•	187·7 (7·5)[16·3]	•	—	37·1
7	•		—	—	120·0 (59·3)[151]	•	—	35·2
8	•	129·0 (47·2)[117]	—	•	166·0 (8·4)[9·1]	•	—	39·5
9	•		—	—	131·0 (64·8)[160]	•	—	37·7

† Based on DSC cooling thermograms.
‡ Smectic layer spacing observed by X-ray diffraction.
§ Molecular length calculated as the carbon to carbon distance between the ends of all-*trans*-molecules.

Based on the above study, we can conclude the following concerning common features of the transition behaviour and phase structure. (i) The materials with even n form nematic and S_A phases, whereas the materials with odd n show the S_{C_A} phase. (ii) The isotropization temperatures, enthalpies and entropies of the smectic phases exhibit a marked odd–even oscillation, with higher values for the materials with even n.

3.3. Influence of the terminal chain length

Next we turn our attention to the reverse situation, namely the effect of the terminal chain length on the mesophase properties; this can be examined by holding the spacer length constant. As the types of mesophase appeared different for the even- and odd-membered series of materials, as mentioned above, the effect was examined for each of the series.

3.3.1. Even-membered materials with even n

Figures 6 (a), (b) and (c) show the dependence of m on the phase behaviour observed for the even-membered materials, mOAz4AzOm, mOAz6AOm and mOAz8AzOm, respectively. In all the figures, a common dependence of the terminal chain length on the transition temperatures can be found. The isotropization temperature gradually decreases with m, while the crystal melting temperature decreases initially and then increases with further increase in m. A common tend can also be observed with respect to the phase behaviour. The materials with the short terminal chain of $m = 2$ show the nematic phase. The nematic phase then changes to S_A with an increase of m to 4 or 8, but reappears with a further increase of m to 12.

3.3.2. Odd-membered materials with odd n

Figures 7 (a), 7 (b) and 7 (c) show the dependence of m observed for the odd-membered series mOAz5AzOm, mOAz7AzOm and mOAz9AzOm, respectively. It is also seen here that all the series exhibit a common feature regarding the phase behaviour. The isotropization temperature increases initially and then decreases gradually with m. In contrast, the crystal melting temperature decreases markedly and then increases with a further increase of m. As a result, the mesophase temperature range is considerably expanded for the materials with $m = 4$ and 8. A most distinct feature of the phase behaviour in this odd-membered series is that the S_{C_A} phase is invariably observed for all of the mesogenic materials.

4. Discussion

Smectic phase formation may be thought of as a microphase separation of the aromatic cores and the aliphatic chains [10]. There exist two possible driving forces for this separation, either the specific mesogenic unit-mesogenic unit interaction or the poor miscibility of the mesogenic unit with the flexible alkyl chains. In conventional monomer compounds which consist of a mesogenic core and an alkyl terminal chain, the smectic layer structure in the segregated from can be easily envisaged and, as a general rule, its stability can be enhanced by extending the length of the terminal alkyl chain [10, 11]. In the dimeric compounds, on the other hand, there are two kinds of aliphatic chain, the spacer and the tail. In order to picture their layer structure, we must therefore first consider how the two aliphatic parts are accommodated into the spaces within a layer.

