Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713926090

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Online publication date: 11 November 2010

To cite this Article Folcia, C. L. , Ortega, J. and Etxebarria, J.(2003) 'On the interpretation of the racemic states of the B 2 phase of banana-shaped mesogens', Liquid Crystals, 30: 10, 1189 — 1191
To link to this Article: DOI: 10.1080/02678290310001599206
URL: http://dx.doi.org/10.1080/02678290310001599206

LIQUID CRYSTALS, VOL. 30, NO. 10, OCTOBER, 2003, 1189–1191

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On the interpretation of the racemic states of the B_2 phase of banana-shaped mesogens

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(*Received 25 February 2003; accepted 24 May 2003*)

We show that the racemic states of the B_2 phase of liquid crystals composed of banana-shaped molecules do not satisfy the Curie principle. Thus it is argued that these states cannot exist in bulk samples and the homochiral states constitute the only stable microscopic structures. A reinterpretation of the racemic states with the same macroscopic optical behaviour is proposed in terms of mixtures of the homochiral structures.

The B_2 phase is the most studied of the mesophases exhibited by banana-shaped mesogens. According to the Boulder model for this phase [1], bulk samples can contain both chiral and racemic states. In the chiral state the chirality of the neighbouring smectic layers is the same, while in the racemic case the chirality alternates in between consecutive layers. The different structures in the absence and in the presence of a strong electric field have become widely accepted in the field of banana-shaped mesogens, and are denoted by SmC_iP_j, where $i=A$ (anticlinic) or S (synclinic), and $j=A$ (antiferroelectric) or F (ferroelectric). The model has had a remarkable success in explaining the electro-optic behaviour of the B_2 phase [1–4].

However, despite all these successes, we have found some serious theoretical difficulties with the racemic states. We will show here that the very existence of these states is untenable, at least if they are interpreted in the usual way. The purpose of this note is to present these difficulties and propose an alternative interpretation for the molecular structures of the racemic states.

The difficulties have their origin in the so-called Curie principle. Some other problems derived from thermodynamical considerations have also been pointed out recently [5, 6] but will not be treated here. We will restrict ourselves to present some simple arguments which lead to inconsistencies and are based on pure symmetry grounds. The Curie principle is one of the most celebrated principles in condensed matter physics and determines the change in a crystal symmetry when it is under any external influence [7]. It can be stated as: *the symmetry group of a medium subjected to an applied field is equal to the intersection between the point group of the medium without the field and the point group of the field without the medium*. The principle has a broad scope of application and the 'field' can be a rather general quantity, such as a stress field, a magnetic field, or an electric field, each with its own symmetry group (see figure 1). Here we want to apply this principle to the B_2 structures under an electric field, whose point group is $C_{\infty v}$.

Figure 2 shows the four SmC_iP_j states. SmC_SP_A and SmC_AP_F are racemic; SmC_AP_A and SmC_SP_F homochiral. Let us first consider the racemic state without field (SmC_SP_A). Its point group is C_{2h}, i.e. there is a two-fold axis parallel to the dipole moments and a mirror plane perpendicular to the axis which transforms one smectic layer into the adjacent. Now let us take the racemic structure with an applied field (SmC_AP_F). Its point group is C_{2v}, i.e. the two-fold axis is maintained

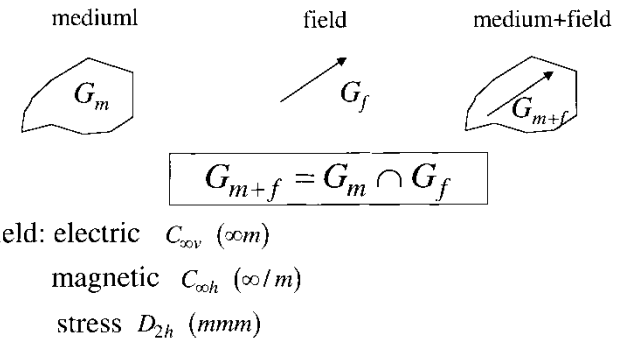

Figure 1. Schematic illustration of the Curie principle. G_m is the point group of the medium in the absence of field, G_f the point group of the field and G_{m+f} that of the medium subjected to the field. Several point groups of some important fields are also indicated.

