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Novel Modulated Hexatic Phases in Symmetric Liquid Crystal Dimers

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(Received 24 October 1994, received in final form 9 January 1995, accepted 10 January 1995)

Abstract. — Homologues of the dimeric \( \alpha, \omega \)-bis(4-\( n \)-alkylanilinebenzylidene-4'-oxy)alkanes (\( m \).OnO.m) have been synthesised with spacer lengths \( n \) ranging from 9 to 12 methylene units and with terminal alkyl chain lengths \( m \) of 10, 12 and 14. Characterisation of these materials has been carried out by X-ray diffraction, differential scanning calorimetry and optical microscopy. In six of these compounds a novel modulated tilted hexatic phase, denoted \( S_1 \), has been identified, in which the smectic layers have a periodic modulation in their structure, analogous to the \( S_2 \) ribbon phase. This modulated hexatic phase is only observed for dimers with an odd parity spacer, suggesting that the average molecular shape, believed to be bent for the odd spacer dimers but linear for the even ones, is responsible for its formation. The compound 10.090.10 exhibits a second modulated hexatic phase denoted \( S_3 \), which is monotropic, and which cannot be distinguished from the \( S_1 \) phase by polarizing microscopy or by calorimetry. These long chain dimeric liquid crystals have been found to have a strong tendency to form tilted hexatic phases; indeed two of the compounds studied here are the first dimers to undergo a transition directly from a tilted hexatic phase to the isotropic liquid.

1. Introduction

A rich source of smectic polymorphism appears to result from a competition between different characteristic length scales in liquid crystal systems, which can lead to the formation of re-entrant, incommensurate or modulated phases [1–3]. For polar molecules, there is an incompatibility between periodicities corresponding to the molecular length \( L \), and to the length \( L' \) of antiparallel molecular pairs, which usually lies in the range \( L < L' < 2L \). Packing with the former periodicity fills space efficiently, but leads to an unfavourable dipolar interaction between head-to-head antiparallel molecular pairs. The latter periodicity, which arises from an

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antiparallel association of the mesogenic cores, allows the dipolar energy to be minimised, but fills space less efficiently. Prost and co-workers have developed a phenomenological Landau model [1,2] to explore the occurrence of smectic structures such as the monolayer \( S_{A1} \), partial bilayer \( S_{Ad} \), or bilayer \( S_{A2} \) phases. Furthermore, incommensurate \( S_{A,inc} \) phases, in which the two competing periodicities coexist along the layer normal, can occur, and the first apparently genuine example of such a phase has recently been reported, for a non-symmetric liquid crystal dimer [4].

An alternative compromise between the competing periodicities is to form one of the two dimensional modulated phases such as the centred rectangular \( S_{\AA} \) phase [5], shown schematically in Figure 1a. When the director is tilted with respect to the layer normal, the oblique \( S_{\CC} \) phase results, as shown in Figure 1b [6-8]. These \( S_{\AA} \) and \( S_{\CC} \) structures are also known as “antiphases” and “ribbon phases”, respectively [9,10]. Closely related to the \( S_{\AA} \) phase is the simple rectangular modulated \( S_{\AA,cren} \) phase [11]. This occurs when the antiferroelectric cluster in the centred position is of a different lateral extent to those at the corners of the unit cell, thus lowering the symmetry. Although less common, modulated phases have also been observed for more ordered smectic phases, such as the hexatic \( S_B \) phase formed by the polar mesogen 4-(4'-cyanobenzyloxy) benzylidene-4'-n-monyloxyaniline [12]. For the cyano bicyclohexanes, evidence has been found for a local antiphase structure in the crystal B phase, but only extending laterally for approximately 70 \( \AA \), or about two wavelengths of the modulation [13].

Although these effects have been discussed in terms of antiparallel pairing of dipolar molecules, and have been most thoroughly studied in strongly polar mesogens [7,8,10,14-16], it is in fact only necessary that the molecules have some kind of structural asymmetry, which could also be steric [2,16,17]. An example of how an \( S_{\AA} \) phase may arise from packing frustration arising from purely steric effects is shown in Figure 1c. In this case, the lateral association of meso-

![Schematic structures](image)

Fig. 1.— Schematic structures of modulated smectic phases. a) the centred rectangular \( S_{\AA} \) phase (2D spacegroup \( cmm \)), b) the oblique \( S_{\CC} \) phase (2D spacegroup \( p2 \)), c) an \( S_{\AA} \) phase induced by purely steric effects, d) a rectangular phase (2D spacegroup \( pmg \)) induced by steric pairing of bent molecules.
genic cores which are bulkier than the terminal chains leads to a build up of packing strain, which can be relieved by the system transforming to a modulated smectic structure, as shown in the Figure. A different kind of steric effect may occur for bent molecules, which could tend to pack as shown in Figure 1d, to give molecular pairs with a length $L < L' < 2L$, analogous to the dipolar pairing of polar molecules. Note that for the structure shown in Figure 1d, the value of $L'$ has to equal 1.5 $L$. Modulated fluid smectic phases arising from such steric effects have been observed for mesogens with fluorinated terminal chains which are more rigid and bulky [18], for polymeric mesogens [19, 20] and for a main chain polymer containing two alternating spacers of different lengths [21]. Furthermore, modulated crystal B phases, arising from steric effects rather than from dipolar associations, have been found in the monomeric N-(4-n-alkyloxybenzylidene)-4'-n-alkylanilines [22, 23].

