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The effect of molecular chirality on the incidence of twisted smectic A phases

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Four chiral chloro-esters were synthesized in order to examine systematically the effect that molecular chirality has on the temperature range and incidence of the twisted smectic A phase or the twist grain boundary phase as it has become known. We find that when the motion of the chiral centre is restricted by rotational hindrance, thereby increasing the chirality of the system, the twisted S_A phase range is increased. At low chirality the twisted S_A phase disappears altogether. Furthermore, it is shown that the transition temperatures of the chiral compounds are lower than their racemic analogues.

1. Introduction

Recently the discovery of a new liquid crystal variant, the twisted S_A phase, was reported [1]. In this phase the molecules are packed in layers with their long axes perpendicular, on average, to the layer planes. In the direction normal to the long axes of the molecules, and parallel to the layers, a macroscopic helix is formed. The formation of such a helical structure in the plane of the layers is difficult to conceive without disruption of the layer planes. However, Renn and Lubensky predicted that the formation of a helix would be possible if a lattice of screw dislocations is incorporated into the structure of a normal smectic A phase [2]. The helical twist is effected by a small rotation of blocks of the smectic A phase about an axis perpendicular to the director. A shift in registry between the individual blocks is produced by the inclusion of screw dislocations. A periodic array of such defects was predicted to form grain boundaries. Hence the twisted smectic A phase has become known as the twist grain boundary phase.

Initially Renn and Lubensky suggested that under certain circumstances the twist grain boundary phase could mediate the cholesteric to smectic A transition [2]. Later they expanded their model to include the smectic A to C* phase transition as well [3]. The first experimental evidence for such a phase existing came with the synthesis of some phenyl propiolates [1, 4]. However, these materials were found to exhibit direct isotropic liquid to smectic A* phase transitions and no cholesteric–smectic A*–smectic A phase sequences were observed. Subsequent investigations revealed that a new class of chiral chloro compounds [5] gave some examples of the Ch–S_A^*–S_A phase sequence predicted by Renn and Lubensky [2].

In this study we examine the properties of some chiral (*S*)-2-chloroalkyl 4′-(4″-*n*-nonyloxybenzoyloxy)biphenyl-4-carboxylates with particular reference to the effect that molecular chirality has on the stabilization of the S_A^* phase. For instance, it is thought that the occurrence of a smectic A* phase is critically dependent on the chirality of the liquid crystal molecules. In order to investigate this effect we have

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prepared a series of four materials, each one having the same basic molecular structure with the exception of the terminal aliphatic chain attached to the asymmetric centre. The structures of the materials studied are shown in figure 1. On moving down the series from compound **1** to compound **4** the chirality of the materials is believed to increase due to the reduced freedom of rotation of the chiral centre. It can be seen from figure 1 that compounds **2** and **4** have a branching methyl group attached to the carbon atom adjacent to the asymmetric centre that carries the chlorine atom. With reference to compound **1**, the extra methyl group essentially restricts the independent rotation of the chiral centre about the long axis of the molecule. Compound **3** also has a greater restriction of rotation in comparison to compound **1** because it has a longer terminal aliphatic chain [6]. Thus this series of materials can be used to investigate the effects of molecular and phase chirality on liquid crystal properties. As the tendency to form twisted S_A phases is predicted to be dependent on chirality, so the temperature range of the phase is expected to increase as the series is descended. Here we report the results of our studies on these four materials and also the racemic modification of compound **3**.

2. Experimental

The materials were prepared by the same method described previously for (*S*)-2-chloro-4-methylpentyl 4′-(4″-*n*-nonyloxybenzoyloxy)biphenyl-4-carboxylate, (compound **3**) [5]. The first step in the synthesis was the preparation of the diazonium salt of the appropriate amino acid. The amino acids used were *S*-alanine, *S*-valine, *S*-leucine, and 2*S*,3*S*-isoleucine. Each diazonium salt was treated with hydrochloric acid to produce the analogous chiral 2-chloro acid. The acids produced were then reduced to their respective alcohols in the presence of lithium aluminium hydride and then each was esterified with 4-methoxycarbonoyloxy-4′-hydroxybiphenyl in the presence of diethylazodicarboxylate (DEAD) and triphenylphosphine. The 4-methoxy-

