Liquid Crystals

A chiral induced ferroelectric liquid crystal phase transition with a vanishingly small enthalpy

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A chiral induced ferroelectric liquid crystal phase transition with a vanishingly small enthalpy

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Information on molecular interactions that give rise to the stabilization of various ferroelectric, liquid-crystalline mesophases is important to the realization of their potential utility in a wide variety of optical devices. Understanding the roles that optical activity and optical purity play in the formation and properties of the various smectic phases is therefore of particular interest. In order to study this relationship three new liquid-crystalline materials were prepared, one as a racemic mixture, the other two as the optically active analogues. The optically active isomers appear to exhibit a different mesophase morphology from the racemate. The chiral compounds apparently possess two extra ferroelectric mesophases in comparison to the racemic mixture. The transitions to and from these phases have extremely small enthalpies. An attempt is made to explain the results for the chiral compounds in terms of differing dipolar couplings in the chiral ferroelectric phases. In the racemic mixture these interactions are compromised or scrambled by a loss of asymmetry thus destabilizing these extra phases.

Ferroelectric liquid-crystalline mesophases show potential as the electrically active media in a wide variety of applications, such as displays [1], light-valves [2], spatial light modulators [3], optical processing [4], and pyroelectric detectors [5]. However, the fulfilment of the promise that these novel media have generated is greatly dependent on the physical properties of the actual substances involved in producing the mesophase. Therefore, the synthesis and blending of materials, and an understanding of their physical properties is of central importance to the success of this infant technology.

Symmetry arguments predict, when a smectic C liquid crystal is composed of chiral material, that the possibility of ferroelectric behaviour exists [6]. This manifests itself in the form of a spontaneous polarization which acts along the C_2 axis of the phase. The magnitude of this effect has been suggested to be related to the size and time dependent couplings of the dipoles at the chiral centres with the other dipoles in their local chiral environments [7, 8].

A material that exhibits ferroelectric properties can have one or more chiral centres. However, a multiplicity of chiral centres can produce diastereoisomers which in turn can induce unusual physical properties for the mesophase. For example, in phase diagrams between racemates and diastereoisomers of the same parent compound strong non-ideality sometimes can be observed, occasionally culminating in the racemate and diastereoisomers exhibiting different phase types [9, 10]. In this preliminary article we report three new liquid crystal substances, two enantiomers and

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an independently synthesized racemic mixture of the two enantiomers. The enantiomers have a single chiral centre, and yet are still found to exhibit completely different phase sequences from the racemic mixture.

The materials investigated were discovered as part of an ongoing study into the morphology of biphenyl carboxylic esters. The three compounds reported, racemic, R- and S-1-methylpentyl 4-n-decyloxybenzoyloxybiphenyl-4'-carboxylates, are in fact similar in structure, but not identical, to materials prepared previously [11]. The materials were synthesized from 4-methoxy-4'-cyanobiphenyl (M3, BDH Chemicals) by first hydrolyzing the nitrile to the acid, demethylating, and then protecting the free hydroxyl group with methyl chloroformate as described previously [12]. The protected acid was then esterified with R- or S-2-hexanol (Chemical Dynamics) or ($\pm$)-2-hexanol (Aldrich), deprotected and re-esterified with 4-n-decyloxybenzoyl chloride to give the desired products. The chemical purities of the final products were determined to be in excess of 99 per cent by reverse and normal phase H.P.L.C. Their structures were confirmed by N.M.R., I.R., and M.S. The optical purities of the two enantiomers were inferred from the optical purities of the starting 2-hexanol as shown in the table.

n-$C_{10}H_{21}OC_6H_4COOC_6H_4C_6H_4COOCH(CH_3)C_4H_9$											
Isomer	J*†		X_2		X_1		C*		A		Iso	m.p.	$[\alpha]_D^{23}$‡	ee (per cent)
(R)	●	(48·1)	●	74·2	●	86·6	●	106·5	●	135·5	●	65·6	9·5	89·45
(S)	●	(48·5)	●	85·0	●	87·3	●	106·7	●	133·9	●	65·7	9·9	91·1
($\pm$)	●	(46·1)	—	—	—	—	●	105·4	●	132·4	●	65·0	—	—

† J phase is non-chiral for the racemate.
‡ $[\alpha]_D^{23}$ is the optical rotation of the 2-hexanol starting material. Optically pure starting material has a value of 12·04.
( ) monotropic transition temperature.

