

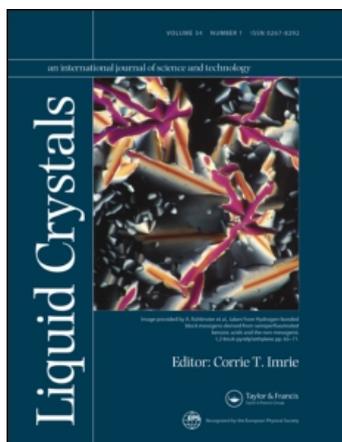
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## Liquid Crystals

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## Preliminary Communications

# A chiral material with a new phase sequence: Twist grain boundary smectic A phase—blue phases

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A new phase sequence: twist grain boundary  $S_A$  phase to blue phases was observed in a chiral compound (*R*)- or (*S*)-1-methylheptyl 3'-fluoro-4'-(3''-fluoro-4''-octadecyloxybenzoyloxy)tolan-4-carboxylate. It is the first time that blue phases have been found to occur above the TGBA phase in the absence of a cholesteric phase. These phases were characterized by microscopic observation, differential scanning calorimetry, the contact method and study of the racemic system.

Chirality has profound effects on the phase behaviour of liquid crystals. Nematic and tilted smectics have their chiral variations. Chirality may cause the appearance of fundamentally new phases—the blue phases (BPs) and the recently discovered twist grain boundary smectic A and smectic C phases (TGBA and TGBC).

Theoretical and experimental work has demonstrated that cholesteric liquid crystals of short pitch can form up to three distinct blue phases [1–3]. In order of increasing temperature they are named blue phase I (BPI), blue phase II (BP II) and blue phase III (BP III). BPI and BP II have, respectively, body-centred cubic and simple-cubic symmetry. BP III is seemingly amorphous with a still unknown local structure. In the cubic blue phases, the basic unit is thought to be a double twist tube—a cylinder of liquid crystal in which the director is parallel to the axis at the centre and rotates spatially about any radius. Fitting these double twist cylinders into a three dimensional structure so that the directors match everywhere is topologically impossible, so disclinations, defects in the orientational arrangement of the molecules, are necessary to relieve the elastic strain energy. The cubic blue phases can therefore be described as lattices of double twist tubes or, equivalently, lattices of defects.

The twist grain boundary phases (TGB) are another kind of frustrated phase derived from chiral molecules, which may occur at the transition from smectic A ( $S_A$ ) or helical smectic  $C^*$  ( $S_C^*$ ) phases to cholesteric ( $N^*$ ) or isotropic phases. The TGBA phase was predicted in 1972 by de Gennes [4] from an analogy between the

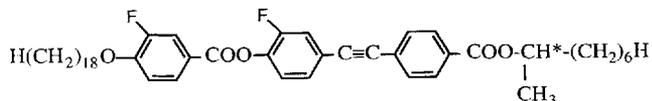
cholesteric to smectic A transition and the normal to superconductor transition in metals under an external magnetic field. The theoretical structures of this new phase were proposed in 1988 by Renn and Lubensky [5]: slabs of  $S_A$  material are regularly stacked in a helical fashion along an axis parallel to the smectic layers. Adjacent slabs are continuously connected via a grain boundary which consists of a grid of parallel equispaced screw dislocation lines to allow for the helical twist. The authors also proposed the existence of TGBC and TGBC\* [6, 7] in which the smectic slabs are, respectively,  $S_C$  and  $S_C^*$ . After the first discovery of a TGBA phase in 1989 by Goodby *et al.* [8] and the discovery of the TGBC phase in 1992 by Nguyen *et al.* [9], these phases have been found in various chiral systems [10–16]. Structural studies, especially by X-ray [17, 18] have proved the above theoretical structures of TGB phases.

Up to now, the blue phases have been found between the isotropic liquid phase and cholesteric phases of sufficiently short pitches, except in mixtures of cholesteryl myristate and 4,4'-di-*n*-decylazoxybenzene, where a direct  $S_A$ –BPI transition was observed [19]. In the binary diagram of these mixtures, the phase sequence varies from  $S_A$ – $N^*$ –BPI to  $S_A$ –BPI upon increasing the concentration of the achiral compound 4,4'-di-*n*-decylazoxybenzene. Then in 1987, we observed a direct BP– $S_A$  transition in a pure compound on cooling; however, on heating a cholesteric phase existed in a very narrow temperature range [20]. Twist grain boundary smectic phases are often demonstrated to occur between smectic phases and the cholesteric or isotropic liquid phase. In this communication, we report the observation of a new

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phase sequence Cr-S<sub>C</sub>\*-TGBA-BPs-I in a chiral compound: (*R*) or (*S*)-1-methylheptyl 3'-fluoro-4'-(3''-fluoro-4''-octadecyloxybenzoyloxy)tolan-4-carboxylate. It is the first time that BPs have been found to occur above the TGBA phase in the absence of a cholesteric phase.