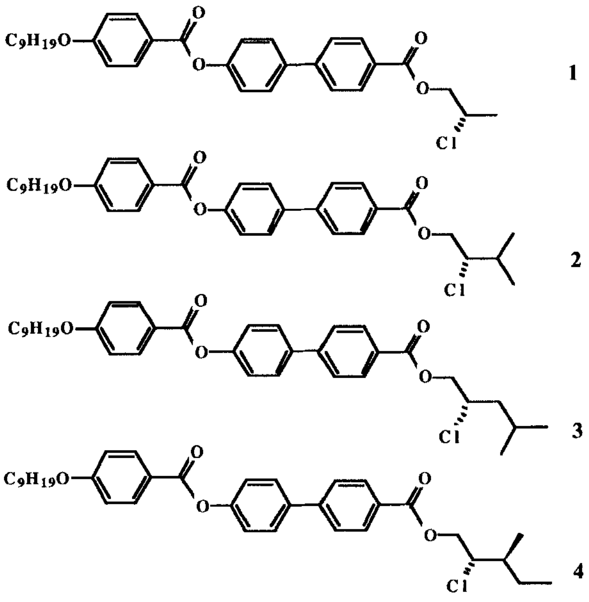

Figure 1. Structures of the materials studied.

carbonoyloxy-4′-hydroxybiphenyl was prepared from 4-cyano-4′-methoxybiphenyl by demethylation of the methoxy group and hydrolysis of the nitrile in one step using a mixture of acetic acid and hydrobromic acid. Protection of the resulting 4′-hydroxybiphenyl-4-carboxylic acid was achieved with methyl chloroformate in the presence of aqueous sodium hydroxide [7]. After esterification with the chiral alcohols the products were purified by flash chromatography over silica gel. The carbonate protecting group was then removed in the presence of an ethanol–ammonia mixture to yield the corresponding biphenol ester. Each of the biphenols was in turn esterified with 4-*n*-nonyloxybenzoic acid in the presence of dicyclohexylcarbodiimide and 4-(N,N-dimethylamino)pyridine (DMAP) to yield the final, liquid-crystalline products **1** to **4**. The racemic modification of compound **3** was prepared by the same process, but in this case racemic leucine was used as the starting amino acid.

The final products were purified by flash chromatography over silica gel (200–400 mesh) using dichloromethane as the eluent. This process was repeated until the isolated product gave a single spot by thin layer chromatography. The materials were then recrystallized successively from petroleum ether (40–60°) and acetonitrile until the transition temperatures were found to be constant. The purity of each chiral ester was determined by a combination of normal and reverse phase high pressure liquid chromatography. Reverse phase chromatography was carried out over octadecylsiloxane (5 μm pore size, 25 × 0·46 cm, ODS Microsorb Dynamax 18 column) using both acetonitrile and methanol water (9 : 1) as the eluents. Normal phase chromatography was carried out over silica gel (5 μm pore size, 25 × 0·46 cm, Dynamax Scout column) using acetonitrile as the eluting solvent. Detection of the eluting products was achieved using a Spectroflow 757 UV/VIS detector ($\lambda = 254$ nm). Each of the final products was found to have a chemical purity that exceeded 99·5 per cent.

The chemical structures of all of the materials prepared, intermediates and final products, were determined by a combination of nuclear magnetic resonance spectroscopy (Joel JNM-GX 270 MHz Spectrometer), infra-red spectroscopy and mass spectral analysis. The results obtained were found to be consistent with the predicted structures of the target materials.

The optical purity of compound **3** was investigated by NMR chiral shift reagent techniques using europium (D-3-heptafluorobutyryl camphorate) as the shift reagent. The chemical shift reagent was added incrementally to the racemic form of compound **3** in order to achieve a separation of peaks arising from the protons in the phenyl ring adjacent to the chiral centre. Both ortho and meta doublets were found to be split. The separation of the ortho H was determined to be 8 Hz (~ 0·03 ppm) whereas for the meta H the value of 3 Hz (~ 0·01 ppm) was obtained. Further additions of the shift reagent caused excessive broadening. The optically active form of compound **3** was examined under decoupling conditions such that the peaks for the H_{ortho}, and the H_{meta} protons were reduced to singlets. Within the limitations imposed by the broadened lines neither singlet (H_o, H_m) showed any doubling, indicating 100 per cent enantiomeric purity. A much more conservative estimate, however, would be a purity of 90 ± 10 per cent. Further experiments with *S*-(+)-2,2,2-trifluoro-1-(9-anthryl)ethanol, revealed no separation of enantiomers. HPLC studies confirmed the shift reagent experiments, and showed that the optically active version of compound **3** was better than 95 per cent optically pure.

The initial phase assignments and corresponding transition temperatures (for the final products) were determined by thermal optical microscopy using a Zeiss Universal Polarizing light microscope equipped with a Mettler FP 52 microfurnace and FP 5 control unit.

