Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl16

A Chiral Smectic B Phase

D. Coates [a] & G. W. Gray [a]
[a] Department of Chemistry, The University, Hull, HU6 7RX, England
Version of record first published: 21 Mar 2007.

To cite this article: D. Coates & G. W. Gray (1976): A Chiral Smectic B Phase, Molecular Crystals and Liquid Crystals, 34:1, 1-5

To link to this article: http://dx.doi.org/10.1080/15421407608083213

Mol. Cryst. Liq. Cryst., Vol. 34 (Letters), pp. 1–5

Printed in the United States of America

A CHIRAL SMECTIC B PHASE

D. COATES AND G.W. GRAY
Department of Chemistry, The University, Hull, HU6 7RX, England

(Submitted for publication April 18, 1976)

Abstract Terephthalylidene-bis-((+)-4'-methylhexyloxy)aniline, a chiral analogue of TBBA has been prepared. The compound forms a chiral smectic C phase and, at a lower temperature, a tilted smectic B phase. Evidence is presented which shows that the S_B phase, consisting of ordered layers, is also chiral.

Introduction The biaxial nature of a smectic C (S_C) liquid crystal is due to the tilt of the long axes of the molecules with respect to the planes of the smectic layers. Theoretical considerations by Saupe[1] predicted that if the molecules were optically active, the tilt directions would spiral about a direction normal to the layer planes on passing through a series of layers. This prediction was verified experimentally in 1971 by Helfrich and Oh[2] for an optically active compound that gave a S_C phase. A thin film of this chiral S_C phase, pressed out to form the equivalent of the non-chiral S_C schlieren texture, i.e., with the layers parallel to the glass surfaces, showed optical activity and rotatory dispersion. For convenience in this communication, we refer to this texture as a planar S_C texture.

Also in 1971, Levelut and Lambert[3] showed that the smectic B (S_B) phase which occurs on cooling the S_C phase of the non-chiral compound, terephthalylidene-bis-4-n-butylaniline (TBBA), is tilted and biaxial. Indeed, it is now accepted that any S_B phase occurring on cooling a S_C phase will be tilted.

We reasoned therefore that if an optically active compound showed a tilted S_B phase, then that phase might also involve a helical distribution of the tilt directions and be optically active in the same manner as a chiral S_C phase, except that the molecules within each layer would be hexagonally packed. However, the interlayer forces operating in the more viscous S_B phase are probably more effective in giving structural correlations over a number of layers than those in the higher entropy S_C phase. If the forces causing these correlations tend to constrain the system to adopt a uniform tilt direction, then the chiral forces may not be strong enough to overcome them and allow a spiral twist of the tilt directions to propagate through a stack of layers. As these possibilities had not hitherto been investigated, we prepared an optically active analogue of TBBA which gave a tilted S_B phase on cooling its S_C phase. The optical properties of the S_C and S_B phases are now described.

Results and Discussion Terephthalylidene-bis-4-((+)-4'-methylhexyloxy)aniline (TBMHA) has the constants, C-S_B, 144°; S_B-S_C, 160.4°; S_C-Ch, 207.6°; Ch-I, 224.5°. The cholesteric phase transforms into and forms from the isotropic liquid via elongated, banana-shaped particles[4] similar to bâtonnets. The cholesteric texture (plane or 'focal-conic') changes on cooling into a S_C texture usually consisting of both coloured, planar areas and focal-conic areas. The focal-conic regions are crossed by pronounced black lines which pass continuously from one fan-like area to another. These periodic lines are very different in appearance from the concentric arcs (or bands) of a smectic E fan texture[5]. The spacing of these lines is presumably related to the pitch or half-pitch of the helical structure. Moreover, the observed spacing will be a function of the orientation of a particular focal-conic domain relative to the glass surface on which the microscope is focused. If the spacing is to give a measure of the actual pitch-length, it is therefore necessary to range over the preparation and measure the maximum line spacing. At the high temperature at which this S_C phase exists, an accurate measurement of the separation of these lines is quite difficult, but we estimate the pitch length to be about 4.6μ.