The physical properties of these two materials were probed thermally, optically, and electrically. However, as the phase morphology of these compounds is the topic of this discussion only the thermal and optical studies are reported in detail.

The materials were initially investigated by thermal optical microscopy using a Mettler FP52 hot-stage and FP5 control unit. The transition temperatures for the three are shown in the table. Oddly, the chiral compounds were apparently found to exhibit five mesophases, whereas the racemic mixture has one or two phases less.

Homogeneous preparations of the chiral compounds gave the usual focal-conic texture of the A phase which gave way on cooling to the typical banded texture of the C* phase. Homeotropic preparations of the same material, however, gave unusual results. The A phase appeared homeotropic, and the transition to the C* phase was marked by the introduction of an iridescent texture. Further cooling produces two subsequent transitions, one to a non-iridescent phase (X_1) that is suspected of being the I* type, and a second transition back to a strongly iridescent phase (X_2). By a process of elimination this third helical phase X_2 may be expected to be of the F* type. Yet another transition to the G* or J* crystalline modification took place on further cooling (see figures 1 to 4).

Free standing film preparations of the same material confirmed the observations made on the homeotropic textures. An interesting point to note concerning the

photomicrographs is that the X_2 phase shows an uncommonly strong iridescence. This would be unusual if the X_2 phase is of the F* type. Normally, because of the long range bond orientational ordering, the pitch of the helix of the phase would be expected to be relatively long, as in the preceding X_1 phase. However, such a transition X_1 to X_2 (I* to F*) may have the effect of decoupling the layers in the X_2 phase leading to a phase with a shorter pitch. Alternatively, the X_2 phase may not be of the F* type at all. This scenario leads to the possibility that this iridescent phase could be either a new phase or a C* phase with a different local bond orientational order than the higher temperature C* phase. However, the defect structure of the texture suggests that this second proposition is probably unlikely.

The photomicrographs clearly show for both of the enantiomers that one non-iridescent phase (X_1) separates two irridecent phases (C* and X_2) on heating and cooling. When the top polarizer is rotated for these phases it is found that the three phases preceding the formation of the J* phase on cooling are helical, and that the upper and lower phases are apparently of opposite twist senses to the non-iridescent middle phase. However, contact studies indicate that this is not the case and that in fact all three phases are levo, l($-$) for the S isomer and dextro, d($+$) for the R isomer. The reason for this descrepancy is that the pitch is so tight in the upper and lower helical phases that a false result can be obtained by the free-standing film technique. From this experimental evidence it appears that the resurgence of an iridescent phase formed on cooling the X_1 (I*) phase is unlikely to be due to a change in twist direction. Thus, all of the helical phases are expected to conform to the Sol($-$) or Rod($+$) sequencing pattern described previously.

The results obtained for the analogous racemic mixture, in light of the studies on the chiral compounds, were quite surprising. The material was found to exhibit only A, C, and G or J phases, with the possibility that a fourth phase, smectic B, may be present as well. The two lower temperature helical phases (X_1 and X_2) had disappeared and no racemic analogue had replaced them. The textures obtained in homogeneous, homeotropic, and free-standing film preparations were consistent with only the A, C, and J or G phases being present. After formation of the G or J phase, the mosaic texture for a previously homeotropically oriented specimen quickly gave way to the introduction of a homeotropic texture of a fourth phase. The flow properties of this phase, determined when the specimen was subjected to mechanical stress, suggested that it may be of the crystal B class or a plastic phase.

Thermal studies of the materials by differential scanning calorimetry also proved to be extraordinary. The materials appeared almost identical by D.S.C.; no extra enthalpies were detected for the chiral substances for the two helical phases that were present but not observed for the racemic mixture. Figures 5 and 6 show the heating and cooling cycles for one of the chiral compounds, and figure 7 shows an expansion of the region between 110 and 50°C for the cooling cycle. The A to C* transition is detected as a second order phase transition with a relatively small enthalpy. However, the transitions to and from the other helical phases are not visible above the level of the background noise. Differential scanning calorimetry of the racemate only differed from the chiral substances by the inclusion of an extra phase below the G or J phase (thought to be B from microscopy studies). Otherwise the other regions of the thermograms were found to be identical.