Tilt angle, polarization and alignment studies were carried out in 2 μm cells that were constructed from electrically conducting glass (ITO coated). The inner surfaces of the glass were coated with polyimide and unidirectionally buffed in order to induce a homogeneous planar alignment of the liquid crystal. Electrical contacts were made directly to the inner surfaces of the cell in order to facilitate the study of the polarization direction and tilt angle in an applied electric field (20 V peak to peak AC) for each compound. These studies were carried out in a Linkam THM 600 hot-stage attached to the polarizing microscope. Pitch measurements in the smectic C* phase were made in cells with a plate separation of approximately 50 μm. The pitch was measured using a Lasico Filar eyepiece with a processor for digital readout that was attached to the microscope and calibrated against a standard 1 mm scale. The temperature of the specimen was controlled to better than 0·1°C in a Mettler FP 52 oven. Differential scanning calorimetry was used to determine both the temperatures and heats of transition. The instrument used in these studies was a Perkin–Elmer DSC Lab I calorimeter equipped with a thermal analysis data station. The instrumental accuracy was calibrated against an indium standard (measured ΔH 28·63 J g^{-1}, literature value 28·45 J g^{-1}). The thermal properties of the materials were investigated under a variety of heating and cooling rates (1°, 2° and 5°) in both aluminium and graphite pans. The effect of optical purity on phase formation, was investigated via miscibility studies between the racemic and enantiomeric versions of compound **3**. These studies were carried out by taking the optically pure and racemic compounds and weighing out small portions of each on to a glass slide, heating the mixture into the isotropic liquid phase, mixing thoroughly and allowing the mixture to cool into its liquid-crystalline phases. Phase identification was once again carried out by thermal optical microscopy.

3. Results

3.1. *Thermal optical microscopy*

The phase sequences and the accompanying transition temperatures determined by thermal optical microscopy for compounds **1** to **4** and the racemic modification of compound **3** are shown in the table. On cooling from the isotropic liquid compounds **2** to **4** inclusive, exhibited blue phases. The transition from isotropic liquid to blue phase III was not easily observed in the microscope, but subsequent transitions to blue phase II and then to blue phase I were clearly discernible. Blue phase II appeared as a characteristic, iridescent platelet texture and on transition to blue phase I the platelets took on a typical wrinkled appearance. Further cooling resulted in the formation of an iridescent cholesteric phase, either in the form of cholesteric fan defects or as a Grandjean plane texture. The blue phase and cholesteric temperature ranges were found to be approximately the same in compounds **3** and **4**, but markedly shorter in compound **2**. Compound **1** did not exhibit a cholesteric phase or blue phases and consequently had a direct smectic A to isotropic liquid transition. For compounds **2** to **4** inclusive, the transition from smectic A to cholesteric was mediated by the formation of filaments. This *vermis* texture closely resembled that of the smectic A* phase reported previously [1, 4]. As with the cholesteric and blue phase range, the range over which filaments were seen was found to be markedly shorter in compound **2** (<0·1°C), in comparison to compounds **3** and **4**. The transition to the chiral smectic C phase in compounds **2**, **3** and **4** was found to be enantiotropic, whereas in compound **1** the transition was monotropic. The chiral smectic C phase was characterized by either a

Transition temperatures for the compounds studied.

Compound	mp/°C	$T_{S_C^*S_A}$/°C	$T_{S_CS_A}$/°C	$T_{S_AS_A^*}$/°C	T_{S_AI}/°C	$T_{S_A^*Ch}$/°C	T_{S_AN}/°C	T_{ChBP_I}/°C	$T_{BP_IBP_{II}}$/°C	$T_{BP_{II}BP_{III}}$/°C	$T_{BP_{III}I}$/°C	T_{NI}/°C
1	90·2	(67·7)†	—	—	192·1	—	—	—	—	—	—	—
2	98·5	128·7	—	159·7	—	159·7	—	160·0	160·8	161·1	161·3	—
3	74·9	121·0	—	144·6	—	145·4	—	145·8	148·6	149·9	150·2	—
4	89·6	123·9	—	150·1	—	150·4	—	151·5	153·8	155·3	155·8	—
±3	77·9	—	121·4	—	—	—	147·5	—	—	—	—	152·7

†( ) indicates a monotropic phase transition.

broken focal conic or a plane pseudo-homeotropic or schlieren texture. On further cooling of the S_C^* phases of compounds **2**, **3** and **4** abnormal changes in texture occurred. These changes were thought to be due to a large change in tilt angle produced on cooling each material.

The helical twist sense in the chiral smectic C phase for each material was determined by polarimetry in the neat phase. In compounds **1** to **3** the rotation of plane polarized light was found to be laevo (*l*) and therefore the helical structures in these compounds were all categorized as right handed. In compound **4** the twist sense was unexpectedly found to be dextro (*d*), thereby suggesting a left handed helix. The result for compounds **1** to **3** classifies these materials as Se*l* (S is the absolute spatial configuration, e signifies an even parity which corresponds to the odd or even atom count that the chiral centre is separated from the core, and *l* is the rotation of plane polarized light through the sample) which is in agreement with a previous hypothesis [8]. Theoretically compound **4** should be classified as Se*l* when we consider the chiral centre closest to the central core of the molecule, or So*l* if we take the other chiral centre into account. Thus the effects should reinforce each other. However, experimental observations of free standing films of compound **4** show that the material is dextro (*d*). Conversely, contact studies with the other compounds of this series seem to indicate that the material is actually laevo (*l*). The surprising dual nature of this material is under further investigation.

