Columnar and smectic ordering in a TGBA phase

A. Ribeiro, A. Dreyer, L. Oswald, J. Nicoud, A. Soldera, D. Guillon, Y. Galerne

Classification
Physics Abstracts
61.30 — 61.30E

Short Communication

Columnar and smectic ordering in a TGB_A phase

A. C. Ribeiro [1,2], A. Dreyer [1], L. Oswald [1], J. F. Nicoud [1], A. Soldera [1], D. Guillon [1] and Y. Galerne [1]

[1] Institut de Physique et Chimie des Matériaux de Strasbourg, Groupe des Matériaux Organiques, ICS, 6 rue Boussingault, 67083 Strasbourg Cedex, France

[2] Centro de Física da Matéria Condensada, Av. Gamma Pinto, 1699 Lisboa Codex, Portugal

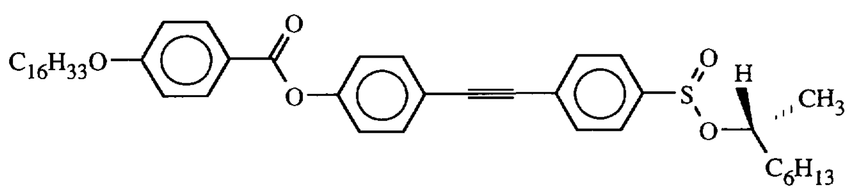
(Received 14 October 1993, revised 21 January 1994, accepted 27 January 1994)

Abstract. — Optical textures characteristic of cholesteric and columnar structures were simultaneously detected for the first time in the same mesophase of a liquid crystal. However, X-ray diffraction measurements show that the mesophase under consideration is smectic A in nature. We show here that the compound presents, indeed, a twist grain boundary (TGB) phase within a large temperature range, and we propose an explanation of the supramolecular organization in this phase.

1. Introduction.

We reported recently the synthesis and the characterization of new ferroelectric liquid crystalline compounds having a tolane rigid core and an optically active sulphinate group [1]. Some of these compounds were shown to exhibit textures with horizontal cholesteric planes (see Fig. 1 in Ref. [1]), and also optical textures [2] very similar to those usually obtained with columnar mesophases [3]. The presence of one or the other textures, or both simultaneously was quite puzzling and led us to analyse these compounds in more detail.

In this paper, we present an optical and structural investigation of one of the following diastereomers:



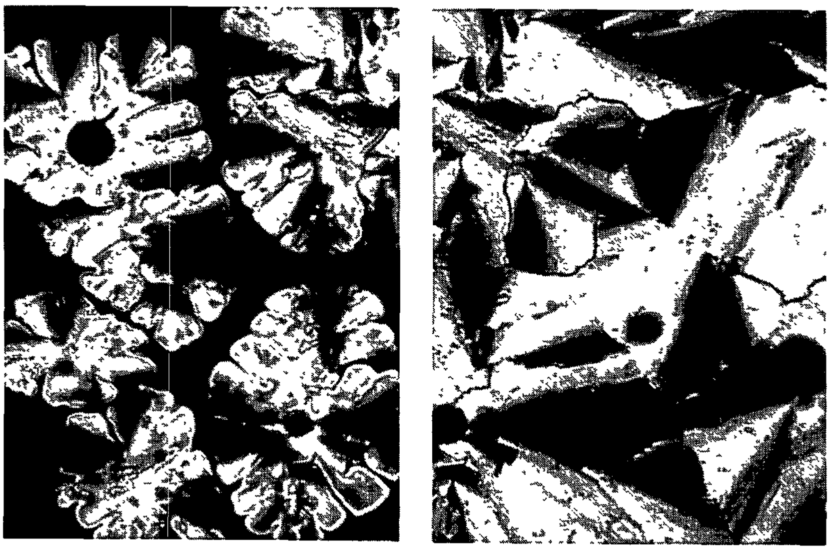
We show, that it presents a twist gain boundary (TGB) phase within a large temperature range and we propose a model of molecular organization in this phase.

2. Experimental results.

The compound under investigation incorporates two chiral centres in its molecule. If the chiral carbon is known to be in the R configuration, the sulphur chiral centre may be either in the S or in the R configuration. The two diastereomers, (R, R) and (S, R) have been separated by high pressure liquid chromatography. Only one of these diastereomers was available in sufficient quantity, and is considered in the present paper. Unfortunately, the actual configuration of its sulphur atom has not yet been determined. However, we can notice that preliminary optical observations obtained with the other diastereomer seem to show that it exhibits properties similar to those observed with the compound studied here.

