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Schlieren textures in free-standing nematic films: evidence of biaxiality

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Conoscopic studies reveal that the nematic phase of 4,4″-(*p*-terphenyl)-bis[2,3,4-tri(dodecyloxy)benzal]imine is biaxial, the biaxial angle increasing with decreasing temperature. The schlieren textures exhibited by the nematic phase have been examined. Films sandwiched between glass plates, as well as free-standing films, exhibit a nematic schlieren texture consisting entirely of $|s|=\frac{1}{2}$ or 2-brush disclinations, confirming an earlier suggestion that the absence of 4-brush disclinations is evidence of biaxiality.

1. Introduction

Based on optical studies [1, 2] we suggested in a previous communication [2] that the absence of disclinations of unit strength, $|s|=1$, in the nematic schlieren texture is evidence of biaxiality in the phase. We were pleased to find that our conclusion is, in fact, corroborated by the initial observations of Yu and Saupe [3] on a ternary lyotropic system consisting of potassium laurate + 1-decanol + D_2O, in which they established for the first time the existence of the biaxial nematic (N_b) phase. They have remarked that the N_b phase shows a nematic schlieren texture, 'but integer-numbered-singularities which are common in many uniaxial nematics were not observed by us'.

We proposed the following explanation for the absence of $|s|=1$ in the N_b phase: in the uniaxial nematic (N_u) the singularity at the origin of $|s|=1$ as given by the planar model can be avoided by a non-singular continuous structure of much lower energy by allowing the director to escape in the third dimension (figure 1) [4]. On the other hand, in the case of the orthorhombic nematic, there are three mutually perpendicular director vectors, so that if one of the directors is allowed to escape, it automatically gives rise to another planar configuration (figure 2). Hence the singularity at the origin continues to exist and the escape mechanism is unable to remove it [5]. The $|s|=1$ defect is not therefore favoured in the N_b phase.

The observations described in our previous papers [1, 2], were made on thin films sandwiched between glass plates. The question arises as to whether the biaxiality is induced by the glass surfaces. To settle this point we have now examined schlieren textures in free-standing films.

2. Conoscopic observations

The present experiments were all conducted on 4,4″-(*p*-terphenyl)-bis[2,3,4-tri(dodecyloxy)benzal]imine (**I**, figure 3).† The compound was prepared as described in

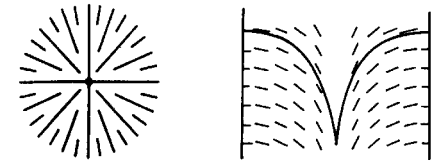

Figure 1. (i) Director field around a disclination of unit strength $s=1$, $c=0$ for a uniaxial nematic as given by the planar model. (ii) Director escape at the centre of the disclination when the sample is contained in a capillary; the alignment is homeotropic at the wall and changes by 90° from wall to axis.

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†Alternatively named 4,4″-di-(2,3,4-tridodecyloxyoenzylidene)amino-*p*-terphenyl.

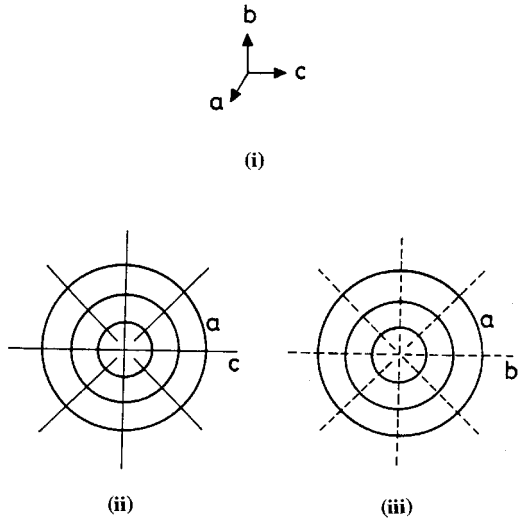
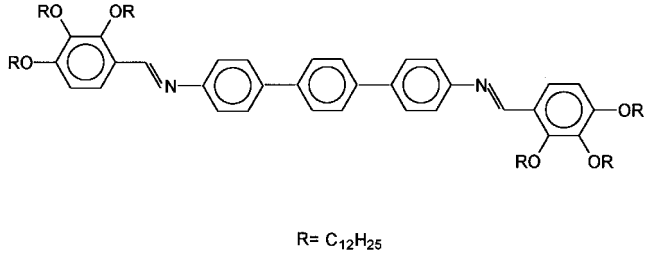


