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Liquid-crystalline Abrikosov flux phase with an antiferroelectric structure

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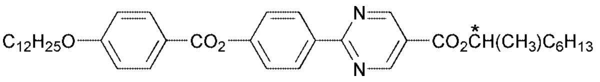
(*S*)-1-Methylheptyl 2-[4-(4-dodecyloxybenzoyloxy)phenyl]-pyrimidine-5-carboxylate and its racemic modification are synthesised; miscibility studies, investigations of defect textures, differential scanning calorimetry and electrical field studies show that this material exhibits an antiferroelectric twist grain boundary TGBC*$_\text{A}$ analogue of the Abrikosov flux phase found in superconductors.

The prediction[1,2] and discovery[3,4] of the twist grain boundary smectic A* (TGBA*) phase led to the unification of phase transition theory in liquid crystals with those of superconductors. Subsequent to these seminal contributions, TGB phases were found to be ubiquitous in the field of self-organising systems where they have been encountered at transitions from either the isotropic liquid or the chiral nematic (N*) phase to the lamellar, smectic (Sm) state.[5–7] At the normal chiral nematic to smectic transition, the helical ordering of the chiral nematic phase collapses to give the layered structure of the smectic phase. However, for strongly chiral systems, there can be competition between the need of the molecules, due to their chiral packing requirements, to form a helical macrostructure and the need for the formation of a lower energy layered structure. This frustration is relieved by the formation of a helical structure with its heli-axis parallel to the planes of the layers. The helix and lamellar structures are, however, incompatible with one another and cannot co-exist without the formation of defects. The co-existence is achieved by having small blocks/sheets of molecules, with a local smectic structure, which are rotated with respect to one another *via* sets of screw dislocations located at their interfaces, thereby giving a quasi-helical structure.[2] In this way the twist distortions are localised in defects that periodically punctuate the normal smectic state which is analogous to how lines of flux punctuate the Abrikosov vortex state in type II superconductors.

Frustrated equivalents of the smectic A* and C* phases have been found, with both having commensurable or incommensurable variants that are dependent on the rational number of smectic blocks/sheets with respect to the pitch of the phase.[8,9] For the TGBC modification a number of subphases have been discovered which are dependent on; (i) the presence (TGBC*) or expulsion (TGBC) of the local heli-axis of the smectic C* phase which is oriented perpendicular to the layers of molecules and to the heli-axis of the TGB phase; (ii) the direction of the local spontaneous polarization relative to the heli-axis (parallel or perpendicular); (iii) the inversion of the handedness of the helix in the TGBC phase as a function of temperature;[10] and (iv) the formation of a 2D modulated structure with respect to the tilt.[11]

Here we report on the liquid crystal properties of (*S*)-1-methylheptyl 2-[4-(4-dodecyloxybenzoyloxy)phenyl]pyrimidine-5-carboxylate **A**, and its racemic modification **B**. Through miscibility studies, investigations of defect textures, differential scanning calorimetry, and electrical field studies, we suggest this material exhibits the first example of a twist grain boundary (TGBC*$_\text{A}$) phase that has a local antiferroelectric structure.

The transition temperatures, and the associated enthalpies for each phase transition, for (*S*)-1-methylheptyl 2-[4-(4-dodecyloxybenzoyloxy)phenyl]pyrimidine-5-carboxylate **A**, and its racemate **B**, were determined by thermal polarized microscopy and differential scanning calorimetry, and are given together in Table 1. Firstly, we note from the Table 1 there are considerable differences in transition temperatures between the enantiomer and the racemate, however, we also emphasise that the purities of the materials were found to be better than 99.5%. Therefore the differences in temperatures are real, as are the variances in phase sequences and phase types, and both are associated with the effects of chirality on the self-organising processes. Importantly the isotropization temperature for the racemate is higher than that for the enantiomer, whereas the transition to a tilted smectic phase is lower, these results are at variance with problems associated with the effects of impurities.