In recent studies of symmetric [24] and non-symmetric [25–27] liquid crystal dimers, we have discovered a wealth of smectic phases, as well as striking odd–even effects in their transitional behaviour, as the length of the spacer is varied. These effects are believed to be related to a difference in the average molecular shape of the dimers, linear for the even parity spacers, but bent for the odd parity ones. The former system, the $\alpha, \omega$-bis(4-n-alkylanilinebenzilidene-4'...
oxy)alkanes tend to form monolayer smectic phases \(d \approx L\). Their chemical structure is

\[
C_mH_{2m+1} \quad N=CH \quad O(CH_2)_nO \quad CH= \quad C_mH_{2m+1}
\]

and they are the dimeric analogues of the widely studied monomers, the \(N\)-(4-\(n\)-alkyloxybenzylidene)-4'-\(n\)-alkylanilines [28]

\[
H_{2n+1} C_nO \quad CH= \quad C_mH_{2m+1}
\]

The monomeric compounds are referred to as the \(nO.m\)'s, where \(n\) and \(m\) denote the number of carbon atoms in the alkyloxy chain, and in the alkyl chain, respectively. For the dimeric compounds, we therefore use the mnemonic \(mOnO.m\), where \(n\) and \(m\) denote the number of carbon atoms in the central spacer, and in the terminal chains, respectively. In our previous study [24] we prepared homologues with values of \(m\) ranging from 0 to 10 over the range of \(n\) values from 1 to 12, and characterised their liquid crystalline behaviour. This turned out to be particularly important, because they were the first liquid crystal dimers to possess a rich variety of smectic phases.

In addition, we have found that the non-symmetric dimer system, the \(\alpha\)-(4-cyanobiphenyl-4'-oxy)-\(\omega\)-(4-\(n\)-alkylanilino-benzylidene-4'-oxy)alkanes (denoted \(CBO\)OnO.m), can form either intercalated phases \(d \approx L/2\) or interdigitated (partial bilayer) phases \(d \approx 1.7 - 1.9 L\) depending on the length of the spacer [27]. The intercalated structure is believed to result from a specific, favourable interaction between the unlike mesogenic groups. Indeed, intercalated phases are not observed for the \(mOnO.m\) symmetric dimers, possibly because the terminal chain–spacer chain interaction is unfavourable [24]. As expected, equimolar mixtures of certain \(mOnO.m\) and \(BCBO.n\) (\(\alpha,\omega\)-bis(4-cyanobiphenyl-4'-oxy)alkane) symmetric dimers do form intercalated phases, due to the favourable interaction between unlike mesogenic groups [27].

Intercalated phases have also been reported for a different type of symmetric dimer, the \(\alpha,\omega\)-bis(4-butoxybiphenyl-4'-carbonyloxy) alkanes [29]. For these dimers, an intercalated \(S_2\) phase is formed when the spacer has an even parity, whereas an intercalated alternating \(S_{C2}\) phase is formed when the spacer parity is odd. In the latter phase, the mesogenic cores tilt in opposite directions in adjacent layers. Note that this \(S_{C2}\) structure contains the pairing of bent molecules of the type shown in Figure 1d. Similarly, for the non-symmetric \(CBO\)OnO.m dimers, tilted intercalated phases are seen only for odd parity spacers (with nine and eleven methylene units) [27] (in this latter work, the use of the label \(S_{C2}^+\) is proposed to denote an intercalated alternating smectic C phase).

An interesting question is that of whether liquid crystal dimers might form modulated smectic structures. In our work on the \(mOnO.m\) symmetric dimers [24], we found that the compounds 10.09O.10 and 10.011O.10 exhibit an enantiotropic smectic phase, which we denoted \(S_1\), and which we deduced from polarizing microscopy and unaligned X-ray diffraction studies to be a tilted hexatic phase with a periodic modulation in the lateral structure of the layers. The 10.09O.10 compound also formed another modulated hexatic phase, denoted \(S_2\), which appeared similar to the \(S_1\) phase, although its diffraction pattern was not indexed.

We now present a more detailed study of the modulated hexatic phases formed by the \(mOnO.m\) symmetric dimers. We extended the range of compounds to cover the 12.0nO.12 and 14.0nO.14 homologues, for \(n\) values over the range from 9 to 12, in the expectation that some
of them would also form modulated hexatic phases. This is indeed the case, and four of these new compounds have been found to exhibit the modulated hexatic $S_1$ phase. Homologues of the series 11.O$n$.O.11 and 13.O$n$.O.13 were not prepared, as neither the appropriate alkylanilines nor the precursor materials to make them were available. These homologues might, however, also be of interest as we expect that some of the odd spacer members should also exhibit modulated hexatic phases. Our new results on the 12.O$n$.O.12 and 14.O$n$.O.14 homologues allow us to build up a consistent picture for the structure of the $S_1$ phase, and we also now propose a structure for the $S_2$ phase.