The coloured, planar S_C areas do not become extinct between crossed polarisers on rotation of the sample, indicating that the optic axis is parallel to the direction of viewing. However, these areas do give extinction in monochromatic light when the analyser is rotated, showing that the phase is indeed optically active. When the chiral S_C

phase is agitated mechanically, the coloured, planar texture is adopted uniformly over the field of view, but does not exhibit cholesteric-like peacock colours because the pitch is too long. Helfrich and Oh[2] did not quote a pitch length for their S_C phase. However, using their optical rotations and the de Vries' equation, and assuming a plausible value for the birefringence of a layer for normally incident light, Dr. N.H. Hartshorne has calculated the pitch of their chiral S_C phase to be about 3.2μ. Again this pitch is too great to give selective reflection of visible light.

Despite the uniformity of the planar S_C texture of TBMHA, an optic sign could not be obtained for the phase. Indeed, when phase diagrams for mixtures of TBMHA (Ch-S_C-S_B) with either TBBA (N-S_A-S_C-S_B-S_G)[6] or with n-butyl 4-(4'-methoxybenzylideneamino)cinnamate (N-S_A-S_B) were constructed, the S_A-S_C transitions were characterised by a change from a homeotropic S_A texture giving a positive, uniaxial interference figure to a coloured, planar S_C texture showing no interference figure. These phase diagrams showed that TBMHA exhibits cholesteric, S_C and S_B phases, and also that the compound has strong latent S_A tendencies.

When the chiral S_C phase of TBMHA is cooled to give the S_B phase, a mosaic texture results, irrespective of the S_C texture. The mosaic areas are small compared with those given by non-chiral, tilted S_B phases. In the mosaic texture of the tilted S_B phase of TBBA, the molecules lie in flat layers whose planes are inclined at various angles to the glass surfaces. However, none of the mosaic areas of TBBA appear to involve an arrangement of the molecules <u>orthogonal</u> to the glass, i.e., no areas are homeotropic. When the sample is rotated, the mosaic areas simply pass through extinction positions every 90°. However, with the mosaic texture of the S_B phase of TBMHA, although a few areas simply change colour a little, most areas do show extinction every 90°. It seems then that none of the mosaic areas consist of layers <u>strictly</u> parallel to the glass, and because of this the optical rotatory power could not be examined. The mosaic texture of the S_B phase is very viscous, and pressure and agitation fail to change it to a texture in which the layers lie parallel to the glass surfaces. Even with different treatments and cleaning procedures for the glass surfaces, the mosaic S_B texture still formed, and the phase has not been seen in any other texture.

However, when miscibility experiments were carried out on TBMHA, it was found that for concentrations of TBBA >10%, the S_B textures obtained from the planar, chiral S_C textures of the mixtures were also planar and exhibited the same properties as those of the planar, chiral S_C phase, i.e., optical activity was shown. Also, when n-butyl 4-(4'-methoxybenzylideneamino)cinnamate was the diluent, then in the region of the phase diagram where direct S_A-S_B changes occurred (<70% TBMHA), a change from a black homeotropic S_A texture (optically positive uniaxial) to a coloured, optically active, planar S_B texture occurred.

Thus, even though pure TBMHA does not exhibit a S_B texture in which optical activity can be observed, mixtures of this S_B phase with either orthogonal or tilted S_B phases produce planar textures which show optical activity. Therefore, even for these diluted, more weakly optically active, tilted S_B phases, the chiral centres in the molecules of a given layer can influence the tilt directions of the molecules in neighbouring layers, producing a helical distribution of the tilt directions which propagates through the bulk phase of structured S_B layers. A chiral, tilted S_B phase is therefore capable of existence.

Acknowledgements The authors thank the Ministry of Defence for a research grant. We also acknowledge the valued collaboration with Dr. N.H. Hartshorne, and thank members of the Materials and Components Laboratory, S.T.L. Limited, Harlow for their interest in the work.

References

1. A. Saupe, Mol. Cryst. Liquid Cryst., 7, 59 (1969).

2. W. Helfrich and Chan S. Oh, Mol. Cryst. Liquid Cryst., 14, 289 (1971).

3. A.M. Levelut and M. Lambert, C. r. hebd, Séanc. Acad. Sci., (Paris) 272, 1018 (1971).

4. D. Coates and G.W. Gray, Phys. Lett., 45A, No. 2, 115 (1973); 51A, No. 6, 335 (1975).

5. D. Coates, K.J. Harrison and G.W. Gray, Mol. Cryst. Liquid Cryst., 22, 99 (1973).

6. L. Richter, D. Demus and H. Sackmann, J. Phys. (Paris), in the press.