The racemic version of compound **3** possesses only three phases, nematic, smectic A and smectic C. The clearing point of the racemic form was found to be considerably higher (2·5°C) than for the chiral compound as was the nematic (or cholesteric) to smectic A or A* transition temperature (2·1°C). However, the transition from smectic A to smectic C was found to be only slightly higher in the racemate (0·4°C). The possibility that impurities might be the cause of these differences in transition temperatures was eliminated by detailed HPLC investigations of both substances: HPLC showed that their chemical purities were in excess of 99·5 per cent pure.

3.2. *Thermal investigations*

The materials were studied by differential scanning calorimetry at various heating and cooling rates. The clearing points and the transitions immediately below the clearing points were of great interest because of the nature of the smectic A to cholesteric phase transition, and so were studied extensively. On heating, the clearing point of compound **1** showed a single peak corresponding to the transition from smectic A to isotropic liquid. Figure 2 shows the clearing point transitions for compounds **2**, **3** and **4**. For compound **3** five peaks corresponding to the smectic A to smectic A*, smectic A* to cholesteric, cholesteric to blue phase I, blue phase I to blue phase II and blue phase II to isotropic liquid transitions can be seen. The transition from blue phase II to blue phase III could not be detected by calorimetry. For compound **4** only four peaks were detected which corresponded to smectic A to smectic A*, smectic A* to cholesteric, cholesteric to blue phase and blue phase to isotropic liquid. The transitions between blue phases are not resolved for this compound. The thermogram for compound **2** shows only two peaks which are very close together and partially overlap. These peaks correspond to the smectic A to cholesteric and

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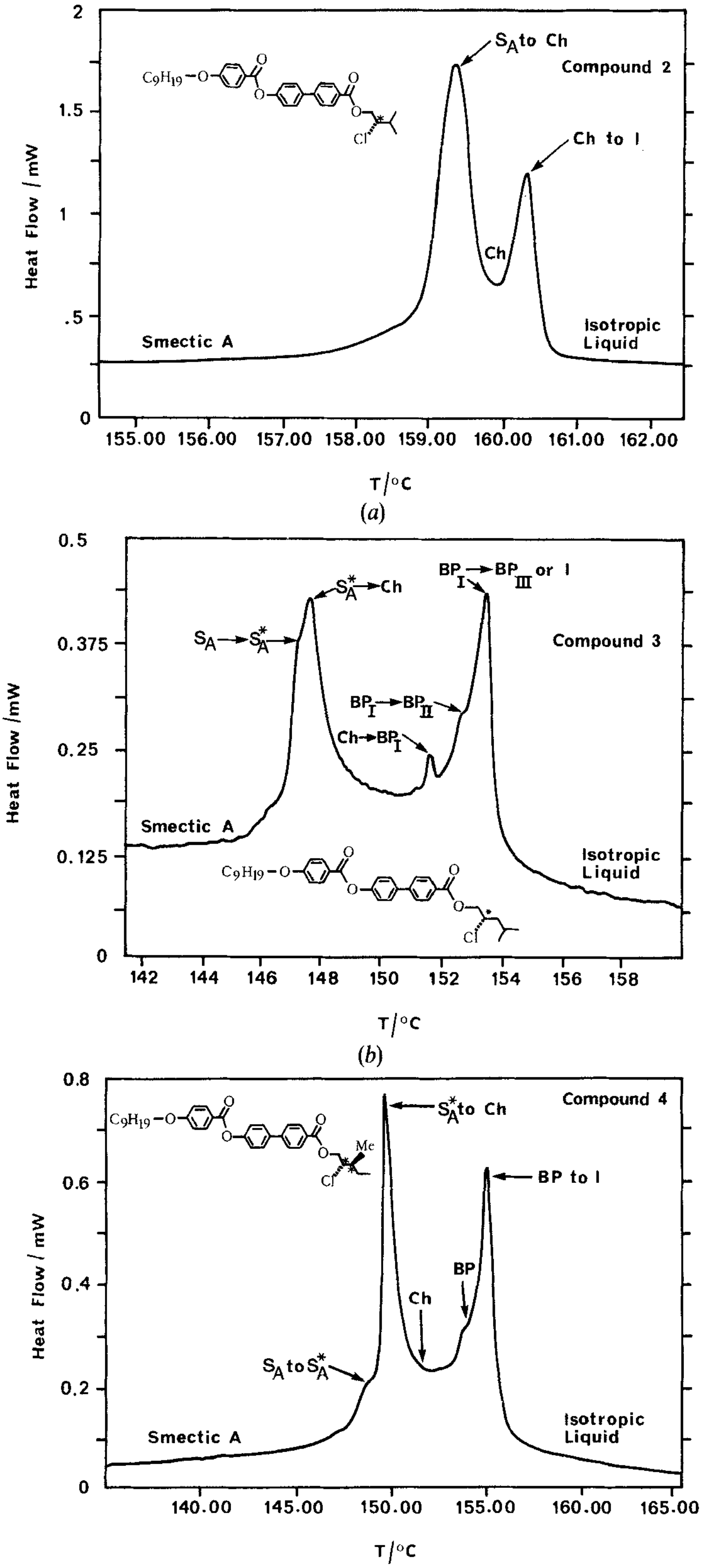
Figure 2. The differential scanning thermograms near the clearing points for the heating cycles of compounds **2**, **3** and **4**, figures (*a*), (*b*) and (*c*) respectively. The heating rate was 2° min^{-1} in each case.