2. Experimental

Details of the synthesis of the $m$.O$n$.O.$m$ symmetric liquid crystal dimers have been given previously [24]. The thermal behaviour of the compounds was characterised using a Perkin-Elmer DSC-2C differential scanning calorimeter, interfaced to a microcomputer for data analysis, and a Nikon polarising microscope with a Linkam THM-600 hot stage. The X-ray diffraction patterns were recorded using a Guinier camera fitted with a bent quartz monochromator (R. Huber, Germany) set to isolate CuK$_{α1}$ radiation ($λ = 1.5405$ Å). The non-aligned samples were contained in a thermostatted sample holder, with temperature gradients of less than $0.5$ °C across the region of the sample in the X-ray beam. The diffraction patterns were recorded using several layers of Kodak DEF2 film, and the optical densities were subsequently measured with a Joyce-Loebl IIIc microdensitometer. The intensities in Tables I to III are given on an arbitrary scale after correcting for the line geometry of the X-ray diffraction camera using the approximate formula $I = y(Q_{hk}^{3/2})$, where $I$ is the corrected intensity, $y$ the uncorrected peak height and $Q_{hk} (= Q_{hk}/2π)$ the reciprocal spacing of the $(hk)$ Bragg peak.

3. Results and Discussion

The behaviour of the compound 10.O9.O.10 is discussed in detail below prior to those of the other dimer compounds, because its phase behaviour is the most complex. Its phase sequence is

\[
\begin{align*}
105 °C & \quad \text{C} & \quad \text{S}_1 & \quad 114 °C & \quad \text{S}_A & \quad 126 °C & \quad \text{I} \\
\text{S}_2 & \quad 105 °C & \quad \text{S}_1 & \quad \text{S}_A & \quad \text{I}
\end{align*}
\]

where $S_1$ and $S_2$ denote modulated hexatic phases.

As shown in Plate 1, the optical texture of the $S_A$ phase of 10.O9.O.10 formed on cooling from the isotropic liquid exhibits focal conic fan and homeotropic textures, the latter feature confirming the uniaxial nature of this phase [30]. Upon cooling at $0.1$ °C min$^{-1}$ into the $S_1$ phase (Plate 2) the focal conic fans develop fine arc lines, and a mosaic pattern of grey coloured platelets develops from the homeotropic regions of the smectic A phase. The appearance of birefringence in the previously homeotropic regions implies that the $S_1$ phase is tilted (although strictly speaking does not prove it). There is no observable change on subsequent cooling into the $S_2$ phase. The optical texture of these phases is similar in appearance to that which we have previously reported for the tilted hexatic phases of the $m$.O$n$.O.$m$ compounds [24]. However, a
Plate 1. — Focal conic fan and homeotropic textures of the $S_A$ phase of 10.O9O.10 at 119 °C.

Plate 2. — Focal conic fan and mosaic textures of the modulated hexatic $S_1$ phase of 10.O9O.10 at 113 °C.
slow cooling rate is essential for the formation of a well-defined texture in the $S_1$ phase; in our previous study, where a cooling rate of 0.5 °C min$^{-1}$ was employed, a much less well-defined optical texture was obtained.

The intensity profile of the X-ray diffraction pattern of a non-aligned $S_A$ phase of 10.090.10 at 125 °C is shown in Figure 2. A diffuse maximum, of breadth $\Delta Q = 0.39$ Å$^{-1}$ (FWHM) is located in the wide angle region, centred at a spacing of 4.7 Å. In the low angle region, two sharp diffraction peaks are observed, corresponding to a smectic layer spacing of 54.6 Å, which is nearly independent of temperature (the weak second order peak is not visible in Figure 2, but appears with longer exposure times). Such a diffraction pattern is typical for the $S_A$ phase [31], and when compared to the all-trans molecular length of 60.0 Å (estimated from molecular models), the periodicity indicates a monolayer $S_A1$ structure (note that in our previous study [24] we mistakenly gave the all-trans length as 56.0 Å). The fact that the layer spacing is some 10% less than the all-trans molecular length is presumably largely due to conformational disorder in the long terminal chains.

The intensity profile of the X-ray diffraction pattern of the $S_1$ phase of 10.090.10 at 114 °C is shown in Figure 3. The single wide angle diffraction peak centred at 4.6Å is much sharper, $\Delta Q = 0.08$ Å$^{-1}$ (FWHM), than that obtained for the smectic A phase, but broader than the peak observed for hexatic $S_B$ phases for which typically $\Delta Q = 0.03$ Å$^{-1}$ (e.g., 5.040.5) [24]. This broadening is characteristic of the tilted hexatic $S_F$ or $S_T$ phases, although it is not in itself diagnostic of them. In the low angle region of Figure 3 several sharp reflections are observed, which are seen more clearly in an expansion of the low angle region, shown in Figure 4. The reflections index (see Table I) as a two dimensional oblique lattice (2D spacegroup $p2$), with dimensions $a = 143$ Å, $b = 59.3$ Å and $\gamma = 102^\circ$, for which the reciprocal spacings, $S_{hk}$, are given by

$$S_{hk}^2 = h^2a^{*2} + k^2b^{*2} + 2hk a^{*}b^{*} \cos \gamma^*,$$

where

$$a^* = 1/(a \sin \gamma), \ b^* = 1/(b \sin \gamma), \ \gamma^* = (180^\circ - \gamma),$$
Fig. 3. — Densitometer scan of the powder X-ray diffraction pattern of the modulated hexatic $S_1$ phase of 10.O9O.10 at 114 °C.

and the angle $\gamma$ is obtuse.