The chemical structure of the compound is given below:



Apart from the fluorine substitution, this molecule has basically the same chemical structure as those of compounds published previously which exhibit the TGBA phase [13]. The core is benzoyloxytolan (BT) and the chiral centre is linked to the core via an ester group: 1-methylheptyl carboxylate (MHC). We assign a simple name to the compound: FH/FH/HH-18BTMHC in which FH/FH/HH describes the fluorine substitution in the three aromatic rings from left to right and 18 the number of carbons in the aliphatic chain. By using 2-fluoro-4-bromophenol as the starting reagent, we have used the same process of synthesis as that described in [13] (see reaction scheme in [13]).

The final compounds (*R*)- and (*S*)-FH/FH/HH-18BTMHC were purified by chromatography on silica gel with toluene as eluent and were recrystallized from absolute ethanol. Chemical structures of the purified compounds were confirmed by IR (Perkin-Elmer 78 spectrophotometer) and proton NMR (Bruker 270 MHz spectrometer). <sup>1</sup>H NMR (CDCl<sub>3</sub>): 0.86(t, 6H, 2CH<sub>3</sub>), 1.25(m, 38H, 19CH<sub>2</sub>), 1.31(d, 3H, CH<sub>3</sub>-CH), 1.8(m, 4H, OCH-CH<sub>2</sub>, OCH<sub>2</sub>-CH<sub>2</sub>), 4.11(t, 2H, OCH<sub>2</sub>), 5.15(m, 1H, CH-CH<sub>3</sub>), 7.02(t, 1H arom. ortho to OR), 7.2-8.0(m, 9H arom.).

The mesomorphic properties of FH/FH/HH-18BTMHC were studied by thermal optical polarizing microscopy and differential scanning calorimetry (DSC). For the microscopic observations we used a Leitz Ortholux equipped with a Mettler FP5 hot stage and for the calorimetric study a Perkin-Elmer DSC7. We have used the same temperature rate (0.2°C min<sup>-1</sup>) in the microscopic observations and the DSC measurements. The calibration shows that the shift in temperature between the two techniques is around 0.4°C.

When cooling from the isotropic phase, two blue phases have detectable textures in a narrow temperature span (~2.5°C). Upon decreasing the temperature to 71.7°C, we observe first some large, blue-grey, square-shaped single domains of BPII which grow very rapidly from the dark background. Growth can result in an elongated platelet (see figure 1). Then growth of the domains or crystals is limited by mutual contact when

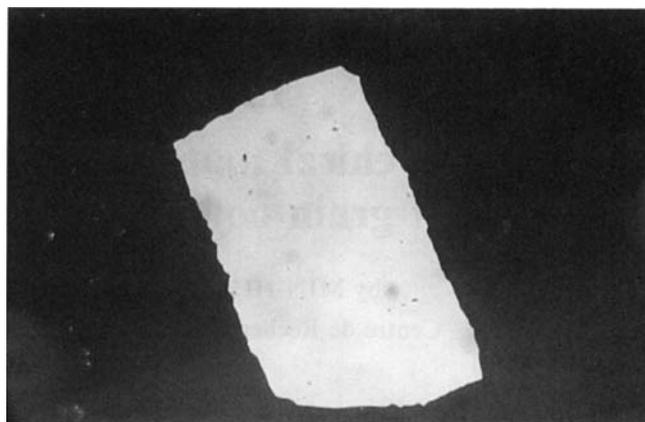


Figure 1. Crystal of BPII for (*R*)-FH/FH/HH-18BTMHC at 71.7°C.

their edges merge. As a result, the typical mosaic texture of BPII is observed (see figure 2). On cooling further down to 71.1°C, a cross-hatching appears in the platelets (see figure 3) and this texture persists only over an