Figure 2. (i) The three mutually perpendicular director vectors **a**, **b** and **c** in an orthorhombic nematic. (ii) Director field for $|s|=1$ disclination in an orthorhombic biaxial nematic. Concentric circles represent the **a**-director and radial lines the **c**-director. (iii) The structure that results when the **c**-director in (ii) escapes by a rotation of $\pi/2$ about the **a**-axis. The dashed lines represent the **b**-director. Notice that the singularity at the origin continues to exist.

I



R= $C_{12}H_{25}$

Figure 3. Structural formula of 4,4″-(*p*-terphenyl)-bis[2,3,4-tri(dodecyloxy)benzal]imine (compound **I**).

§4. The transition temperatures, as determined by optical microscopic observations, are: crystal–nematic ~82°C and nematic–isotropic ~117°C.

Conoscopic studies using a Leitz polarizing microscope Model DMRXP were made on films (~25 μm thick) taken between glass plates coated with transparent conducting electrodes. Homeotropic alignment was achieved by means of an electric field (1 kHz 250 V) applied across the 25 μm sample. With electric fields of this order, large areas of uniform orientation, sometimes covering the entire field of view, were seen and it was conveniently possible to carry out conoscopic observations on a monodomain. Typical biaxial patterns were obtained, the separation between the arcs (isogyres) increasing with decreasing temperature, indicating an increase in the biaxial angle (figure 4). The reverse trend is seen on heating the sample.

3. Observations on free-standing films

When the nematic sample was taken between two clean untreated glass plates, one invariably obtained a schlieren texture consisting entirely of 2-brush ($|s|=\frac{1}{2}$) disclinations. An example of this type of texture is shown in figure 5.

Free-standing nematic films were prepared by spreading the fluid over a circular hole, less than about 1 mm in diameter, drilled in an aluminium plate. The thickness of the film was measured to be about 350 μm. With a film of this thickness, the influence of the nematic–air interface on the orientational order in the bulk of the sample may be expected to be quite small. Again, the schlieren textures in free-standing films consisted only of 2-brush disclinations. Two examples are presented in figure 6.

For comparison, textures obtained with free-standing films of a uniaxial nematic, 4′-*n*-octyl-4-cyanobiphenyl (8CB), were examined. Large 4-brush disclinations appeared readily in the N_u films (figure 7). Interestingly we did not observe any 2-brush disclinations in any of the samples that we examined.

4. Synthesis and characterization

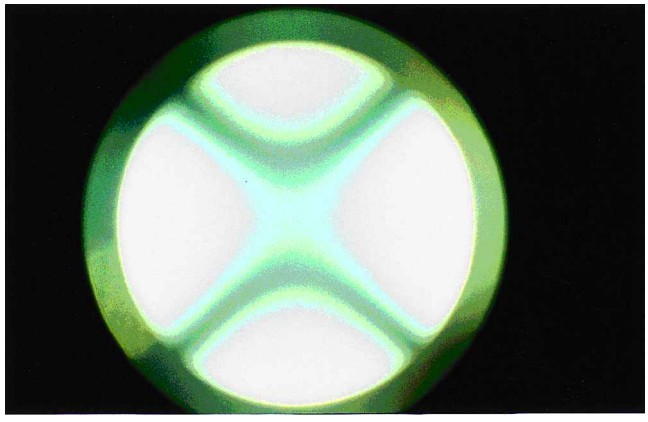
We give below a brief description of the preparation of 4,4″-(*p*-terphenyl)-bis[2,3,4-tri(dodecyloxy)benzal]imine.