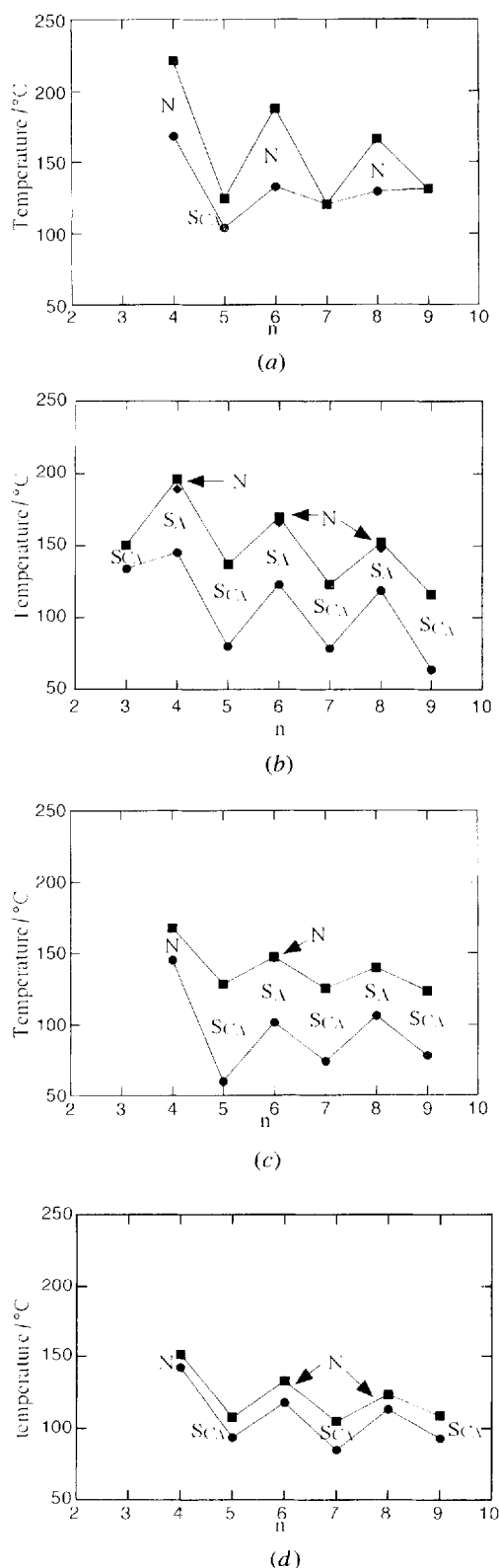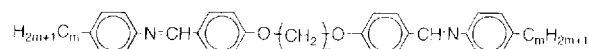Depending on the compatibility of the two aliphatic

groups, the formation of two possible layered structures
can be considered [5, 12–14], as illustrated in figure 8.
One is a single layer smectic phase in which the two
different types of aliphatic chain are compatible and so are
randomly mixed with each other (see figure 8(*a*)). The
other is a bilayer smectic phase in which the spacer and tail
groups are segregated into different spaces so that there are
two maxima in the density modulation within a real repeat
length of the layer structure (see figure 8(*b*)). These two
layer structures can be distinguished from each other by
measuring the layer thickness; in the random mixing
system, the layer thickness should have a value corre-
sponding to half the molecular length, while in the bilayer
system it approximates to the molecular length.

In order to clarify this, the layer reflection profiles were
examined by X-ray measurements. The values of the layer
thickness elucidated from the first order layer reflections
are listed in tables 1 to 4 and also plotted against *n* for each
series with constant *m* in figure 9. From figure 9, we first
recognize a marked odd–even oscillation of the spacings,
with the larger values for the materials with even *n*. This
odd–even oscillation reflects the different types of smectic
phase, as mentioned above [1, 5, 6]. Further, all these
values of the layer spacings were found to approximate to
half the molecular length which was calculated for the
molecule in an all-*trans*-conformation (see tables 1 to 4).
These facts indicate that the layer structure in all cases is
constructed by a random mixing of the two aliphatic parts,
in such a manner that the molecular ends do not
significantly overlap with each other.

Such an intercalated structure with a single layer
character may be considered reasonable since a random-
ized arrangement of the spacer and tail can maximize the
combinatorial entropy of the system. Further, the inter-
calated structure in the present system might be favoured
partly by a dipole interaction between the carbonyl groups
which link the spacer to the mesogenic units and the ether
groups which connect the terminal chains to the mesogenic
moieties [5].