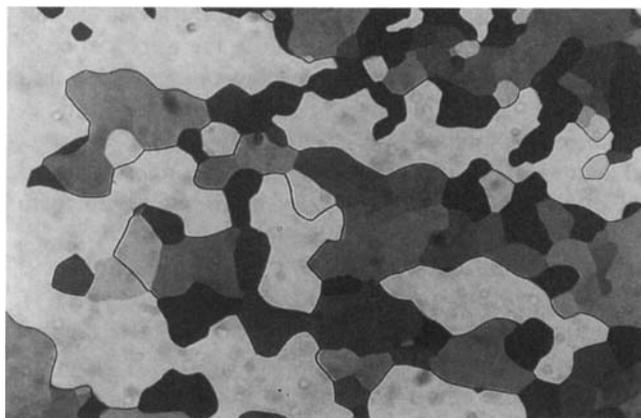


Figure 2. Mosaic texture of BPII for (*R*)-FH/FH/HH-18BTMHC at 71.6°C.

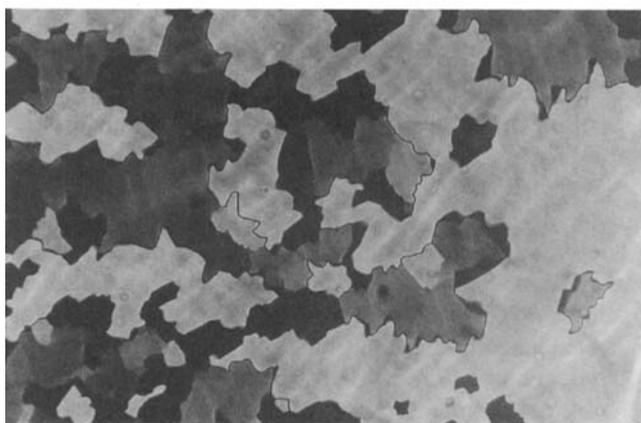


Figure 3. Mosaic texture with cross-hatching of BPII for (*R*)-FH/FH/HH-18BTMHC at 71.1°C.

interval of 0.2°C. We assign this texture to the BPI phase. At 70.9°C, a bright and coloured texture develops rapidly, which gives evidence of either a BP-TGBA transition or a BP-N\* transition. If the sample is heated now, this texture vanishes at 71.3°C and a mosaic texture, with smaller platelets than those shown in figure 2, is restored. No striation is visible. Due to superheating of the TGB (or N\*) phase, we think that BPII is obtained directly. The edges of the platelets change a little in their shape and become more rounded on heating; the reverse phenomenon was observed on cooling. This feature indicates the fluid properties of the BPII crystals. On heating further, BPII melts at 71.8°C to give a seemingly isotropic sample.

At a lower temperature (68°C), the helical smectic C\* phase occurs with a broken fan-shaped texture and large pseudo-homeotropic domains.

The final assignment of the phases, especially of the TGB phase, relies on studies of the racemic mixture and contact preparations.

Figure 4 shows the polarizing microscopic texture of the contact sample of the (R)- and (S)-enantiomers at 71.1°C. On cooling from the isotropic phase, the racemic mixture in the middle of the contact preparation displays directly the S<sub>A</sub> phase with focal-conic, 'noyaux' and homeotropic textures as shown in figure 4 in the temperature range between 73.4°C and 70.3°C. At lower temperatures, the racemic mixture exhibits the S<sub>C</sub> phase with a whitish broken focal-conic and schlieren texture. As usually found, the transition temperatures of the racemic mixture are a little higher than those of the pure enantiomers (see also the table). The observed phase sequence I-S<sub>A</sub>-S<sub>C</sub> with the absence of the nematic phase means that in the pure enantiomers the phase above S<sub>C</sub>\* is TGBA, but not N\*. Moving away from the middle in figure 4, we observe a continuous change of texture, first

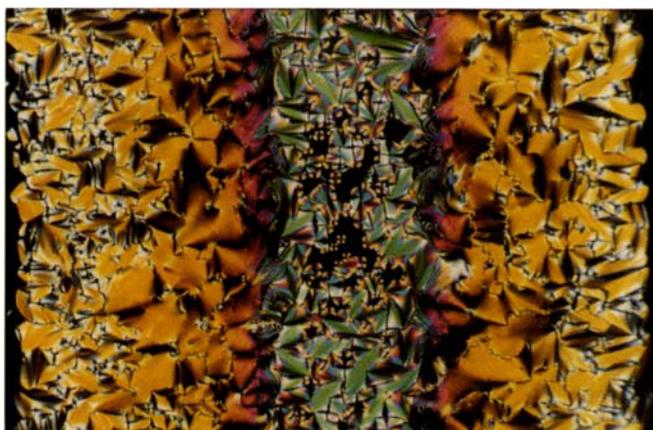


Figure 4. Contact preparation between (R)- and (S)-FH/FH/HH-18BTMHC at 71.1°C (see text).