Electric field studies [13], however, show unusual behaviour for the chiral compounds through these phase transitions, thus confirming the optical investigations. Consequently, in this case optical studies are quite definitive concerning the
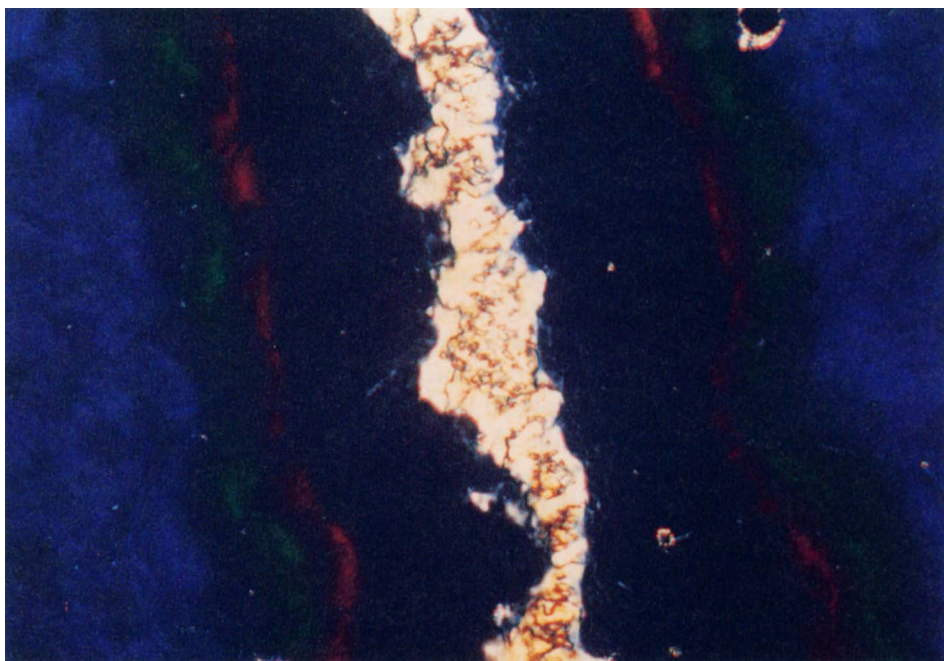
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Figure 1.   A contact preparation between the R- and S-1-methylpentyl 4-*n*-decycloxybenzoyl-
oxybiphenyl-4′-carboxylates. The materials are both in their C* phases. In the central
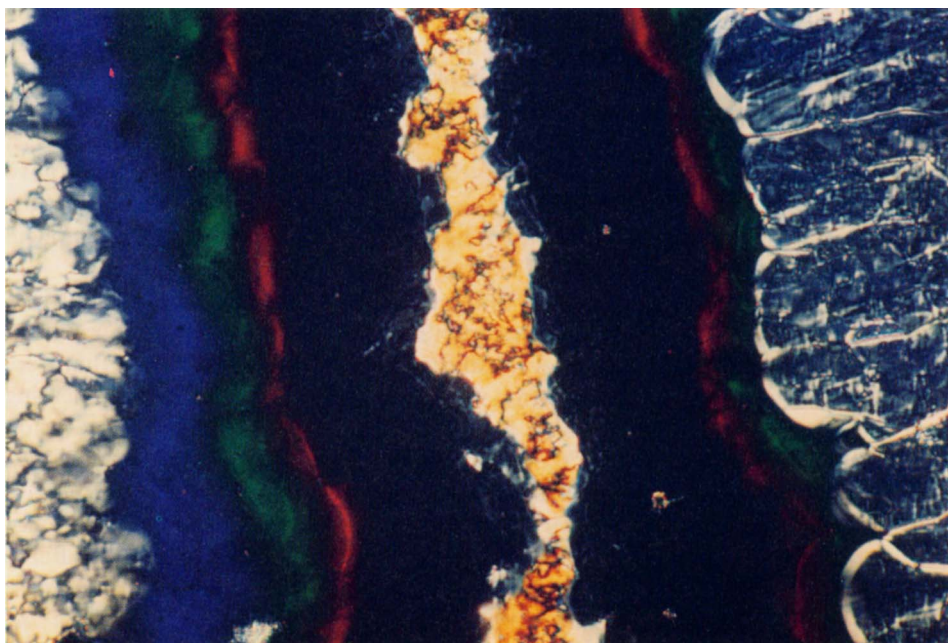region of the contact the pitch becomes compensated.