A

Homogenous, homeotropic, uncovered droplets, and free-standing film specimens of **A** were examined by transmitted, polarized-light, thermal microscopy. The phase first formed from the isotropic liquid was iridescent and clearly helical. The phase did not exhibit either focal-conic, platelet or *schlieren* defect textures, and was not typical of either the TGBA or TGBC phase. Nevertheless, at lower temperatures the transition to and from the smectic C*$_\text{A}$ phase was characterised by the formation of filaments typical of a TGB phase.[12] A Grandjean plane texture, typical of a helical phase was obtained for **A** in a homogeneously aligned (perpendicularly oriented layers) cell with a *ca.* 5 μm spacing that had been antiparallel-buffed. The fact that the heli-axis forms normal to the glass substrates of the cell indicates that the twist is in the direction of the planes of the layers, *i.e.* typical of a TGB phase. The presence of filaments and a heli-axis in the plane of the layers confirm that the phase formed first on cooling the isotropic liquid of the enantiomer is a twist grain boundary phase, however, the lack of a characteristic texture suggested that the phase was not of the same class as those characterised so far.

Table 1 The transition temperatures (°C) and the associated enthalpies of transition [Δ*H*/kJ g^{-1}] for (*S*)-1-methylheptyl 2-[4-(4-dodecyloxybenzoyloxy)phenyl]pyrimidine-5-carboxylate **A** and its racemic modification **B**; * denotes the enthalpies that were too small to be evaluated.

Chiral compound **A**				
Iso–TGBC*$_\text{A}$	TGBC*$_\text{A}$–SmC$_\text{A}$*	SmC$_\text{A}$*–Cryst		Mp/°C
93 [−0.87]	91.6 [−0.22]	68.3 [−28.8]		86.4
Racemic modification **B**				
I–SmA	SmA–SmC	SmC–SmC$_\text{alt}$	SmC$_\text{alt}$–Cryst	Mp/°C
96 [−9.12]	90.5 [−]*	89.2 [−]*	43.6 [−34.8]	72.6 [75.6]

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Comparing the results obtained for racemate **B** with those for enantiomer **A** yields some interesting and contrasting observations. The mesophase formed first on cooling the isotropic liquid of the racemic modification exhibits a focal-conic texture that is characterised by its elliptical and hyperbolic lines of optical discontinuity, and a homeotropic optically extinct texture. The presence of these defect textures characterises the mesophase as smectic A. Subsequent cooling leads to the homeotropic areas becoming *schlieren*, and the focal-conic domains becoming broken, both of these textures are characteristic of the formation of a smectic C phase. As the temperature is lowered there is the formation of a third phase, again characterised by the presence of a *schlieren* texture, but this time the focal-conic domains are not as broken as they were in the smectic C phase. These observations are in keeping with the third phase being an *anticlinic* smectic C_{alt} phase, where the tilt directions of the molecules alternate on passing from one layer to the next, *i.e.* the tilt direction rotates through an angle of 180° on passing from one layer to the next. Thus racemate **B** appears to exhibit a SmA, SmC, SmC_{alt} phase sequence, whereas the enantiomer **A** exhibits a TGB and SmC^*_A sequence.

Differential scanning calorimetry was used to investigate the nature of the phase transitions and to determine their associated enthalpy values, see Table 1. Fig. 1 shows the cooling scans for both the racemate and the enantiomer. For the racemate (dotted line) the smectic A phase forms first on cooling from the isotropic liquid at 96 °C. On further cooling a smectic C phase is formed at 90.5 °C, but as the transition is second order it is detected only as a baseline step in the DSC. As the temperature is lowered a weak first order transition is found for smectic C to smectic C_{alt} at 89.2 °C.