Optical observations and differential scanning calorimetry (DSC) show only two phase transitions, one between the crystalline (K) and the mesophase (M), and the other between the mesophase (M) and the isotropic phase (I). The thermal behaviour is thus the following:

$$K \xrightarrow[66\ \mathrm{J/g}]{72\ ^\circ\mathrm{C}} M \xleftrightarrow[5.5\ \mathrm{J/g}]{98\ ^\circ\mathrm{C}} I$$



a) b)

Fig. 1. — Optical textures showing the growing of developable units on decreasing the temperature from the isotropic state a) $T = 96.4$ °C; b) $T = 96$ °C.

Several types of texture can be obtained when cooling the sample from the isotropic phase. One is very indicative of a columnar structure as shown in figure 1, with developable units growing slowly from the isotropic liquid; it is observed when the preparation is cooled slowly. Another texture observed is typical of a twisted phase, as shown in figure 2, with the helical axis perpendicular to the preparation glass plates; it is very easy to observe it when a slight pressure is applied to the preparation (which probably results in shear flows). The last texture can appear either as platelets of homogeneous colour, with the eventual presence of fibrilla. These

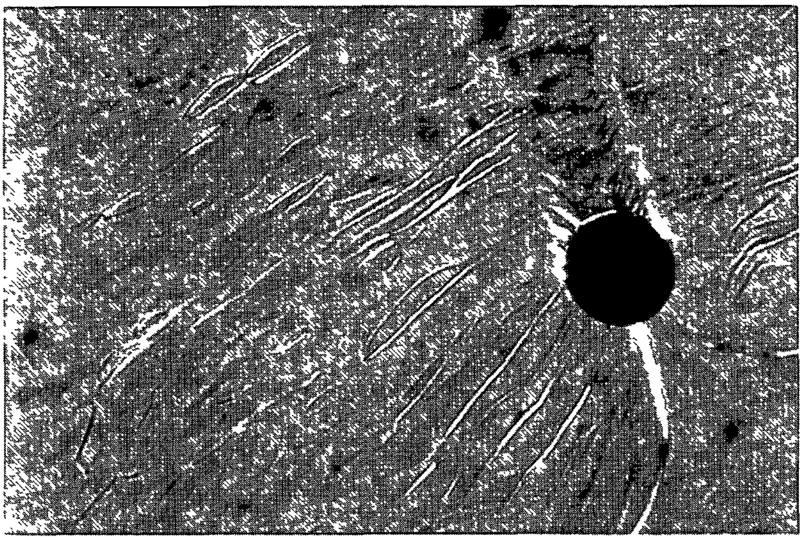
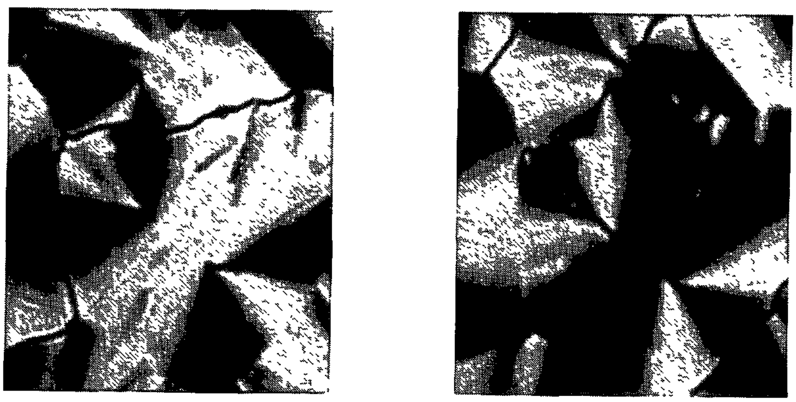


Fig. 2. — Optical texture observed at $T = 96$ °C after a shear force has been applied to the preparation shown in figure 1b. Note the presence of fibrilla reminiscent of the TGB phases.

two characteristic textures can coexist in the same preparation and remain quite stable for a long time (over several hours), suggesting that they belong to the same phase. Moreover, they remain the same (except for the colours) on the whole stability domain of the mesophase from 96 °C down to 72 °C, and even below when supercooling effects occur before recrystallization.



a) b)

Fig. 3. — Optical textures observed with crossed nicols at $T = 95.4$ °C with the nicols in a 0° (a) and 45° positions (b).