As previously noted [24], the (01) and (02) peaks of the $S_1$ phase are nearly continuous with the 1st and 2nd order layer reflections from the $S_A$ phase, although they actually correspond to slightly larger spacings. The (01) peak of the $S_1$ phase has the strongest intensity (see Table I), which is reasonable since it is the peak which is most directly associated with the layer periodicity. The similarity of the $b$ lattice parameter of 59.3 Å to that of the all-trans molecular length of 60.0 Å suggests that the molecules pack with a monolayer periodicity within the smectic layers, and with a tilt angle close to zero; however, the $b$ lattice vector need not lie along the layer normal, and thus the tilt angle may be larger. It should be noted that the tilt angle cannot be directly determined from the diffraction pattern for an unaligned sample; even for an aligned sample, it may be necessary to pin the director along a known external field direction. In fact, the only real evidence we have at present which indicates that the molecules are tilted is that the optical texture of the homeotropic regions of the $S_A$ phase become birefringent upon cooling into the $S_1$ phase. The $a$ and $b$ lattice parameters decrease with decreasing temperature (vide infra); the former change might reflect an increased tilt angle on cooling, but could also be due to a change in the angle between the $b$-axis and the layer normal.

It is striking that the $(h0)$ reflections are absent (but note that the position of the (10)
reflection is actually below the angular range of our Guinier camera), which implies that the modulation is purely displacive along the b-axis, such that the density projected onto the a*-axis (i.e., normal to the b-axis) is uniform. It is typical for modulated phases such as S_A that the equatorial reflections are all absent [10,16]. The fact that (hk) reflections beyond the lowest order are observed for the S_1 phase of 10.090.10 implies that the modulation is less smooth than a pure sine wave.

Two possible models for the modulated S_1 structure are shown schematically in Figure 5. In Figure 5a the molecules are taken to be linear, whereas in Figure 5b they are taken to have a bent shape, with the mesogenic groups tilted symmetrically with respect to the layer normal. In reality the walls between neighbouring domains may be less well defined; an “asymmetric ripple” structure could be an alternative description of the S_1 phase to the displaced ribbon structures shown in Figures 5a and 5b. Such rippled hexatic phases are quite common in lyotropic systems, where they are denoted P_{β'} gel phases [32]. A similar analogy between the P_{β'} gel phase and the S_C phase has previously been made [9], although in this latter case the analogy is more tenuous.

A modulated phase with tilted hexatic molecular ordering is novel, although one with a mod-
ulation of hexatic $S_B$ layers has been reported previously for the polar mesogen 4-(4'-cyanobenzyloxy)benzylidene-4''-n-alkoxyaniline [12]. In keeping with the nomenclature for the modulated fluid smectic phases, the $S_1$ phase could be denoted as $S_p$ or $S_l$. However, it is not possible from powder diffraction patterns to determine the tilt direction of the director with respect to the local hexagonal lattice; indeed it could even lie at some intermediate angle between the edge and the centre of the face of the hexagon. Such a tilted hexatic phase, denoted an $S_L$ phase, has been detected in a lyotropic gel phase between an $S_F$ and an $S_l$ phase with increasing water content [33,34]. Interestingly, this lyotropic system then adopts a modulated hexatic phase (rippled $P_{bb'}$ gel phase) on moving to the excess water region. Although there is no example as yet of a bulk $S_L$ phase in a thermotropic system, modulated optical textures have been observed in free standing hexatic films of non-chiral liquid crystals, which have been identified as chiral surface splay domains of the $S_L$ phase [35,36].

Oblique "ribbon" phases have been reported in anhydrous potassium carboxylate soaps [37]. However, the packing of the soap headgroups is crystalline, and the hydrocarbon chains are fluid, so the analogy with the modulated hexatic phases is somewhat tenuous. Periodic defect structures have also been seen by scanning probe microscopy in Langmuir-Blodgett films of fatty acid salts (see review in [38]). However, the analogy with the modulated hexatic phases is even more tenuous, since the molecular packing in the films is crystalline.

Upon cooling, 10.09O.10 transforms at 105 °C from the $S_1$ phase to a phase denoted $S_2$. Although the wide angle diffraction peak of the $S_2$ phase is identical to that found for the $S_1$ phase, in the low angle region, shown in Figure 6, nine sharp peaks are present. It could be argued that the additional diffraction peaks are simply due to an evolution of the modulation profile, rather than a true phase transition. However, the fact that the onset of the additional reflections with cooling is quite sudden suggests that there is indeed a discontinuous change in the structure. From continuous X-ray temperature scans (not shown) it appears that certain reflections are due to residual coexisting $S_1$ phase, which remains until crystallisation occurs.