This type of bisimine is prepared in the usual way by a 4-toluenesulphonic acid (100 mg) catalysed condensation of 2,3,4-tri(dodecyloxy)benzaldehyde (8 mmol) with 4,4″-diamino-*p*-terphenyl (4 mmol, commercially available) in toluene (120 ml) under reflux conditions during 4 h. The solvent is evaporated in vacuum; the residue is dissolved in methylene chloride, washed twice with an aqueous solution of sodium hydrogen carbonate, and crystallized from ethanol. Yield around 76% of yellow product.

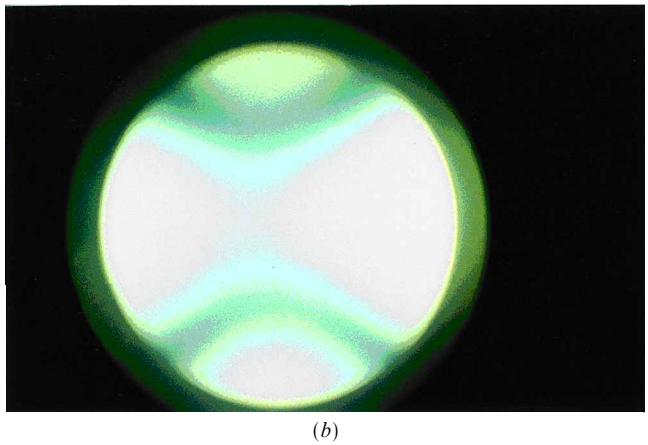
IR (Beckman IR9, CCl_4): $\nu=1621\ cm^{-1}$ (HC=N); ^1H NMR (Bruker WH 400, $CDCl_3$): $\delta=8{\cdot}83$ (s, 2H, HC=N), 7·89 and 6·76 (2 d, J ~9 Hz, 2×2 aromatic H of the tridodecyloxy part), 4·13, 4·05, and 4·00 (3 t, J ~7 Hz, 3×4H, $3OCH_2$); 0·88, and 0·83 (2 t, J ~7 Hz, 12H or 6H, respectively, CH_3); ^{13}C NMR (Bruker AM 270, $CDCl_3$): $\delta=156{\cdot}44$ (d, HC=N). $C_{102}H_{168}N_2O_6$, m.w. 1518·4: calc. C 80·68, H 11·15, N 1·85; found C 80·37, H 11·09, N 1·87.

5. Concluding remarks

These studies demonstrate the occurrence of the N_b phase in a thermotropic liquid crystal and confirm that



(*a*)



(*b*)

Figure 4. Conoscopic patterns obtained with a homeotropically aligned sample of the nematic phase of compound **I** at (*a*) 110°C, (*b*) 85°C.