It should be emphasized here that the intercalation of the
two aliphatic groups does not always occur in dimeric
compounds. As reported by Imrie *et al.* [12–14], the
following materials,

$$H_{2m+1}C_m\text{—}\bigcirc\text{—}N\text{=}CH\text{—}\bigcirc\text{—}O\text{—}(CH_2)_n\text{—}O\text{—}\bigcirc\text{—}CH\text{=}N\text{—}\bigcirc\text{—}C_mH_{2m+1}$$

form the smectic phase with a bilayer character such that
the aromatic units, flexible spacer and terminal chains,
each constitute a microphase as illustrated in figure 8(*b*).
We have also found the formation of the bilayer smectic
phase in the following materials [15];

$$H_{2m-1}C_mO\text{—}\bigcirc\text{—}N\text{=}CH\text{—}\bigcirc\text{—}\overset{\text{O}}{\underset{\text{O}}{C}}\text{—}O\text{—}(CH_2)_n\text{—}O\text{—}\overset{\text{O}}{\underset{\text{O}}{C}}\text{—}\bigcirc\text{—}CH\text{=}N\text{—}\bigcirc\text{—}OC_mH_{2m+1}$$

Figure 5.   The dependence of the transition temperatures on the
length of the polymethylene spacer, *n*; (*a*) 2OAznAzO2, (*b*)
4OAznAzO4, (*c*) 8OAznAzO8 and (*d*) 12OAznAzO12.
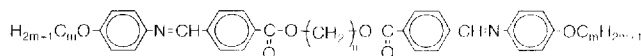
Table 2. Characterization of 4OAznAzO4 compounds.

n	Cr		S_{C_A}	S_A		N		I	$d_{obsd}/\text{Å}$	$d_{calcd}/\text{Å}$
		Transition temperature/°C (enthalpy/kJ mol^{-1}) [entropy/J mol^{-1} K^{-1}]								
3	•	133·7 (31·8) [78·2]	•	—	—	150·2 (15·9) [37·6]		•	17·8	32·7
4	•	145·1 (36·8) [88·0]	—	• 188·9 (5·0) [10·8]	•	195·8 (9·2) [19·6]		•	21·0	39·2
5	•	79·8 (18·0) [51·0]	•	—	—	136·9 (13·0) [31·7]		•	19·2	35·2
6	•	122·7 (41·4) [105]	—	• 165·9 (4·6) [10·5]	•	169·3 (9·6) [21·7]		•	22·2	42·0
7	•	78·5 (25·1) [71·4]	•	—	—	122·7 (10·9) [27·5]		•	20·8	37·7
8	•	118·7 (52·7) [135]	—	• 147·9 (3·8) [9·0]	•	152·2 (10·0) [23·5]		•	23·7	43·6
9	•	63·7 (26·3) [78·1]	•	—	—	115·8 (10·0) [25·7]		•	22·8	40·2

Table 3. Characterization of 8OAznAzO8 compounds.

n	Cr		S_{C_A}	S_A		N		I	$d_{obsd}/\text{Å}$	$d_{calcd}/\text{Å}$
		Transition temperature/°C (enthalpy/kJ mol^{-1}) [entropy/J mol^{-1} K^{-1}]								
4	•	145·0 (43·9) [105]	—	—	•	167·5 (10·5) [23·8]		•	—	48·2
5	•	60·0 (2·0) [6·0]	•	—	—	128·2 (20·9) [52·1]		•	22·8	40·2
6	•	101·5 (48·5) [130]	—	• 146·1 (7·5) [17·9]	•	147·0 (12·5) [29·8]		•	26·8	50·2
7	•	74·0 (28·0) [80·7]	•	—	—	125·0 (20·5) [51·5]		•	24·1	42·8
8	•	105·9 (48·1) [127]	—	•	—	139·5 (25·9) [62·8]		•	27·9	52·3
9	•	78·2 (21·7) [61·8]	•	—	—	123·3 (13·8) [34·8]		•	25·3	45·2

Table 4. Characterization of 12OAznAzO12 compounds.