Figure 2.   The same contact area as in figure 1. Now the materials are in their non-iridescent
X₁ phases. The central portion of the contact still remains in the C phase.
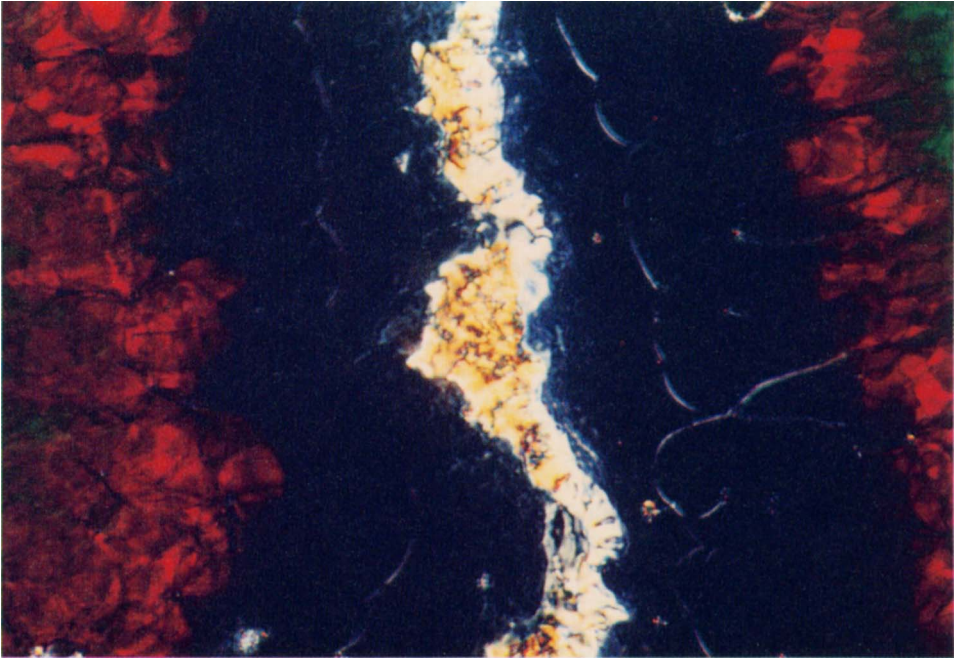
Figure 3. The same contact region as in figures 1 and 2, but now at a lower temperature. The area that was in the X_1 phase has undergone a transition apparently to X_2. This phase is again iridescent, but the central contact region still remains in the C phase. The two phases are separated by a wall that appears as a light line in the photomicrograph. At the outside edges of the preparation a transition from X_1 to the iridescent X_2 phase has occurred.