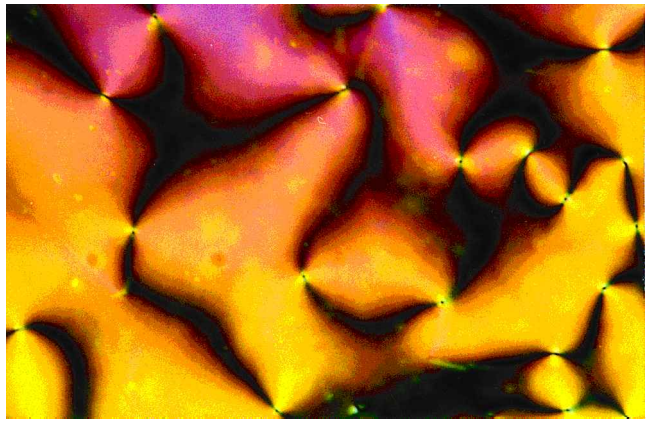
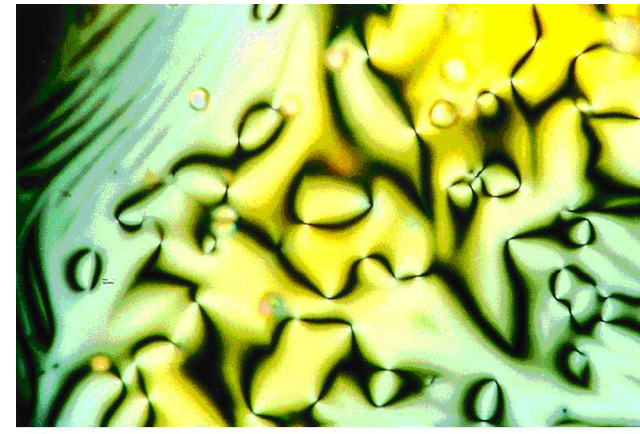
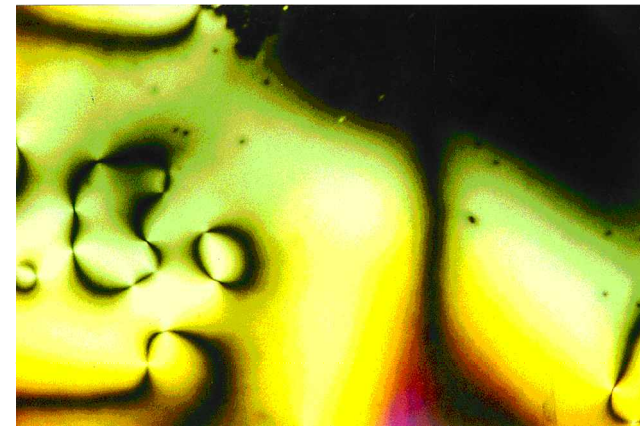


Figure 5. Schlieren texture exhibited by the nematic phase of compound **I**, sandwiched between glass plates. Note that only 2-brush disclinations, $|s|=\frac{1}{2}$, are seen.



(*a*)



(*b*)

Figure 6. Schlieren textures exhibited by a free-standing film of the nematic phase of compound **I**. Note that only 2-brush disclinations, $|s|=\frac{1}{2}$, are seen.

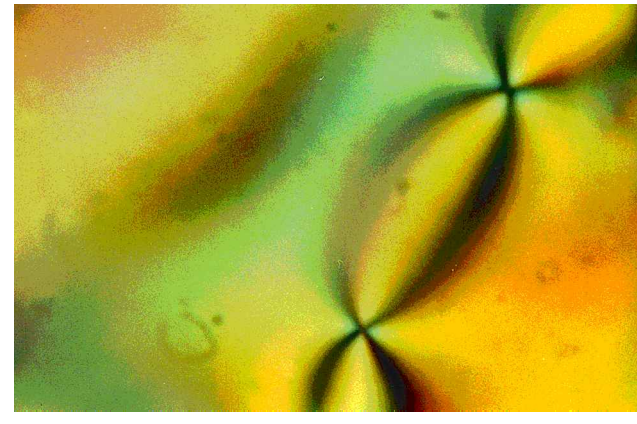


Figure 7. Schlieren texture exhibited by a free-standing film of the ordinary uniaxial nematic phase of 8CB, showing 4-brush $|s|=1$ disclinations.

the absence of disclinations of unit strength in the schlieren textures is evidence of biaxiality.

However, the existence of the N_b phase in thermotropic systems still appears to be the subject of some debate. In lyotropic systems, however, deuterium NMR spectroscopy gives unambigous proof of the existence of the N_b phase, as was first shown by Yu and Saupe [3]

in potassium laurate + 1-decanol + D_2O mixtures. The technique has been used by Fan *et al.* [6] to study 2,3,4-trihexyloxycinnamic acid dimer, which is believed to show a thermotropic N_b phase [7]. However, the NMR study failed to reveal any evidence of biaxiality in the nematic phase. This is a problem that still remains to be resolved.

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