Table I. — Calculated and measured reciprocal spacings $S_{hk}(=Q_{hk}/2\pi)$ for the modulated hexatic $S_1$ phase of 10.09O.10 at 115 °C. All calculated spacings up to the 22/42 reflection are shown. Lattice parameters: $a = 143 \pm 5$ Å, $b = 59.3 \pm 1$ Å, $\gamma = 102 \pm 1^\circ$, $a^* = 0.0072 \pm 0.0003$ Å$^{-1}$, $b^* = 0.0172 \pm 0.0002$ Å$^{-1}$, $\gamma^* = 78 \pm 1^\circ$.

<table>
<thead>
<tr>
<th>$hk$</th>
<th>$S_{hk}(\text{calc}) / \text{Å}^{-1}$ (± 0.0003)</th>
<th>$S_{hk}(\text{obs}) / \text{Å}^{-1}$ (±0.0001)</th>
<th>Intensity / arb. units</th>
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<td>1000</td>
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<td>-</td>
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<td>40</td>
<td>0.0288</td>
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<tr>
<td>31/4 $\bar{T}$</td>
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<td>-</td>
<td>28</td>
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<tr>
<td>1 $\bar{2}$</td>
<td>0.0337</td>
<td>0.0332</td>
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<tr>
<td>02/2 $\bar{2}$</td>
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<tr>
<td>50</td>
<td>0.0360</td>
<td>-</td>
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<td>0.0366</td>
<td>0.0370</td>
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(close to 100 °C), while the remainder are due to the $S_2$ phase. One of the peaks, (12/32), seems to arise solely from the coexisting $S_1$ phase (based on the indexing of the $S_2$ phase given in Table II), five peaks solely from the $S_2$ phase, and three peaks may contain overlapping contributions from both $S_1$ and $S_2$ phases (on some X-ray exposures, a weak $1\bar{2}$ reflection from the $S_1$ phase was also observed). The structure of the $S_2$ phase appears to be similar to that of the $S_1$ phase, except that it has lattice dimensions $a$, $b$ and $\gamma$ at 102 °C of 116 Å, 69.8 Å and 128°, respectively. As for the $S_1$ phase, the (01) peak of the $S_2$ phase has the strongest intensity (see Table II), which is again reasonable. The coexisting $S_1$ phase at this temperature has dimensions $a$, $b$ and $\gamma$ of 121 Å, 56.7 Å and 103°, respectively. Thus the $a$ and $b$ parameters are decreased somewhat from their values at 114 °C, whereas the angle $\gamma$ is unchanged. The calculated and measured positions of the $S_{hk}$ reflections for the $S_2$ phase are given in Table II, and those for the coexisting $S_1$ phase in Table III. For the indexing given in Table II, the following reflections below 23 were not observed: 2\bar{1}, 3\bar{1}, 1\bar{2}, 32, 30, 4\bar{1}, 42, 21, 3\bar{3}, 40, 12, 43. The X-ray data presented in Tables I-III were obtained without continuous rotation of the sample in the beam; the relative intensities of the peaks, particularly the 10 and 11 reflections of the $S_2$ phase, were altered somewhat when sample rotation was employed. The value of 69.8 Å for the $b$ dimension of the $S_2$ phase is significantly greater than the all-trans molecular length (60 Å). This is, however, still consistent with a monolayer structure, if the defect walls between the domains are tilted away from the director by an angle of approximately 30° (cf. Fig. 1d), similar to the model proposed by Hardouin for the $S_C$ phase [10]. A further point is the apparent observation for the $S_2$ phase of the lowest order $(h0)$ Bragg peaks, the (10) and (20) reflections (see Table II), which indicates that the structure projected onto the $a^*$-axis (i.e., normal to the $b$-axis) retains some modulation in density.

Further characterisation of the modulated hexatic phase transitions in 10.090.10 was attempted by differential scanning calorimetry, as shown in the cooling scan given in Figure 7. Inset in the scan over the temperature range of approximately 110 to 95 °C is a trace with the

Fig. 5. — Schematic possible models for the modulated hexatic $S_1$ phase: a) linear molecules, b) bent molecules
Fig. 5. — (continued)

Fig. 6. — Densitometer scan of the low angle region from the first and third films in a film stack exposure of the powder X-ray diffraction pattern of the modulated hexatic $S_2$ phase of 10.000.10 at 102 °C. Reflections with bracketed indices are assumed to arise from the coexisting $S_1$ phase.
Table II. — Calculated and measured reciprocal spacings for the modulated hexatic $S_2$ phase of 10.090.10 at 102°C, coexisting with the $S_1$ phase. Lattice parameters: $a = 116 \pm 5 \text{ Å}, b = 69.8 \pm 1 \text{ Å}, \gamma = 128 \pm 1^\circ, a^* = 0.0107 \pm 0.0003 \text{ Å}^{-1}, b^* = 0.0181 \pm 0.0002 \text{ Å}^{-1}, \gamma^* = 52 \pm 1^\circ$.

<table>
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<tr>
<td>02</td>
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<td>0.0363</td>
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<tr>
<td>23</td>
<td>0.0446</td>
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<td>7</td>
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</table>

(a) Intensity includes a contribution from the coexisting $S_1$ phase.