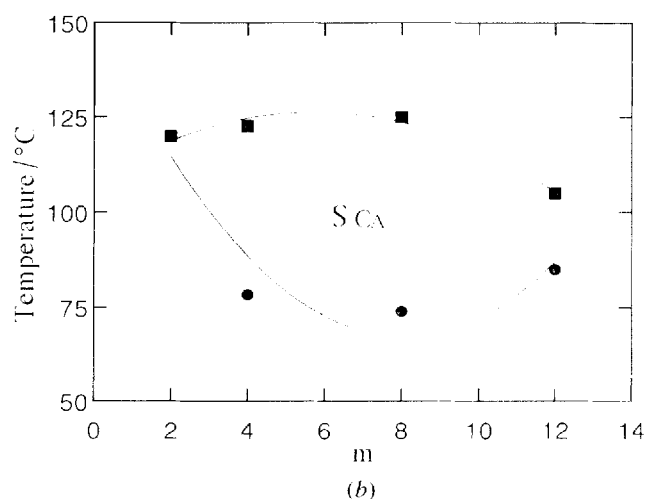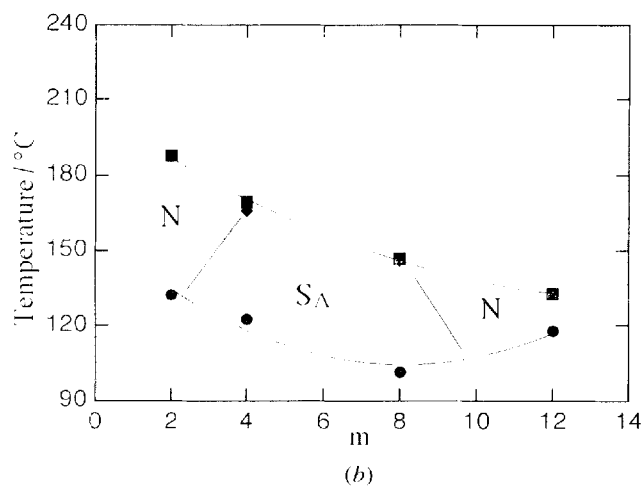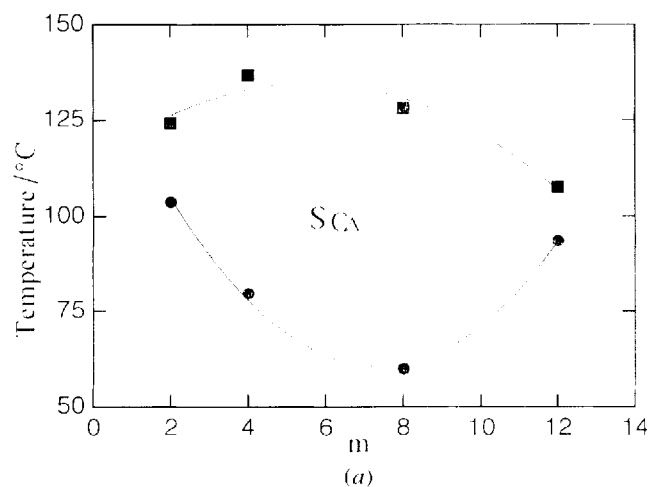| n	Cr		S_{C_A}	N		I	$d_{obsd}/\text{Å}$	$d_{calcd}/\text{Å}$
		Transition temperature/°C (enthalpy/kJ mol^{-1}) [entropy/J mol^{-1} K^{-1}]						
4	•	142·0 (122) [294]	—	•	151·0 (17·6) [41·5]	•	—	57·5
5	•	93·7 (36·4) [99·3]	•	—	107·6 (22·2) [58·3]	•	25·3	45·3
6	•	117·9 (185) [474]	—	•	132·8 (20·1) [49·5]	•	—	59·4
7	•	85·0 (48·1) [134]	•	—	105·0 (23·5) [62·2]	•	27·2	47·8
8	•	113·4 (82·3) [213]	—	•	123·3 (15·9) [40·1]	•	—	61·4
9	•	93·1 (89·9) [246]	•	—	108·8 (30·5) [79·9]	•	28·9	50·3
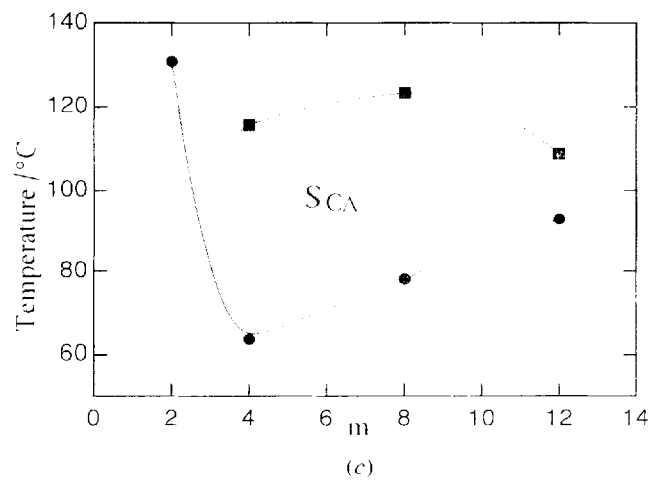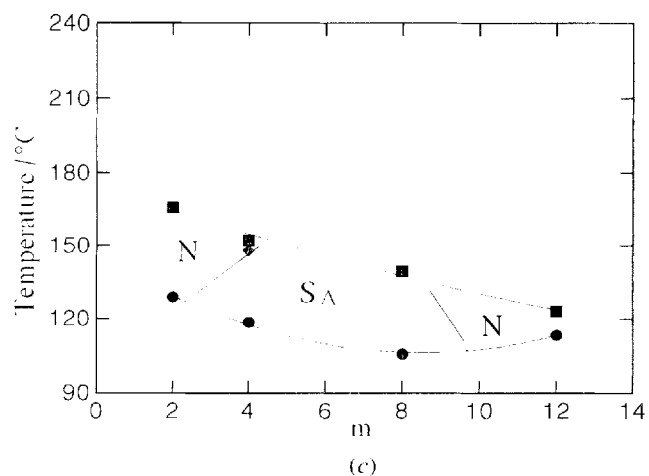
Figure 6.   The dependence of the transition temperatures on the length of the alkyl tail, *m*, as observed for the even-membered series, also with *n* = even; (*a*) *m*OAz4AzO*m*, (*b*) *m*OAz6AzO*m* and (*c*) *m*OAz8AzO*m*.