A, solid line in Fig. 1, shows strong pretransitional effects in the isotropic liquid just before the transition to the TGB phase. Transitional effects in the isotropic liquid are typical for systems that are about to form TGB phases and are associated, like those of superconductors, with entangled or disentangled flux phases, *i.e.* the amorphous liquid has some long range order associated with it.[13] The transition to the TGB phase is strongly first order, but the associated enthalpy is much lower than that obtained for the clearing point of the racemate. However, the enthalpy for the isotropic liquid to smectic A transition is approximately equal to the sum of the enthalpies associated with the pretransitional effect in the liquid and the isotropic liquid to TGB phase of the enantiomer.[3,4]

The magnitude of the spontaneous polarization for **A**, determined using the triangular wave method, was found to reach a maximum value of approximately 60 nC cm^{-2}. Examination of the current flow as a function of temperature and time showed that as the material is switched from one stable ferroelectric state to the other, two separate events occur which correspond to switching from one ferroelectric state to the antiferroelectric state and on to the other ferroelectric state. As the temperature is reduced, so the antiferroelectric state becomes more stable, which is probably reflected in a higher viscosity. At the transition to the TGB phase there is no appreciable change in the switching process indicating that the phase formed from the TGB phase on cooling is indeed antiferroelectric, confirming the observations made from the miscibility studies, *i.e.* that enantiomer **A** does not exhibit either a smectic A* or smectic C* phase that corresponds to the achiral phases of the racemate. It is also interesting to note the events that take place prior to and during the switching of the TGB phase. When the cell is filled from the isotropic liquid the homogeneous alignment causes the formation of a helical macrostructure, associated with the TGB phase, perpendicular to the glass substrates. As the field is applied the helix unwinds to give a bookshelf-like geometry, as the field is increased a helix, associated with an antiferroelectric phase, now forms perpendicular to the layers and parallel to the planes of the glass substrates. Increasing the field induces this phase to unwind to give a stable unwound antiferroelectric phase, which as the field is increased gives way to a stable switched ferroelectric phase. These investigations suggest that the polarization vector associated with the ferroelectric layers in the antiferroelectric phase lies perpendicular to the heli-axis as shown in Fig. 2.

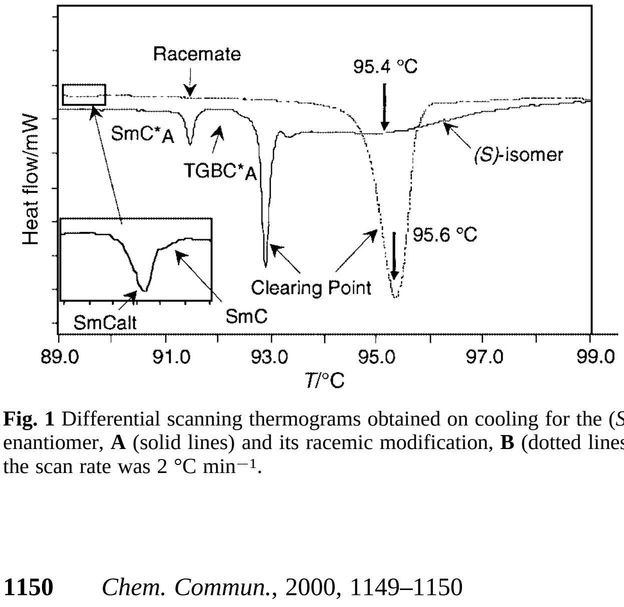

Fig. 1 Differential scanning thermograms obtained on cooling for the (*S*)-enantiomer, **A** (solid lines) and its racemic modification, **B** (dotted lines), the scan rate was 2 °C min^{-1}.

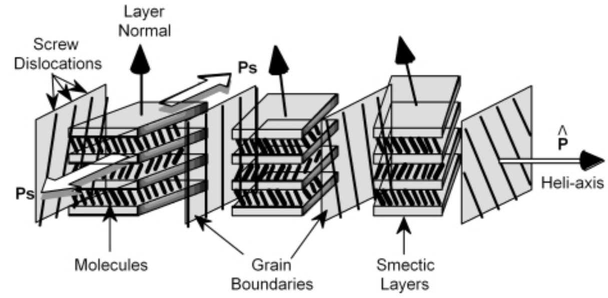

Fig. 2 A cartoon of the proposed structure of the antiferroelectric $TGBC^*_A$ phase.

In conclusion, we have demonstrated that (*S*)-1-methylheptyl 2-[4-(4′-dodecyloxybenzoyloxy)phenyl]pyrimidine-5-carboxylate exhibits a novel TGB which we believe to be antiferroelectric. This result represents the addition of a new frustrated state of matter to the family of twist grain boundary phases.

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