Table III. — Calculated and measured reciprocal spacings for the modulated hexatic $S_1$ phase of 10.090.10 at 102°C, coexisting with the $S_2$ phase. Lattice parameters: $a = 121 \pm 5 \text{ Å}, b = 56.7 \pm 1 \text{ Å}, \gamma = 103 \pm 1^\circ, a^* = 0.0085 \pm 0.0003 \text{ Å}^{-1}, b^* = 0.0181 \pm 0.0002 \text{ Å}^{-1}, \gamma^* = 77 \pm 1^\circ$.

<table>
<thead>
<tr>
<th>$hk$</th>
<th>$S_{hk}(\text{calc}) / \text{Å}^{-1}$ ($\pm 0.0003$)</th>
<th>$S_{hk}(\text{obs}) / \text{Å}^{-1}$ ($\pm 0.0001$)</th>
<th>Intensity / arb units</th>
</tr>
</thead>
<tbody>
<tr>
<td>01,1</td>
<td>0.0181</td>
<td>0.0181</td>
<td>$1000(b)$</td>
</tr>
<tr>
<td>11/2</td>
<td>0.0217</td>
<td>0.0217</td>
<td>236$^{(b)}$</td>
</tr>
<tr>
<td>02,2</td>
<td>0.0362</td>
<td>0.0363</td>
<td>385$^{(b)}$</td>
</tr>
<tr>
<td>12/3</td>
<td>0.0391</td>
<td>0.0394</td>
<td>16</td>
</tr>
</tbody>
</table>

(b) Intensity includes a contribution from the coexisting $S_2$ phase.

sensitivity increased by a factor of 25. The temperature at which the $S_1$-$S_2$ phase transition was detected in an X-ray diffraction continuous temperature scan is indicated on the figure. Even at high sensitivity, the $S_1$-$S_2$ phase transition could not be detected by DSC, implying that the structural rearrangement at the transition involves very little change in molecular ordering, even though the indexing of the X-ray pattern shows a large change in the periodicity (but with no change in the symmetry) of the phase.

There are some problems remaining with the precise nature of the $S_2$ phase, which are exacerbated by the fact that the $S_1$-$S_2$ transition is monotropic and in addition cannot be detected by either polarizing microscopy or DSC. We have indexed the X-ray data on the assumption that the lines which are continuous with those from the $S_1$ phase are at least in part due to some residual $S_1$ phase coexisting with the $S_2$ phase. Although this is thermodynamically forbidden for a single component system, it could be due to a low level of impurity in the sample caused by thermal decomposition. However, the fact that the $S_1$-$S_2$ transition entropy is vanishingly small implies that any coexistence region should occur only over a very small range of temperature. The fact that we observe phase coexistence over more than 5°C suggests that this explanation can probably be ruled out. Another possibility is that the coexistence is a kinetic effect, with the similarity of the two phases leading to a very slow growth of the
Fig. 7. — Differential scanning calorimetry cooling scan of 10 O9O.10 measured with a rate of 5 °C min\(^{-1}\).

Table IV. — The transition temperatures (°C) and entropies of transition for four members of the 10.O9O.10 homologous series. ( ) denotes a monotropic transition.

<table>
<thead>
<tr>
<th>n</th>
<th>( T_C )</th>
<th>( T_{S2S1} )</th>
<th>( T_{S1A} )</th>
<th>( T_{S2A} )</th>
<th>( \Delta S_{C/R} )</th>
<th>( \Delta S_{GS1/R} )</th>
<th>( \Delta S_{S2S1/R} )</th>
<th>( \Delta S_{SAVR} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>105</td>
<td>(105)</td>
<td>114</td>
<td>126</td>
<td>12.5</td>
<td>4.60</td>
<td>3.90</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>124</td>
<td>135(a)</td>
<td>143</td>
<td>160</td>
<td>4.00(a)</td>
<td>5.93</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>99</td>
<td>104(b)</td>
<td>118</td>
<td>11.8</td>
<td>0.18</td>
<td>5.57</td>
<td>3.68</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>119</td>
<td></td>
<td>131(a)</td>
<td>15.4</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

more stable phase upon cooling. In fact, finally, it cannot be completely ruled out that all of the observed lines might belong to the \( S_2 \) phase, and that their continuation from the \( S_1 \) phase is either accidental, or is due to a specific epitaxial relationship between the two lattices. However, we have not been able to find a satisfactory indexing of the diffraction lines, based on this last assumption. Unfortunately, because the \( S_2 \) phase is monotropic and occurs for only one of the symmetric dimer homologues, we are unable to resolve these important issues at present.

The transitional properties of the long chain \( m.O9O.m \) compounds are given in Tables IV–VI. The transition temperatures and entropies to the isotropic phase show similar odd-even effects to those previously reported for the shorter terminal chain homologues [24]. The modulated hexatic phases are found to occur in a variety of phase sequences, summarised in Table VII. The most striking finding is that modulated hexatic phases are found for all of the
Table V. — The transition temperatures (°C) and entropies of transition for four members of the 12.O12 homologous series.