Further evidence of a columnar ordering is given in figure 3 which shows two pictures of the columnar texture taken with crossed nicols. The pictures were obtained in the same observation region but with the polarizers both rotated by 45° in figure 3b. They clearly indicate the directions of the columns between the two "eyes" of the developable domain.

Observations made with the optical microscope in reflective mode after applying a small pressure, as described above, clearly show a progressive change of colour as a function of decreasing temperature, from blue at 96 °C to red at 76 °C. This is an additional information implying the existence of a helical structure, the pitch of which varies approximately from 0.30 to 0.46 μm (see Fig. 4). The pitch is evaluated by comparison of the reflected light colours with a calibrated colour table, and by taking into account the mean refraction index of the liquid crystal (about 1.5).

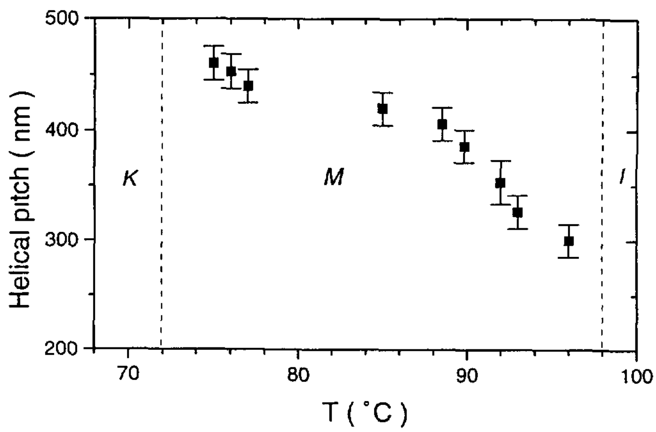


Fig. 4. — Helical pitch as a function of temperature (as deduced from optical observations in reflective mode).

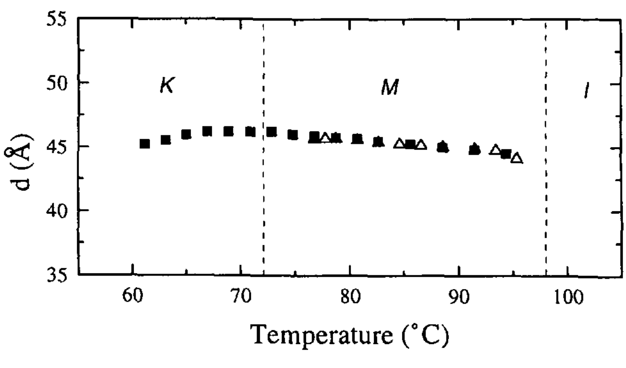


Fig. 5. — Layer spacing as a function of temperature (triangles and black squares correspond to increasing and decreasing temperature respectively).

X-Ray diffraction patterns, registered with a Guinier camera, are typical of a disordered smectic phase for the whole stability domain of the mesophase (Bragg sharp reflections in the small angle region and a diffuse signal in the wide angle region). The corresponding layer spacing, d, does not vary as a function of temperature (Fig. 5) and is found to be around 45.3 Å. This value is slightly smaller than the molecular length (48-49 Å) calculated for the molecule in its most extended conformation by molecular modelling (Sybyl software from Tripos); this difference can be attributed to the desorganized state of the aliphatic chains. These characteristics are typical of a smectic A phase.

The above experimental observations, cholesteric optical textures and smectic A ordering, are thus consistent with a twist grain boundary (TGB) phase of A type, as theoretically predicted [4] and recently observed in other compounds [5]. It is important to remark that the TGB$_A$ phase of the compound under consideration is stable over a temperature range larger than 20 °C. However, it is necessary to understand the existence of columnar textures in a system which is also lamellar.