Heat Flow / mW
2
1.5
1
.5
0
S_A to Ch
Compound 2
Ch to I
Ch
Smectic A
Isotropic Liquid
155.00 156.00 157.00 158.00 159.00 160.00 161.00 162.00
T/°C
C9H19–O
O
Cl
Heat Flow /mW
0.5
0.375
0.25
0.125
0
S_A → S_A*
S_A* → Ch
BP_I → BP_III or I
Compound 3
BP_I → BP_II
Ch → BP_I
Smectic A
Isotropic Liquid
142 144 146 148 150 152 154 156 158
T/°C
Heat Flow / mW
0.8
0.6
0.4
0.2
0
S_A* to Ch
Compound 4
BP to I
BP
Ch
S_A to S_A*
Smectic A
Isotropic Liquid
Me
140.00 145.00 150.00 155.00 160.00 165.00
T/°C

(a)

(b)

(c)

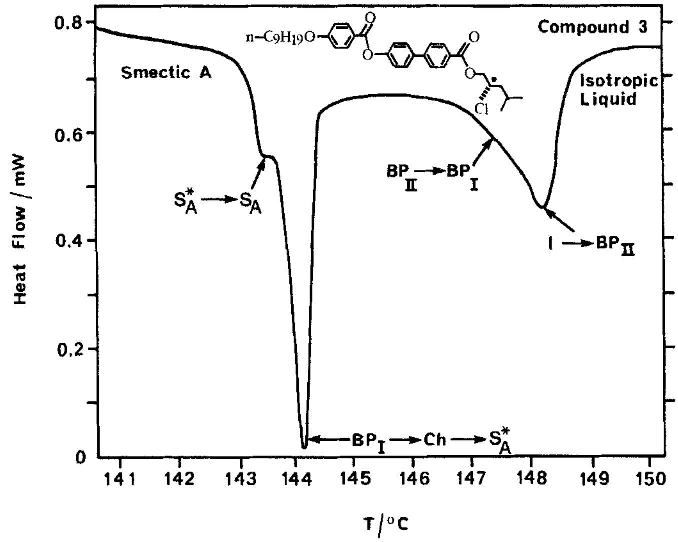


Figure 3. The differential scanning thermogram for the cooling cycle of compound 3. The cooling rate was 2° min^{-1}. This figure shows the supercooling of the BP_I to cholesteric phase transition.

cholesteric to isotropic liquid transitions. A small shoulder on the left hand side of the lower temperature peak may be due to a smectic A* phase that occurs over a very short temperature range. The blue phase transitions are not resolved at all probably because of the very short blue phase temperature range. The cooling cycles for these compounds were in agreement with the heating cycles except for the resolution of the blue phase and smectic A* peaks which were not as clear. Most of the peaks were seen to supercool to some degree; the most striking example of this being for compound **3** where the transition from blue phase I to cholesteric supercooled far enough for the blue phase I to cholesteric phase change to become amalgamated with the smectic A* to cholesteric transition as shown in figure 3.

The racemic modification of compound **3** was found to exhibit only two peaks near the clearing point. These correspond to the transition from smectic A to nematic and nematic to isotropic liquid. The heating thermogram for this compound is shown in figure 4.

From these studies it was found that the optimum conditions to resolve both the smectic A* and blue phase transitions were a moderate sample weight (approximately 6 mg) and a scan rate of 2°C min^{-1}. Slower scan rates had the disadvantage of producing some thermal decomposition. We endeavoured to avoid this by using graphite pans and preheating the sample.