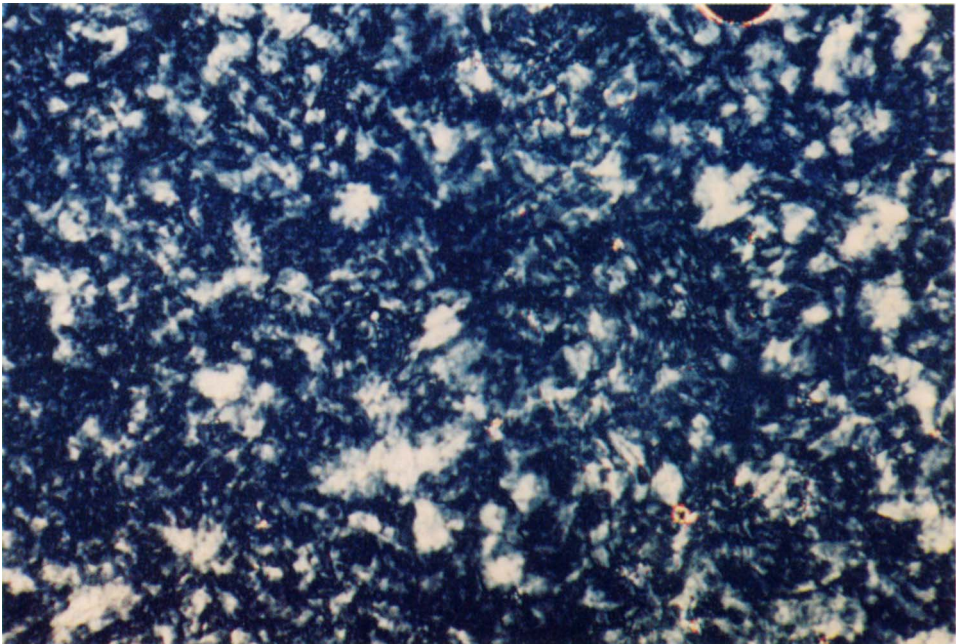
Figure 4. The same region as in figures 1 to 3, but now a transition has occurred to the J* or G* phase. The whole preparation is now in J* or G* phase including the contact region that was previously in the C phase.
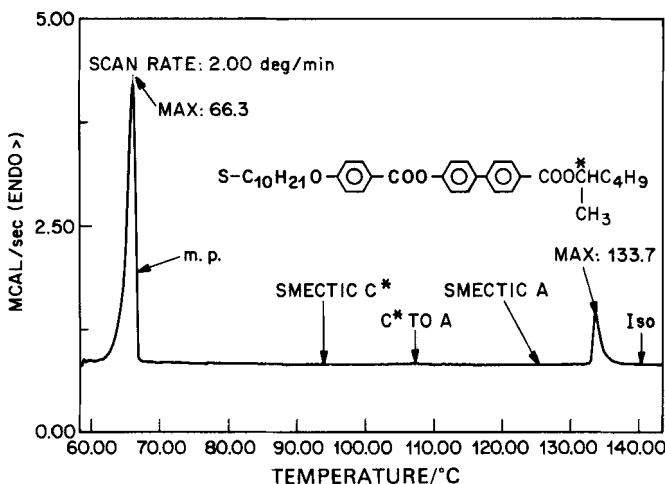
Figure 5.   Differential scanning calorimetry heating cycle for S-1-methylpentyl 4-n-decyloxy-benzoyloxybiphenyl-4'-carboxylate.
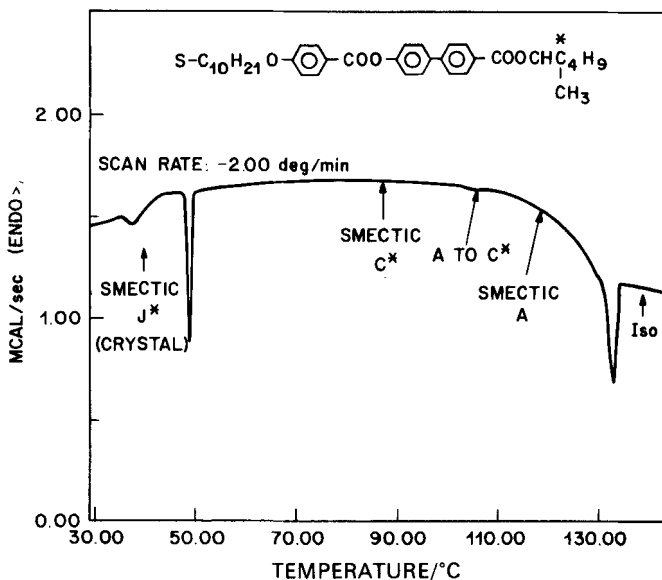

Figure 6.   Differential scanning calorimetry cooling cycle for S-1-methylpentyl 4-n-decyloxy-benzoyloxybiphenyl-4'-carboxylate.

presence of these transitions for the chiral compounds, whereas D.S.C. which would normally be expected to produce definitive evidence instead appears to give continuous behaviour.