Transition temperatures<sup>a</sup> (°C) and enthalpies (in brackets) (kJ mol<sup>-1</sup>) of FH/FH/HH-18BTMHC (temperature rate 0.2°C min<sup>-1</sup>).

	Cr	S <sub>C</sub> <sup>*</sup> (or S <sub>C</sub> )	TGBA (or S <sub>A</sub> )	BPI	BPII	BPII (?)	I
(R) Enantiomer	Heating	• 59.2 (47.9)	• 67.9 (0.101)	• 70.8 (0.69)	• 71.4 (0.32)	• 72.4 (2.72)	•
	Cooling	• 44.6	• 67.7 (0.093)	• 70.2 (0.31)	• 71.2 (0.26)	• 72.3 (2.81)	•
Racemic mixture	Heating	• 68.1 (59.3)	• 70.7 (0.045)	• 74.0 (4.34)	—	—	•
	Cooling	• 49.5 (53.6)	• 70.3 (0.084)	• 73.4 (4.26)	—	—	•

<sup>a</sup> Peak temperatures in the DSC thermograms were taken as transition temperatures.

<sup>b</sup> Sum of all blue phases transition enthalpies.

to a filament texture and then to a more cholesteric-like texture. These textures correspond in fact to the TGBA phase as exhibited by different parts of the contact sample with increasing optical purities. At 71.1°C the pure enantiomers remain in the blue phase (beyond the edges of figure 4).

The DSC thermograms on heating and on cooling are given in figure 5. The transition temperatures and enthalpies are listed in the table. On cooling we observe a large  $C_p$  variation 1 followed by three sharp peaks 2, 3 and 4 within the temperature range 74–69°C, while upon heating, only two sharp peaks 2 and 3 are detected previous to the large  $C_p$  feature. All the transitions are very close to each other. The enthalpy of each one is difficult to determine precisely. Nevertheless, we can evaluate each contribution (see figure 5). Values are given in the table together with the sum of the enthalpies. One can note specially that the sum of  $\Delta H_3$  and  $\Delta H_4$  upon cooling is equivalent to  $\Delta H_3$  upon heating. All the observations confirm the microscopic assignment of the BPI and BPII phases. The broad specific heat variation 1 would correspond to the I–BPIII transition. However, to be fully consistent with the microscopic observations in which no fog phase (BPIII) could be detected, one has to consider that the broad  $C_p$  variation 1 is not a true phase transition. It is more likely a supercritical phenomenon in the vicinity of the I–BPIII tricritical point [21]. The evolution of the shape of this peak 1 as a function of the length of the aliphatic chain (to be published in a forthcoming paper) favours this assumption and indicates that a BPIII [22] phase could exist for longer chain lengths.

The racemic system was also studied by DSC. Its transition temperatures and enthalpies are also listed

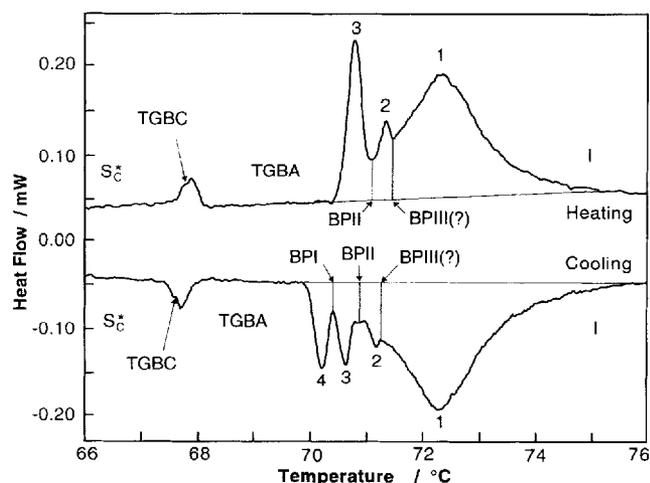


Figure 5. DSC thermograms of (R)-FH/FH/HH-18BTMHC on heating and cooling at 0.2°C min<sup>-1</sup>.

in the table. The phase sequence Cr–S<sub>C</sub>–S<sub>A</sub>–I was confirmed.