3.3. *Pitch and tilt angle investigations*

The variation of both the helical pitch and the tilt angle with respect to temperature, in the chiral smectic C phase, were investigated for compounds **3** and **4**. The tilt angles were determined from electrical switching studies in cells with plate separations of approximately 2 μm. Each material was introduced into the cell by capillary action whilst still in the liquid state. The material was then allowed to cool slowly into the chiral smectic C phase before an electric field was applied. Good alignment was

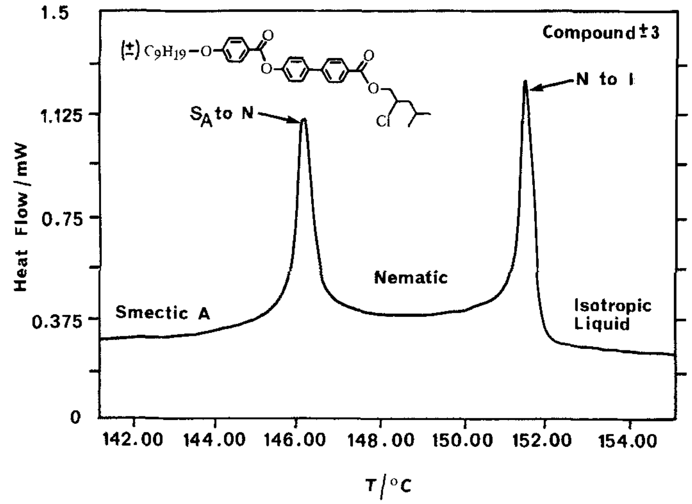


Figure 4. The differential scanning thermogram near the clearing point for the heating cycle of the racemic modification of compound 3. The heating rate was 2° min^{-1}.

achieved for both compounds **3** and **4** by using a cooling rate of 0·2°C min^{-1}, however, when a similar experiment was attempted for compound **2** the alignment was found to be of an extremely poor quality, thereby making it impossible to obtain results for this material. The misalignment was found to be due to the very short smectic A* and cholesteric temperature range in compound **2**. Thus the close proximity of the overlying blue phases perturbs the initial aligning process.

Initial switching studies showed that compounds **3** and **4** have positive polarizations ($P_s(+)$). A plot of tilt angle as a function of temperature for compounds **3** and **4** is shown in figure 5. It was found that the tilt angle for compound **3** saturates at approximately 35° whereas the tilt angle for compound **4** saturates at the lower value of 27°. Assuming that the azimuthal angle is similar in both compounds, this suggests that compound **3** has a greater degree of chirality than compound **4** in the chiral smectic C phase.

Pitch measurements of the helix in the smectic C* phase were carried out for both compounds **3** and **4**. The pitch was determined from the spacing between the dechiralization lines [9] obtained in the focal conic texture of the S_C^* phase. A focal conic texture was obtained by heating the material into the isotropic liquid and cooling slowly between untreated glass plates (plate separation 50 μm). On cooling the material into the chiral smectic C phase, dechiralization lines appeared. The spacing between the lines was determined by measurements over a number of bands and across a wide variety of areas of the sample. The microscope was focused on the top and bottom plates of the cell in order to ensure that the pitch and not the half-pitch was measured. A plot of the pitch versus temperature for compounds **3** and **4** is shown in figure 6. This figure shows that the pitch of compound **4** in the smectic C* phase is found to be considerably longer than that in compound **3**. Furthermore the pitch for compound **4** appears to vary linearly with respect to temperature. Unfortunately the pitch of compound **3** was more difficult to determine accurately because of its must shorter length. However, as a general trend it was found that the pitch decreased quite sharply with decreasing temperature and then saturated.

