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

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Version of record first published: 20 Apr 2011.

Mol. Cryst. Liq. Cryst. Vol. 49 (Letters), pp. 165-168

Printed in the United States of America

THE "UNIAXIAL" SMECTIC E PHASE

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(Submitted for publication 29th November, 1978)

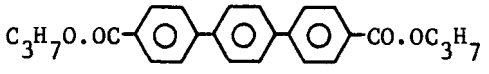
Abstract For many years there have been only two materials reported which exhibit uniaxial smectic E phases; all smectic E phases exhibited by other materials have been shown to be biaxial. Moreover, a number of these biaxial S_E phases are known to have an orthogonal arrangement of the molecules within the layers, proving that the biaxiality is not due to tilting of the molecules within the layers. Therefore, one of the two related materials claimed to give a uniaxial S_E phase was re-examined and the S_E phase has been shown to be biaxial.

Introduction One of the earliest reports of a smectic E phase was made by Sackmann and Demus[1] who discussed the smectic E properties of di-ethyl and di-n-propyl *p*-terphenyl-4,4"-dicarboxylates. In another report,[2] Diele, Brand, and Sackmann described this phase as being uniaxially positive and exhibiting mosaic and pseudoisotropic textures. Moreover, the S_E phases of these materials were shown[3] to be miscible with biaxial S_E phases exhibited by other materials.[4]

In an attempt to clarify this situation which implies that uniaxial and biaxial modifications of a phase can share a common nomenclature (in this case S_E), we prepared a fresh sample of di-n-propyl *p*-terphenyl-4,4"-dicarboxylate by the standard method of Neubert and Carlino.[5]

Results and Discussion The transition temperatures for di-n-propyl *p*-terphenyl-4,4"-dicarboxylate were determined by optical microscopy.

The structure of the ester and the transition temperatures are given below:



$$C \xrightarrow[122^{o}]{} S_E \xrightarrow[142^{o}]{} S_A \xrightarrow[242^{o}]{} I$$

(lit: 122^{o} 137.1^{o} 239.2^{o})

When the sample was subjected to detailed microscopic studies a number of observations which conflicted with earlier reports were made.

On cooling the isotropic liquid of the di-n-propyl ester, we obtained a smectic A phase which exhibited both focal-conic fan and homeotropic textures (Plate 1). On further cooling, the fans became crossed by a number of arcs which persisted throughout the temperature range of the S_E phase. At the same temperature, the homeotropic S_A areas became birefringent and adopted a platelet texture (these textures are shown together in Plate 2). Both of these textures are typical of the biaxial S_E phase. Of course, if the S_E phase of this material were really uniaxial, it should exhibit a homeotropic texture. However, this does not appear to be the case, and even when the S_A phase was obtained in a *totally* homeotropic condition, a platelet texture was again formed at the S_A-S_E transition (Plate 3). Moreover, in this textural condition, the phase was shown to be positive biaxial by conoscopic observation.

Consideration was however given to the possibility that the biaxiality of the phase may be due to uniaxial layers themselves tilting with respect to the surfaces and so destroying the homeotropic alignment of the preceding S_A phase. This was tested by allowing the homeotropic S_A phase to cool and give the platelet texture of the S_E phase. This texture was then examined on a tilting microscope stage. It was found that no matter how much the stage was tilted or in which direction, the S_E phase always remained biaxial and did not give a homeotropic condition. This indicates that the layers do not tilt at the S_A to S_E transition and therefore that the phase is in fact positive biaxial.

PLATE 1 The homeotropic and fan textures of the S_A phase (x200)

PLATE 2 The platelet and arced fan textures of the S_E phase (x200)

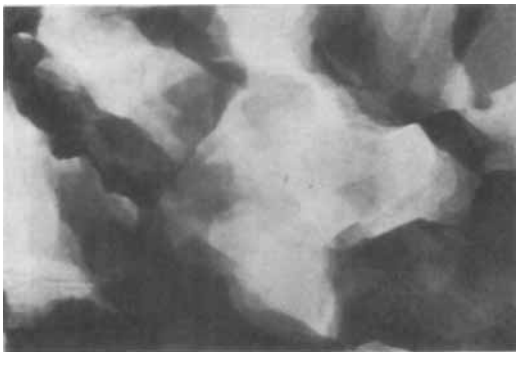


PLATE 3 The platelet texture of the S_E phase (x200)

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Thus, the di-n-propyl ester has been shown to exhibit a positive biaxial S_E phase, and as would now be expected, the phase was miscible with the biaxial S_E phase of n-decyl 4-(4'-phenylbenzylideneamino)cinnamate (S_A, S_B and S_E phases). Therefore, we have to conclude that a uniaxial S_E phase does not exist, and that all known S_E phases are biaxial.

Experimental All the microscopic observations and measurements of transition temperatures made using a Nikon L-Ke polarising microscopic in conjunction with a Mettler FP52 hot stage and temperature control unit.

The purity of the di-n-propyl ester was checked by tlc and its structure was confirmed by mass spectrometry and infra-red analysis.

Acknowledgement The authors wish to thank Barbara Needham of STL Laboratories, Harlow, England, for her microscopic observations made using a tilting stage, and the Science Research Council, London for a research grant.

References

1 H Sackmann and D Demus, *Mol Cryst Liq Cryst*, 21, 239 (1973)

2 S Diele, P Brand, and H Sackmann, *Mol Cryst Liq Cryst*, 17, 163 (1972)

3 A Biering, D Demus, GW Gray, and H Sackmann, *Mol Cryst Liq Cryst*, 28, 275 (1973)

4 GW Gray and KJ Harrison, unpublished results

5 ME Neubert and LT Carlino, *Mol Cryst Liq Cryst*, 42, 353 (1977)