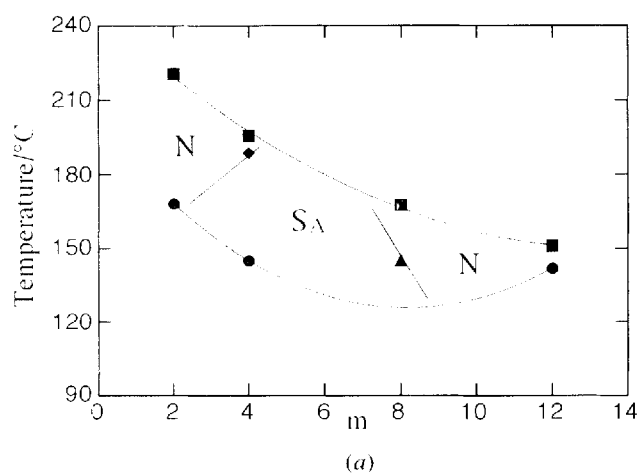
Figure 7.   The dependence of the transition temperatures on the length of the alkyl tail, *m*, as observed for the odd-membered series, also with *n* = odd, (*a*) *m*OAz5AzO*m*, (*b*) *m*OAz7AzO*m* and (*c*) *m*OAz9AzO*m*.
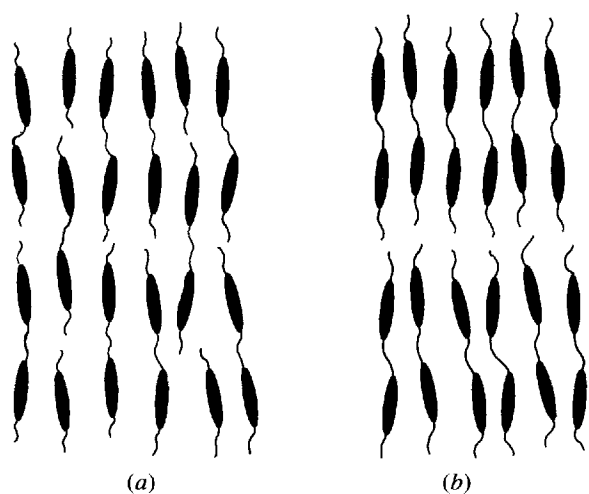
Figure 8. Schematic illustration for two types of smectic phases formed by the dimers; (a) a single layer phase in which the aliphatic spacer and tail are randomly mixed with each other and (b) a bilayer phase in which the two aliphatic moieties groups are segregated into different spaces and so there are two maxima of the density modulation within a real repeat length of the layer.
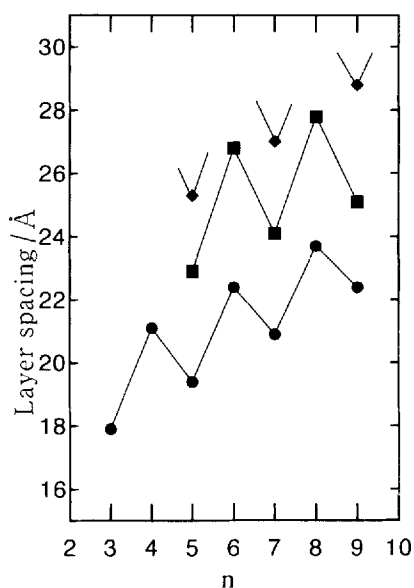