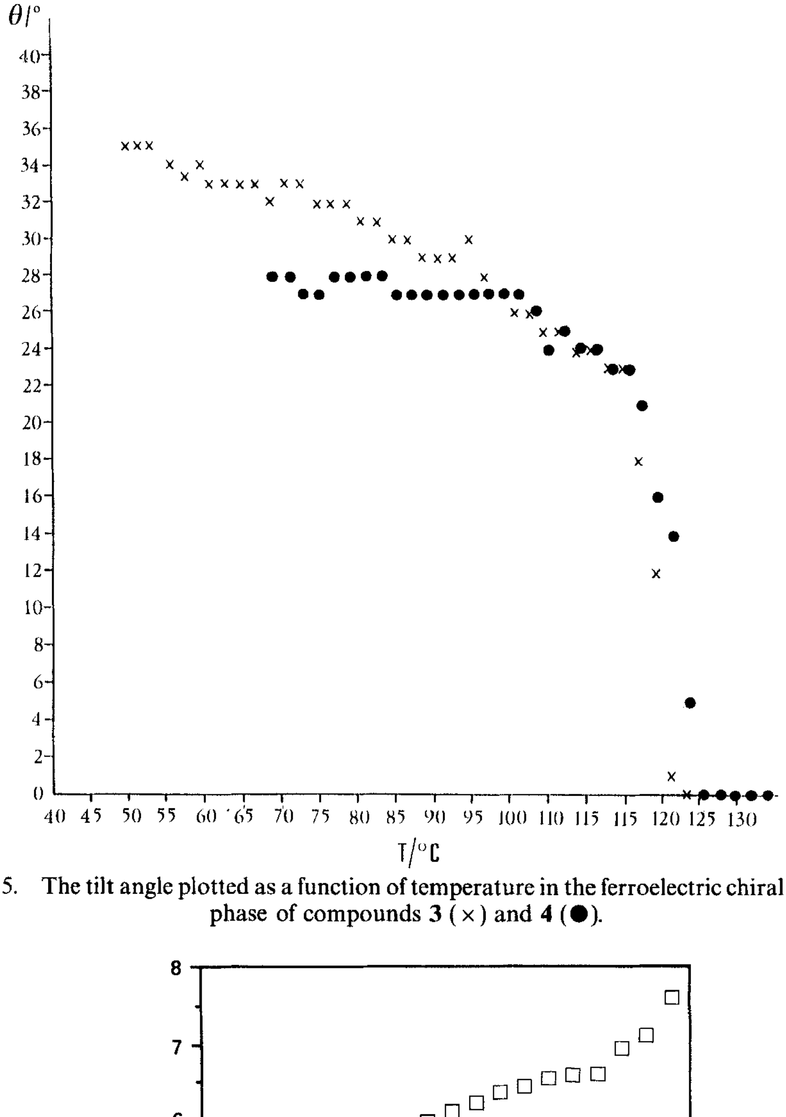


Figure 5. The tilt angle plotted as a function of temperature in the ferroelectric chiral smectic C phase of compounds **3** (×) and **4** (●).

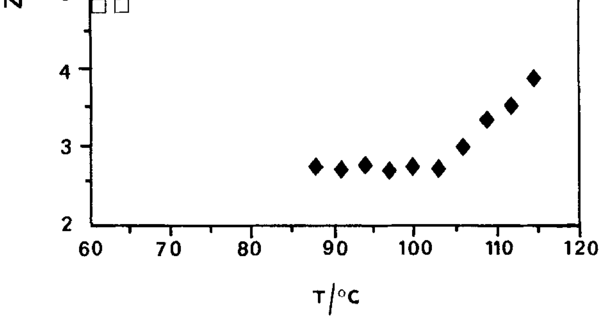


Figure 6. The pitch length measured as a function of temperature in the ferroelectric chiral smectic C phase of compounds **3** (◆) and **4** (□).

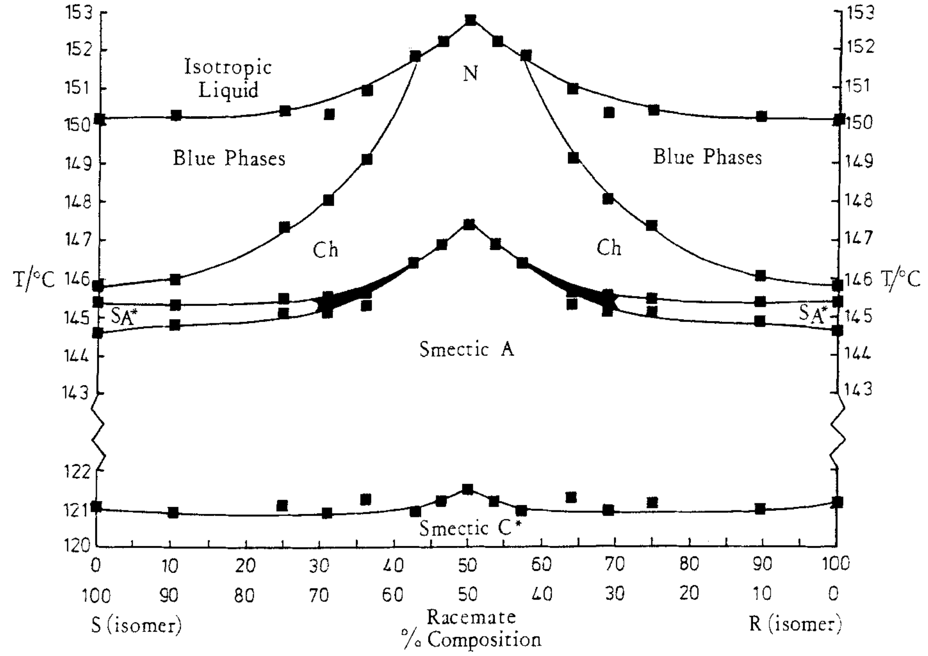


Figure 7. Miscibility phase diagram of binary mixtures (wt %) of the optically active and racemic versions of compound 3. The mixtures between the (*S*) isomer and the racemate have been reflected across the phase diagram for the (*R*) isomer in order to produce a complete miscibility figure for mixtures of (*R*) and (*S*) isomers.