<table>
<thead>
<tr>
<th>n</th>
<th>(T_C)</th>
<th>(T_{S_1})</th>
<th>(T_{S_2})</th>
<th>(T_{S_3})</th>
<th>(\Delta T_{S_1})</th>
<th>(\Delta T_{S_2})</th>
<th>(\Delta T_{S_3})</th>
<th>(\Delta T_{S_4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>105.5</td>
<td>118.5</td>
<td>120.5</td>
<td>129.5</td>
<td>9.95</td>
<td>4.64</td>
<td>4.74</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>120.3</td>
<td>142.5</td>
<td>146.7</td>
<td>147.0</td>
<td>3.38(a)</td>
<td>6.11</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>103.5</td>
<td>118.5</td>
<td>119.5(a)</td>
<td>141.1</td>
<td>10.8(b,c)</td>
<td>10.8(b,a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>119</td>
<td>-----</td>
<td>146(b)</td>
<td>5.81</td>
<td>-----</td>
<td>10.9(b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) represents combined \(S_1\) to \(S_2\) and \(S_2\) to \(I\) transitional entropes

Table VI. — The transition temperatures (°C) and entropies of transition for four members of the 14.O14 homologous series.

<table>
<thead>
<tr>
<th>n</th>
<th>(T_C)</th>
<th>(T_{S_1})</th>
<th>(T_{S_2})</th>
<th>(T_{S_3})</th>
<th>(\Delta T_{S_1})</th>
<th>(\Delta T_{S_2})</th>
<th>(\Delta T_{S_3})</th>
<th>(\Delta T_{S_4})</th>
</tr>
</thead>
<tbody>
<tr>
<td>9</td>
<td>99</td>
<td>112</td>
<td>120</td>
<td>127.5</td>
<td>10.3</td>
<td>4.53</td>
<td>5.43</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>110</td>
<td>-----</td>
<td>145(a)</td>
<td>146</td>
<td>19.8</td>
<td>9.99**</td>
<td>9.99(c)</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>99.5</td>
<td>-----</td>
<td>121(a)</td>
<td>9.80</td>
<td>-----</td>
<td>11.8(a)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>120</td>
<td>-----</td>
<td>130(b)</td>
<td>19.7</td>
<td>-----</td>
<td>10.4(b)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

(c) represents combined \(S_1\) to \(S_2\) and \(S_2\) to \(I\) transitional entropes

odd spacer dimers studied, but for none of the even ones. The terminal alkyl chains need to have a length of at least ten carbon atoms for the modulated hexatic phases to be formed. Interestingly, no modulated fluid smectic phases (\(S_{A1}\), etc.) were observed for any of these symmetric dimers. In addition to forming modulated hexatic phases, certain of the \(m.Om\) dimers also exhibit conventional tilted hexatic \(S_F/S_I\) phases. The compounds 12.0120.12 and 14.0120.14 show a transition from a tilted hexatic phase directly to the isotropic liquid. The modulated hexatic \(S_1\) phase can form on cooling from either \(S_{A}\) or \(S_{C}\) phases, or directly from the isotropic liquid. In the latter case, a large tilt angle is to be expected, by analogy with the behaviour of monomers which transform directly from the isotropic to the \(S_{C}\) phase, although this cannot be directly deduced from the observed lattice parameters. The compound 10.090.10 is the only homologue studied which exhibits two modulated hexatic phases. Upon cooling, most of the dimers crystallize directly from the modulated hexatic phases. Exceptions to this are 14.090.14, which transforms on cooling from the \(S_1\) phase to a tilted hexatic \(S_F/I\) phase before crystallizing, and the dimer 10.0110.10, which transforms first to a crystal smectic \(G/J\) phase from the \(S_1\) phase.

For the \(S_1\) phase of 10.0110.10, nine low angle reflections were observed. These indices are the \(11, 01, 11, 12, 42, 02, 12, 22\) and 13 reflections of an oblique lattice, with cell dimensions \(a, b\) and \(\gamma\) of 162 Å, 61.3 Å and 119°, respectively. In our previous study [24] there was a mistake in the indexing quoted, although the cell dimensions given are similar to those reported here. The \(a\) parameter is somewhat greater than that of the \(S_1\) phase of 10.090.10, and the \(b\)
parameter is approximately 2 Å greater at the same temperature, slightly less than expected for the additional two methylene groups in the central spacer (but note that the $b$ parameter is temperature-dependent, making this comparison problematic).

The diffraction patterns of the modulated hexatic $S_1$ phase of the odd spacer dimers 12.090.12, 12.0110.12, 14.090.14 and 14.0110.14 are very similar to that of the $S_1$ phase of 10.090.10, and the observed lattice parameters are given in Table VIII. Comparison of the values for the $S_1$ phase of the various dimers shows that the $a$ dimension varies over the range 121 to 184 Å, while the $b$ dimension varies between 56.7 and 70.4 Å. As expected, the $b$ dimension tends to increase with increasing length of the $m.O_n.O.m$ dimer, although 12.0110.12 seems to be an exception to this. The angle $\gamma$ has a value close to 100° for most of the compounds, although the value for 10.0110.10 is significantly larger, at 119°. The wide angle pattern for this latter dimer is, in fact, not typical for a hexatic phase, consisting of a poorly resolved cluster of two or three sharper lines, centred at the same diffraction angle as the single, slightly diffuse peak seen in the hexatic phase. This suggests that for this dimer, the modulated $S_1$ phase has a more ordered structure than for the other dimers, and this may be connected with the fact that it is the only one of the dimers to adopt a crystal smectic (G/J) phase below the $S_1$ phase.