Figure 9. The dependence of the smectic layer spacing on the length of the flexible spacer, n; (●) 4OAznAzO4, (■) 8OAznAzO8 and (◆) 12OAznAzO12.

At this stage, we cannot offer a plausible answer to a question as to why the microsegregation arises in these materials.

Keeping in mind that all the smectic phases of the compounds embodied in this paper have the intercalated layer structure, it is interesting to consider how the length of the spacer or the tail affects the phase behaviour and structure. We first refer to the effect of the spacer. This can

be examined for four series of materials, 2OAznAzO2, 4OAznZaO4, 8OAznAzO8 and 12OAznAzO12. In all the series, marked odd–even oscillations with the number of methylene units n of the spacer were observed for the transition temperatures, enthalpies and entropies. The odd–even parity of n also affected the smectic structure: the materials with even n formed the S_A phase, although some also formed the nematic phase, while the materials with odd n exhibit only the S_{C_A} phase. This odd–even behaviour is typical of main chain polymers and can be attributed to the conformational constraint of the spacer which is different depending on the odd–even parity of the carbon number (refer to figure 1 [1,2,6,7]).

We consider next the effect of the alkyl tail length on the intercalated smectic structure. As mentioned above, this effect appeared different for the compounds with even and odd n. In the systems with even n, the nematic phase is formed if the tail attached is short in length. The nematic phase is then replaced by the S_A phase with increase in tail length from $m = 2$ to 8. The change from nematic to smectic phase is similar to that observed for conventional monomeric series and so can be interpreted as a result of the poor miscibility of aromatic and aliphatic moieties [10, 11]. The distinctive behaviour, however, is observed on further increase of m to 12, when the intercalated S_A phase disappears and the nematic phase reappears. This unusual trend may be characteristic of dimeric materials since it is likely that they would form the intercalated smectic phase most effectively if the terminal chain length approximated to half the spacer length. When the terminal chain becomes appreciably longer than the spacer, as in the materials with $m = 12$, two alkyl groups are accommodated with difficulty into the same space within a smectic A layer and this promotes the formation of the nematic phase.

It is interesting that the compounds with odd n exhibit a dissimilar effect. In these compounds, the S_{C_A} phase is invariably formed, irrespective of the length of terminal chain varying from $m = 2$ to 12. This obstinate stability of the intercalated S_{C_A} phase in the odd series is an unexpected result. At this stage, an explanation can be given only on the basis that the bent arrangement of mesogenic moieties strongly stabilizes the smectic layer structure since it is probably very difficult for the bent molecules to pack efficiently into the uniaxial nematic arrangement.

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[8] It should be noted here that a similar conformational constraint has been observed in the nematic phases of the dimers (see HEEKS, S. K., and LUCKHURST, G. R., 1993 *J. chem. Soc. Faraday Trans.,* **89,** 3289) and that the influence of the spacer on the transitional properties is well described by the molecular field theory (see FERRARINI, A., LUCKHURST, G. R., NORDIO, P. L., and ROSKILLY, S. J., 1994, *J. chem. Phys.,* **100,** 146).

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