In order to confirm our observations, we also chose to examine the optical properties of mixtures of one of the chiral substances and the racemic mixture. A phase diagram obtained from thermal optical microscopic studies of individual mixtures of the two materials is shown in figure 8. The A to isotropic transition temperatures in the phase diagram appear to vary almost linearly with concentration. Similarly, both the A to C* and the C* to J* or G* transition temperatures appear
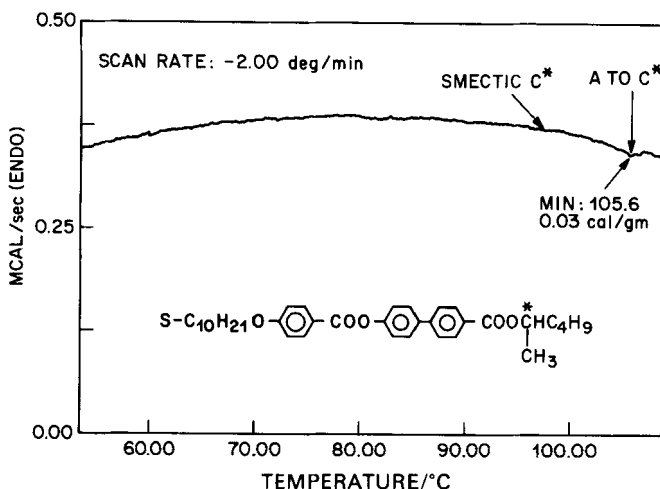
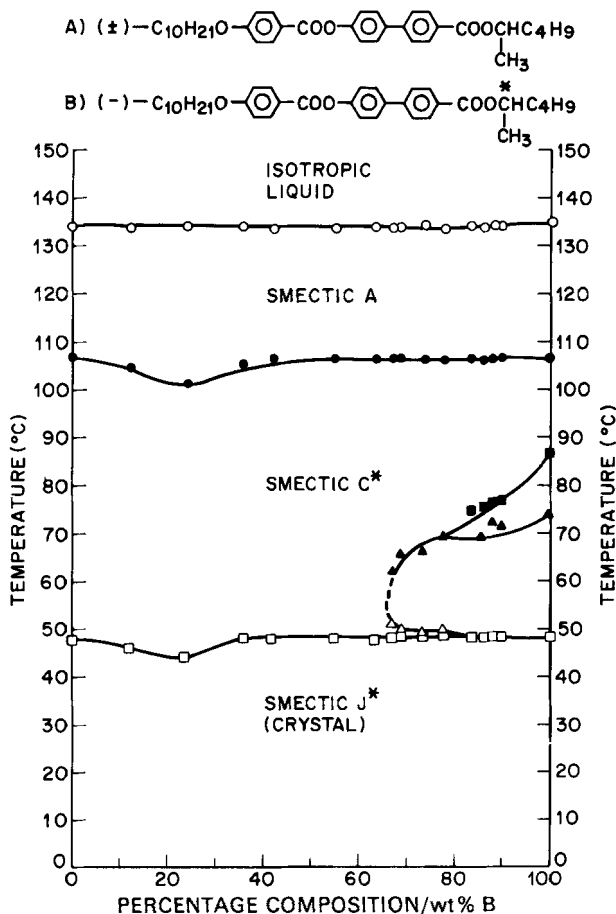Figure 7. Expansion of the D.S.C. cooling cycle shown in figure 6.

Figure 8. Phase diagrams for binary mixtures between S-1-methylpentyl 4-*n*-decyloxybenzoyl-oxybiphenyl-4'-carboxylate (B) and (±)-1-methylpentyl 4-*n*-decyloxybenzoyloxybiphenyl-4'-carboxylate (A).

to vary linearly except for mixtures in the region of 20 per cent by weight of the chiral isomer, where a depression of approximately 5°C in transition temperature was observed. In the region of 70 to 95 per cent by weight of the chiral isomer, transitions similar to those observed for the pure optical isomer were found. The non-iridescent phase X_1 (I*) disappeared at percentages below 78 per cent of the chiral isomer in the mixture. The lower temperature iridescent phase X_2 appears then to wrap around on itself in the region of 70 per cent by weight of the chiral isomer, thus implying a second transition back to the C* phase, and consequently raising the possibility that a re-entrant ferroelectric C* phase may be present, as shown by the dotted lines in figure 8. Thus, this miscibility study confirms our earlier observation that the chiral isomers exhibit two additional helical phases besides the C* phase in comparison to the racemic mixture which only possesses the C phase out of the three. In a final study we examined the textures obtained for a contact preparation between the R and S enantiomers. The contact region between the isomers is shown in figures 1 to 4. These figures are essentially self explanatory, and clearly demonstrate the major point of this preliminary disclosure which is that the contact region, where the racemic mixture exists, remains in the C phase, whereas the neighbouring regions of the pure enantiomers go through a number of other transitions as the temperature is changed.