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Liquid Crystals ISSN 0267-8292 print/ISSN 1366-5855 online © 2003 Taylor & Francis Ltd
http://www.tandf.co.uk/journals
DOI: 10.1080/0267829031000159206

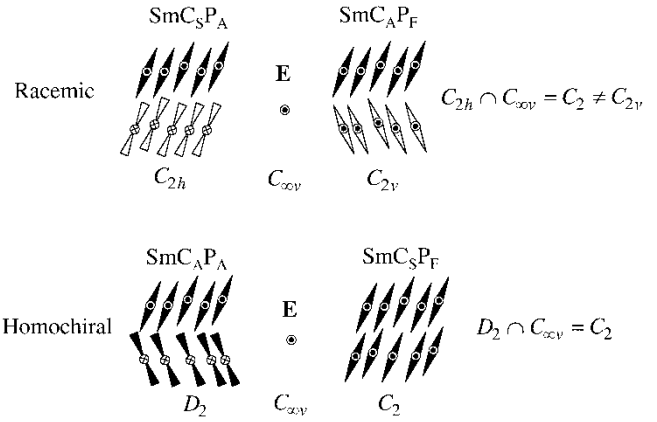

Figure 2. Structures of the B_2 phase in the antiferroelectric states and in the ferroelectric states under the influence of the electric field **E**. The point group of each structure is indicated together with the symmetry predicted by the Curie principle when the field is applied.

and two perpendicular planes containing the axis appear, which relate one layer and the next one. However, the intersection of C_{2h} and $C_{\infty v}$ is C_2, which does not coincide with C_{2v}, as it should according to the Curie principle.

This problem does not arise with the homochiral states. The point group of the structure without field (SmC_AP_A) is D_2, i.e. we have three two-fold axes perpendicular to each other, one of them parallel to the dipole moments. On applying an electric field we obtain the SmC_SP_F structure, which has only one two-fold axis, C_2. In this case the intersection of D_2 and $C_{\infty v}$ is C_2, so the Curie principle is satisfied.

The problem can also be appreciated starting from the racemic structure with an applied field (SmC_AP_F) and analysing the behaviour of the material when the field is removed. According to the Curie principle all the symmetry elements must be preserved upon field removal. Now, the existence of the mirror planes in the group C_{2v} means that the molecules in successive layers must behave in exactly the same way, i.e. we cannot expect that only those which are tilted in a given direction will switch when the field is turned off. From this point of view also, the SmC_AP_F structure can only remain ferroelectric in the absence of field. All the molecules should either switch or not, and the antiferroelectric synclinic structure can never be achieved.

We are led to conclude that the racemic states contradict the Curie principle and their existence in a bulk sample should be rejected or, at least, reinterpreted. It should be clarified that this argument refers exclusively to the bulk structure of the B_2 phase and cannot be applied in principle to other 'non bulk' systems such as freely suspended films. In the case of

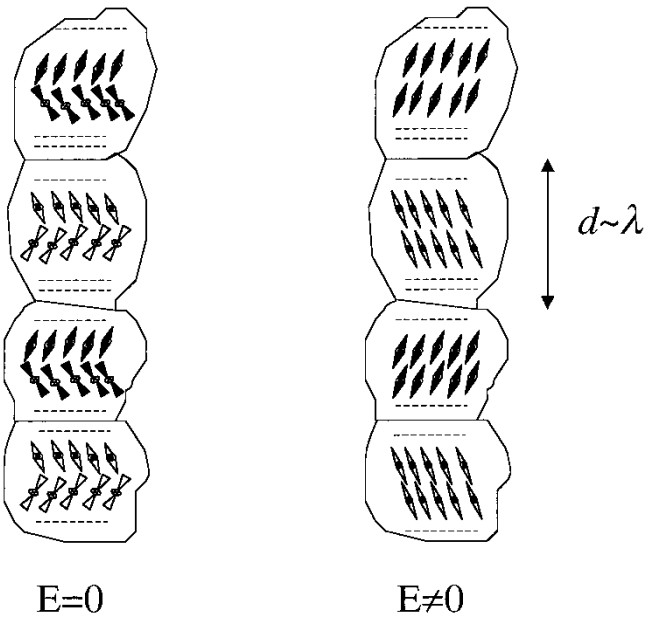

Figure 3. Structure proposed for the racemic state of the B_2 phase. The size of the domains is assumed to be mesoscopic.

films (which have a small number of layers) surface effects are important and the mere existence of a point group for the structure can be questioned. However, the bulk structure of the phase can only be homochiral. One conservative way of keeping a racemic-like state is to reinterpret it by considering it as a statistical 50–50 mixture of mesoscopic domains of homochiral states of opposite handedness, which are the only truly existing structures with thermodynamic stability (see figure 3). By mesoscopic we mean a region of size of the order of the optical wavelength (several tens of layers). In this way all macroscopic optical properties (both linear and nonlinear [8]) appear averaged in this kind of mixture. In particular, it can be seen that the electro-optic behaviour is identical to that found for the racemic states originally proposed.

This work was supported by the CICYT of Spain (Project No. MAT2000-1293-C02) and the University of the Basque Country (Project No. 9/UPV 00060.310-13562/2001).

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