It is now well-accepted that modulated thermotropic smectic phases arise from a tendency for competing periodicities resulting from competing intermolecular forces, stabilising different packing arrangements [3]. Such phases have been seen most frequently in compounds which contain polar end groups, for example nitro or cyano; these may form monolayer, partial bilayer or bilayer smectic phases. However, the $m.O_n.O.m$ symmetric dimers generally form only monolayer smectic phases, and so it is unclear what the other competing periodicity might be. The fact that the modulated hexatic phases are only seen for dimers with odd parity spacers strongly suggests that the preferred molecular shape must be involved, since this is the most striking difference between the odd and the even spacer dimers. The odd dimers have a bent average conformation, which may lead to a steric pairing of length $L'$, with $L < L' < 2L$, as shown in Figure 1d, giving rise to a tendency for a periodicity $L'$, competing with the monolayer periodicity $L$. Note that if $L' = 1.5L$, the system could in principle adopt
Table VIII. — Lattice parameters of the modulated hexatic phases.

<table>
<thead>
<tr>
<th>Dimer</th>
<th>Phase</th>
<th>T / °C</th>
<th>a / Å (±5)</th>
<th>b / Å (±1)</th>
<th>γ / ° (±1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10.O9O.10</td>
<td>S₁</td>
<td>114</td>
<td>143</td>
<td>59.3</td>
<td>102</td>
</tr>
<tr>
<td>10.O9O.10</td>
<td>S₁</td>
<td>102</td>
<td>121</td>
<td>56.7</td>
<td>103</td>
</tr>
<tr>
<td>10.O9O.10</td>
<td>S₂</td>
<td>102</td>
<td>116</td>
<td>69.8</td>
<td>128</td>
</tr>
<tr>
<td>10.O1O.10</td>
<td>S₁</td>
<td>114</td>
<td>162</td>
<td>61.3</td>
<td>119</td>
</tr>
<tr>
<td>12.O9O.12</td>
<td>S₁</td>
<td>118</td>
<td>165</td>
<td>62.9</td>
<td>101</td>
</tr>
<tr>
<td>12.O1O.12</td>
<td>S₁</td>
<td>107</td>
<td>140</td>
<td>62.6</td>
<td>103</td>
</tr>
<tr>
<td>14.O9O.14</td>
<td>S₁</td>
<td>115</td>
<td>184</td>
<td>66.9</td>
<td>101</td>
</tr>
<tr>
<td>14.O1O.14</td>
<td>S₁</td>
<td>120</td>
<td>167</td>
<td>70.4</td>
<td>102</td>
</tr>
</tbody>
</table>

an intercalated, alternating tilted layer structure with paired bent dimers, analogous to the 
$S_{C2}/S_{C+}$ phase discussed in the Introduction; however, the long terminal chains may prevent
this structure from forming, due to the difficulty of packing two of them alongside each spacer.
It is also striking that for the symmetrical dimers, modulated structures only occur for the
more ordered hexatic phase, and are not observed in the $S_A$ or $S_C$ phases.

4. Conclusions

Novel modulated hexatic phases in which the tilted hexatic smectic monolayers have a per-
odic modulation in their structure, analogous to the $S_C$ ribbon phase, have been found
in long chain homologues of the dimeric $\alpha$,$\omega$-bis(4-$n$-alkylanilinebenzylidene-4'-oxy)alkanes
($m. OnO.m$). Homologues have been prepared with terminal alkyl chain lengths $m = 10$, 12
and 14 and with spacer lengths $n = 9$ to 12; these have been characterised by X-ray diffraction,
differential scanning calorimetry and optical microscopy. Six of the homologues, all with odd
spacers, have been found to form the modulated hexatic phases. The fact that these phases
only seem to occur for dimers with odd spacers suggests that their formation may be driven
by a steric frustration induced by a bent average molecular conformation, present in the odd
but not the even dimers, giving rise to a competition between tendencies for monolayer and
partial bilayer smectic periodicities.

The compound 10.O9O.10 exhibits a second modulated hexatic phase, denoted $S_2$, which is
monotropic. The transition between the two modulated smectic phases was clearly detected
by X-ray diffraction but could not be identified by differential scanning calorimetry, nor by
optical microscopy. An unresolved problem is that some residual $S_1$ phase was observed to
coexist with the $S_2$ phase.

It is clear that it is highly desirable to study aligned samples of these modulated hexatic
phases, to permit a more detailed investigation of their structures by diffraction techniques.
However, because they all lack a nematic phase, we have been unable to produce such aligned
samples by using magnetic fields even as high as 1.5 T. Future experiments will have to employ
either much larger fields to align the $S_A$ phase, or will utilize free-standing films to produce
monodomain samples of the phases.

Acknowledgments

We wish to thank Dr. C. T. Imrie for the synthesis of some of the compounds. We are grateful to the former Science and Engineering Research Council for the award of a research studentship to Dr. R.W. Date and a grant, GR/C/95428, towards the cost of the equipment used in this investigation.

References