These preliminary results suggest that the chiral ester exhibits A, C*, X_1 (I*), X_2 (F*), and J* or G* phases, whereas the racemic mixture possesses only A, C, and J or G phases, The helical phases were all shown to be ferroelectric by electrical studies [13]; thus the optical isomers exhibit chiral induced ferroelectric phase transitions.

One possible explanation of this behaviour is that the two extra phases X_1 and X_2 are in fact smectic I* and smectic F* phases which are being stabilized by either parallel or antiparallel dipolar interactions. For example, in the direction about the director the molecules will be, on average, hexagonally close-packed in the C* phase, but in the plane of the layers they are C-centred rectangularly close-packed. The rectangular packing in the I* and F* phases is more extensive than in the C* phase, with the difference between the two being one of tilt orientation [14]. The tilt in the F* phase is across the shorter edge of the rectangular net, whereas in the I* phase it is across the longer edge. The spontaneous polarization acts at right angles to the tilt orientation, and therefore it is along this direction that the lateral dipoles of the molecules will couple in a parallel or antiparallel fashion. It is possible that the dipolar couplings in the structures for the I* and F* phases are not equivalent, thus leading to a difference in energy between the two phases and also with the C* phase. This difference would be expected to be small, and of course the interactions would be compromised or scrambled in the racemic phase. Thus, the energy differences between the C*, I* and F* phases may be great enough to stabilize these phases for the chiral analogues with respect to the racemic mixture. This effect would also be dependent on the optical purity and the magnitude of the dipoles for the chiral species. In the case we have presented the optical purities of the chiral materials are greater than 85 per cent and the spontaneous polarization is in the region of $80\,\mathrm{nC\,cm^{-2}}$ in the C* phase, which is a relatively large value [13]. Hence some of the factors which could enable these transitions to occur are present for this compound. It is interesting to note that S-1-methylheptyl 4-n-octyloxybenzoyloxybiphenyl-4'-carboxylate prepared previously [11], has a polarization of $50\,\mathrm{nC\,cm^{-2}}$ and a helical pitch of $1\cdot6\,\mu\mathrm{m}$, making it non-iridescent. Moreover, this material does not appear to exhibit any unusual phase transitions. This may be because the optical purity for this material is not great enough for this behaviour to occur.

A second possible explanation for this unusual behaviour is that the X_1 and X_2 phases are separate and different manifestations of the C* phase. For instance, the smectic C* phase can have two forms of short-range bond orientational ordering (I*-like and F*-like). The transition to the X_1 and X_2 phases could be simply changes in the direction of the local bond order. This is similar in some respects to the interlayer stacking variations that occur in the smectic B phase with changes in temperature. Moreover, these stacking changes are not usually accompanied by an enthalpy of transition.

Thirdly, although our studies show that there is probably no inversion of the twist direction of the helices of these materials at the C* and X_1 and X_1 to X_2 transitions, because of the short pitch length of the helix and the accompanying experimental difficulties in determining twist direction, a twist inversion cannot be totally ruled out. This could mean that X_1 and X_2 are simply C* phases with different helical twist senses. However, the rapid changes in the pitch that occur at the C* to X_1 and X_1 to X_2 transitions, as shown by the Becke lines in figure 3, would suggest that this scenario is unlikely as the pitch would normally be expected to change continuously with temperature and not diverge abruptly.

Finally, it is interesting that the transition temperatures given in the table for the two enantiomers are not identical, particularly for the C* to I* and I* to F* phase transitions. This is because the optical purities of the two compounds are not identical, and these transitions are obviously more sensitive to optical purity than the others. Thus, we have the prospect of being able to tune the phase types and control the transition temperatures by optical purity.

Summary

We have shown that molecular chirality can apparently induce ferroelectric phases to occur in optically pure compounds, and that these phases need not be present in the racemic mixture. The transitions between these induced ferroelectric phases have extremely small enthalpies associated with them. The structures of these phases are the topic of our present investigations and we hope that these studies will enable us to produce definitive evidence for the phase classification of the chiral isomers.

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