One can also note that a shoulder appears at the TGB–S<sub>C</sub><sup>\*</sup> transition on the thermograms (see figure 5). This corresponds to a TGBA–TGBC [9] transition confirmed by pitch measurement by the Grandjean–Cano method, which will be discussed in another paper.

By this communication, we report the first observation of a TGBA–BPs sequence. The designation of BPI, BPII and BPIII(?) of this system is based on microscopic observations and DSC profiles. But there is no structural evidence that they are completely similar to the blue phases commonly observed between the cholesteric and isotropic states. The establishment of an experimental temperature–chirality phase diagram, the measurement of the pitch for the helical phases and studies by X-ray diffraction are actually in progress in order to understand better the phase behaviour of this system. The preliminary X-ray analysis hints that a lamellar structure exists in the BPs of this system and suggests that the local molecular arrangement is more or less dependent on the underlying TGB state.

## References

- [1] STEGEMEYER, H., and BERGMANN, K., 1980, *Liquid Crystals of One- and Two-Dimensional Order*, edited by W. Helfrich and A. Heppke (Berlin: Springer), p. 161.
- [2] STEGEMEYER, H., BLÜMEL, T. H., HILTROP, K., ONUSSEIT, H., and PORSCH, F., 1986, *Liq. Cryst.*, **1**, 3.
- [3] CROOKER, P. P., 1989, *Liq. Cryst.*, **5**, 751.
- [4] DE GENNES, P. G., 1972, *Solid State Commun.*, **10**, 753.
- [5] RENN, S. R., and LUBENSKY, T. C., 1988, *Phys. Rev. A*, **38**, 2132.
- [6] RENN, S. R., and LUBENSKY, T. C., 1991, *Molec. Cryst. liq. Cryst.*, **209**, 349.
- [7] RENN, S. R., 1988, *Phys. Rev. A*, **45**, 953.
- [8] GOODBY, J. W., WAUGH, M. A., STEIN, S. M., CHIN, E., PINDAK, R., and PATEL, J. S., 1989, *Nature*, **337**, 449; 1989, *J. Am. Chem. Soc.*, **111**, 8119.
- [9] NGUYEN, H. T., BOUCHTA, A., NAVAILLES, L., BAROIS, P., ISAERT, N., TWIEG, R. J., MAAROUFI, A., and DESTRADE, C., 1992, *J. Phys. II France*, **2**, 1889.
- [10] LAVRETOVICH, O. D., NASTISHIN, Y. A., KULISHOV, V. I., NARKEVICH, Y. S., TOLOCHCO, A. S., and SHYANOVSKII, S. V., 1990, *Europhys. Lett.*, **13**, 313.
- [11] SLANEY, A. J., and GOODBY, J. W., 1991, *J. Mater. Chem.*, **1**, 5.
- [12] SLANEY, A. J., and GOODBY, J. W., 1991, *Liq. Cryst.*, **9**, 849.
- [13] NGUYEN, H. T., TWIEG, R. J., NABOR, M. F., ISAERT, N., and DESTRADE, C., 1991, *Ferroelectrics*, **121**, 187.
- [14] BOUCHTA, A., NGUYEN H. T., ACHARD, M. F., HARDOUIN, F., DESTRADE, C., TWIEG, R. J., MAAROUFI, A., and ISAERT, N., 1992, *Liq. Cryst.*, **12**, 575.
- [15] NAVAILLES, L., NGUYEN, H. T., BAROIS, P., DESTRADE, C., and ISAERT, N., 1993, *Liq. Cryst.*, **15**, 479.

- [16] NGUYEN, H. T., DESTRADE, C., PARNEIX, J. P., POCHAT, P., ISAERT, N., and GIROLD, C., 1993, *Ferroelectrics*, **147**, 181.
- [17] SRAJER, G., PINDAK, R., WAUGH, M. A., GOODBY, J. W., and PATEL, J. S., 1990, *Phys. Rev. Lett.*, **64**, 1545.
- [18] NAVAILLES, L., BAROIS, P., and NGUYEN, H. T., 1993, *Phys. Rev. Lett.*, **71**, 545.
- [19] ONUSSEIT, H., and STEGEMEYER, H., 1984, *Z. Naturf.(a)*, **39**, 658.
- [20] NGUYEN, H. T., SALLENEUVE, C., BABEAU, A., GALVAN, J. M., and DESTRADE, C., 1987, *Molec. Cryst. liq. Cryst.*, **154**, 147.
- [21] GARLAND, C., private communication.
- [22] THOEN, J., 1988, *Phys. Rev. A*, **37**, 1754.