3. Discussion and conclusion.

The apparent contradiction between the optical columnar textures and the lamellar nature of the phase can be understood using the model represented in figure 6. Two adjacent smectic

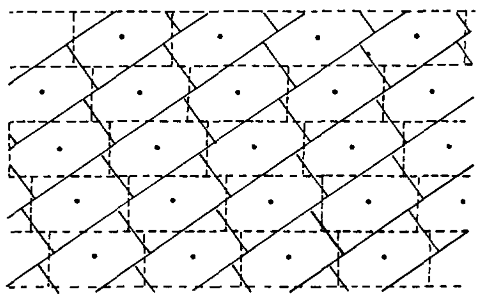
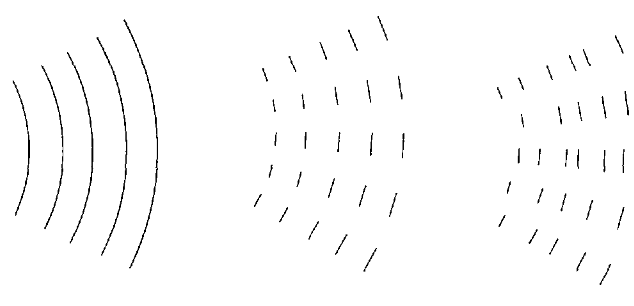


Fig. 6. — Grain boundary between two adjacent smectic slabs, respectively sketched as full and dashed parallel lines, according to whether they are before or behind the grain boundary. An array of equidistant screw dislocations carves out the smectic layers into ribbons or columns perpendicular to the figure. Their local axis is marked by a dot.



a) b) c)

Fig. 7. — Schematic side-views of columnar systems in the cases of: (a) Continuous columns; (b) microcolumns with constant density, located in the grain boundaries. In this case, which corresponds to our model for the TGB$_A$ phase, it is possible to track the columns through the whole sample. It results in the formation of developable domains as in case (a) [7]; (c) microcolumns with variable density inside their transverse plane. This nematic-like structure cannot build up developable domains.

slabs are separated by a grain boundary, the angle α between the two slabs being about 20° as recently observed experimentally [6]. The important feature exhibited by this representation is the presence of common areas between two adjacent slabs, which mark the places where the smectic layers go continuously from one slab to the other, forming kinds of twisted ribbons of molecules. It has to be pointed out that two-dimensional columnar ordering exists only in the grain boundaries. Within the slabs, the columns are interrupted and merge back into smectic layers. Nevertheless, their lateral dimensions d and $d/\sin\alpha$ being fixed, they have a constant density and it is therefore possible to track them from a grain boundary to the next one (Fig. 7b); this ensures the formation of developable domains as in the classical columnar structures made of continuous columns (Fig. 7a). Let us notice that this new structure with broken columns allows easy gliding along planes parallel to the grain boundaries, i.e. normal to the columns. This mechanical property which could seem paradoxical [7], explains that the columns orient normally to the plates when applying a shear stress onto the sample.

In conclusion, we have reported here the mesomorphic behaviour of a TGB_A phase, the stability domain of which is larger than 20 °C, and we have proposed a structural model which accounts for the coexistence of columnar and cholesteric optical textures.

Acknowledgements.

A. C. Ribeiro wishes to thank Dr. Helena Godinho for the use of the reflection microscope of Materials Department of UNL (Lisbon) and the French MRT for a fellowship.

References

[1] Soldera A., Nicoud J. F., Galerne Y., Skoulios A. and Guillon D., *Liq. Cryst.* **12** (1992) 347.

[2] Soldera A., Thesis ULP, University of Strasbourg (1992).

[3] Destrade C., Gasparoux H., Foucher P., Nguyen H. T., Malthete J. and Jacques J., *J. Chim. Phys.* **80** (1993) 137;
Oswald P. and Kléman M., *J. Phys. France* **42** (1981) 1461.

[4] de Gennes P. G., *Solid State Commun.* **10** (1972) 753;
Renn S. R. and Lubensky T. C., *Phys. Rev. A* **38** (1988) 2132.

[5] Goodby J. W., Waugh M. A., Stein S. M., Chin F., Pindak R. and Patel J. S., *Nature* **337** (1989) 449; *J. A. Chem. Soc.* **111** (1989) 8119;
Nguyen H. T., Twieg R. J., Nabor M. F., Isaert N. and Destrade C., *Ferroelectrics* **121** (1991) 187;
Nguyen H. T., Bouchta A., Navailles L., Barois P., Isaert N., Twieg R. J., Maarouji A. and Destrade C., *J. Phys. II France* **2** (1992) 1889.

[6] Navailles L., Barois P. and Nguyen H. T., *Phys. Rev. Lett.* **71** (1993) 545.

[7] The existence of developable domains is equivalent to the local property div $\mathbf{t} = 0$ for the field of the director $\mathbf{t}$ tangent to the columns. This field naturally accepts local continuous translations, and not only the discontinuous ones corresponding to distances between the columns. The existence of gliding planes across the broken columns is therefore consistent with the formation of developable domains.