3.4. *Optical purity studies*

In order to study the dependence of the formation of the smectic A* phase on optical purity, a phase diagram was constructed by studying the phase transitions in various mixtures of chiral and racemic variations of compound 3. The miscibility phase diagram is shown in figure 7. As expected the temperature ranges of the smectic A* phase and the various blue phases were found to decrease with decreasing optical purity. At values of 15 per cent and below of the chiral component in the binary mixtures, no smectic A* phase or blue phases were observed and a S_A–Ch–I phase sequence was obtained. As the 100 per cent level of the chiral component in the mixture was approached the cholesteric phase temperature range decreased, as the temperature of the transition from blue phase I to cholesteric drops quite markedly, thereby increasing the temperature range of the blue phases and decreasing that of the cholesteric phase. Furthermore, it was noted that, in the region of 100 per cent racemate to approximately 40 per cent of the chiral variant in the binary mixtures, the clearing points fell and then levelled off. A similar trend was also observed for the smectic A or A* to cholesteric transition. This unusual trend for the clearing points and S_A or S_A^* phase to cholesteric transitions was not particularly pronounced at all for the smectic C* to smectic A transition. This observation suggests that the clearing points and smectic A to cholesteric transitions are being markedly influenced by the degree of molecular chirality, whereas the smectic C* to smectic A transition is relatively unaffected.

4. Discussion

Optical and thermal results indicate that in compounds **2**, **3** and **4** a novel phase mediates the transition from the smectic A phase to the cholesteric phase. Textural studies suggest that this phase is a chiral smectic A* phase similar to that reported previously [1, 4]. However, for compound **1**, which exhibits a direct smectic to isotropic liquid transition, no S_A^* phase was observed. This and other evidence suggests that for a smectic A* phase to be obtained either an underlying chiral smectic C phase or an overlying cholesteric phase must be in close proximity to the transition to the S_A phase [1, 4, 5]. Furthermore, it appears that the temperature range of the intermediate S_A^* phase is critically dependent on the length and nature of the terminal alkyl chain associated with the chiral group. It is thought that the more restricted the motion of the chiral moiety becomes, then the higher the degree of chirality will be [6], and hence the more likelihood of observing a twisted S_A phase. Other results appear to confirm this hypothesis, for instance, the lower homologues of the series from which compound **1** is an example do in fact possess a cholesteric phase but no smectic A* phase or blue phases. This indicates that when a shorter terminal aliphatic chain is attached to the chiral centre a molecule is yielded that does not have a strong enough degree of chirality to form a twisted S_A phase. An alternative hypothesis is that the layer ordering needs to be relatively weak to form the twisted structure and it may be that the shorter chain attached to the chiral centre aids the packing of the molecules and, therefore, strengthens the layer ordering.

Thermal studies on compounds **3** and **4** clearly indicate the presence of an intermediary phase between the smectic A phase and the cholesteric phase, this is less certain with compound **2** as the existence range of this phase is extremely small. For compound **3**, peaks relating to the transitions from cholesteric to blue phase I, blue phase I to blue phase II and blue phase II/III to isotropic liquid are also resolved. For compound **4** no transitions between the blue phases were observed by DSC. This was also the case in compound **2** where the peaks for the smectic A to cholesteric and cholesteric to isotropic liquid were very close together.

Studies measuring the tilt angle as a function of temperature for compounds **3** and **4**, show that the saturation value for the tilt angle in compound **3** is greater by approximately 8° than that for compound **4**. This supports the view that compound **3** may possess a greater degree of chirality. The result of investigations into the helical pitch of each material appear to confirm this hypothesis. Furthermore it is interesting to note that the smectic A* phase has a greater temperature range in compound **3** which is expected on the hypothesis presented.

From the studies into the effect of optical purity it was found that both the blue phase and smectic A* temperature ranges decrease with decreasing optical purity. This indicates that the conditions necessary for the formation of both types of phase may be similar. The temperatures of the clearing points and the smectic A to cholesteric transitions in mixtures of enantiomers are clearly depressed with increasing optical purity as predicted by de Gennes [10].

5. Conclusions

We conclude that compounds **2**, **3** and **4** in this series of chiral chloro esters exhibit helical smectic A* phases. It appears that, as with blue phases, the stability of this phase is dependent on optical purity and also on the degree of molecular chirality. Results suggest that for the S_A^* phase to exist the layer ordering must be relatively weak and that there must be another helical phase present in close proximity to the transition to the S_A phase.

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