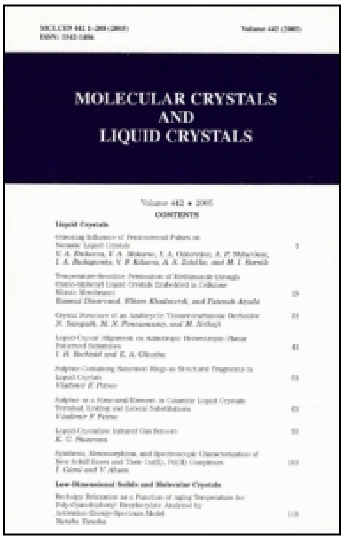

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A Thermotropic Biaxial Nematic Liquid Crystal

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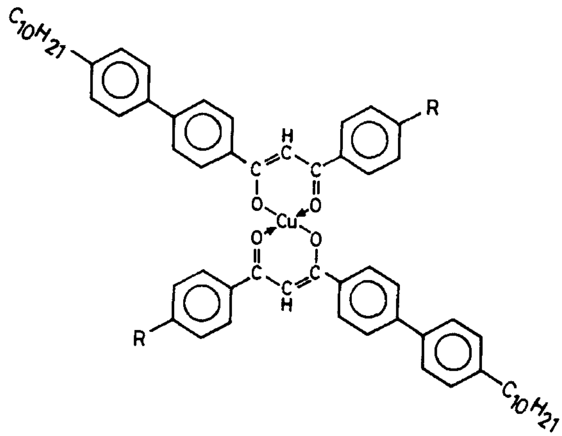
Optical studies have been carried out on a nematogenic copper complex, which incorporates the features of both rod-like and disk-like molecules. Conoscopic figures are presented demonstrating (i) the occurrence of a biaxial nematic phase in the pure complex, (ii) the uniaxial-biaxial (N_u–N_b) transition in binary mixtures, and (iii) the temperature variation of the biaxiality near this transition. The I–N_u–N_b phase diagram has been studied for the binary system.

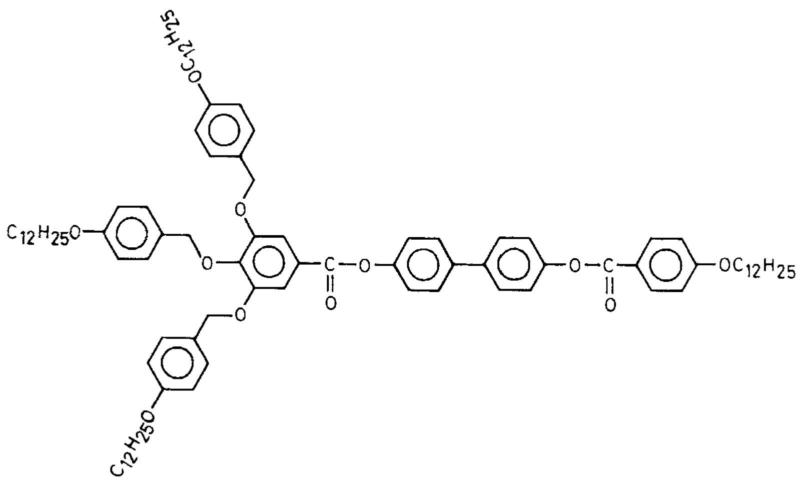
INTRODUCTION

Following the discovery of the biaxial nematic liquid crystal by Yu and Saupe[1] in an amphiphilic system (potassium laurate + 1-decanol + D_2O) there have been a number of investigations on this phase in similar lyotropic materials.[2-14] In these systems, the constituent units are micelles whose size and shape are sensitive to temperature and concentration: over a range of temperature/concentration the biaxial nematic (N_b) phase intervenes between two uniaxial (N_u) phases, one composed of rod-shaped micelles and the other of disk-shaped micelles. Evidence of biaxiality has also been found in certain nematic polymers.[15,16] There are obvious advantages in having a thermotropic N_b phase in a simple low molecular weight system in order to be able to carry out detailed physical studies. It was suggested[17] that a convenient method of achieving this would be by 'bridging the gap between rod-like and disk-like mesogens', i.e., by preparing a mesogen that combines the features of the rod and the disk. We succeeded in producing such molecules—copper complexes having the structural formula I with R = CH_3, C_2H_5, OCH_3, OC_2H_5 and OC_3H_7, which formed nematic liquid crystals with paramagnetic properties.[18,19]



Structural formula I

We have since made careful conoscopic observations which reveal the occurrence of the N_b phase in these complexes. Independently, Malthete et al[20] reported the N_b phase in another compound having the structural formula II, which again combines the features of the rod and the disk.



Structural formula II

Surprisingly, this compound appears to exhibit an *inverted* sequence of transitions, i.e., N_b occurs at a higher temperature relative to N_u, the uniaxial phase, whereas statistical models[21–27] predict a second order transition from N_u to N_b on lowering the temperature.

This paper reports our optical observations on some of these nematogenic complexes.[29] Evidence is presented to demonstrate (a) the biaxiality of the nematic phase, (b) the occurrence of the uniaxial-biaxial transition with decrease of temperature, and (c) the temperature variation of the biaxiality near this transition. The I–N_u–N_b phase diagram has also been studied for a binary system.

OPTICAL STUDIES

The optical textures of N_u and N_b are virtually indistinguishable (Figure 1). Not surprisingly the N_u/N_b phase boundary was missed in the preliminary miscibility studies.[18,19] Very occasionally, zig-zag disclinations[8] were seen in some samples (Figure 2) but these appeared quite unpredictably and we did not regard it as conclusive evidence of biaxiality.[30] We therefore resorted to conoscopic observations on thick films (~100 μm) using Leitz Orthoplan polarizing microscope equipped with a Mettler hot stage (FP82).

The detailed results for one particular complex *I* with R = OC_2H_5 (hereafter referred to as A) are described below. The transition temperatures of **A** are: melting transition 186.6°C, isotropic–nematic

FIGURE 1 Schlieren texture in the nematic phase of complex **A**.

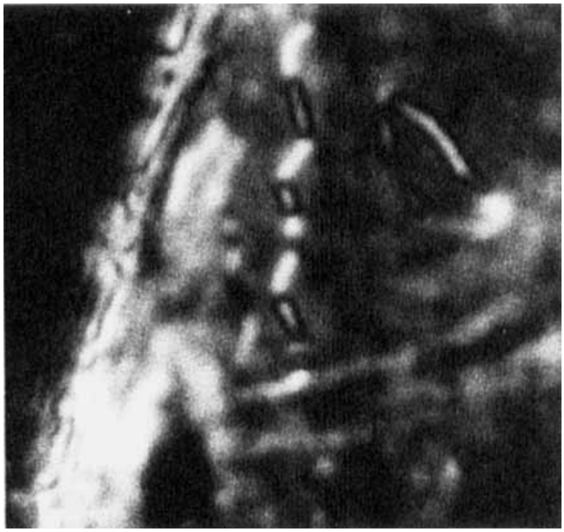


FIGURE 2 Zig-zag disclination in the nematic phase of Complex I with R = OCH_3. The disclination, running vertically in the middle of the photograph, consists of alternately bright and dark segments.

transition 168.5°C. The complex was synthesized by one of us (BKS) according to the procedure outlined in a previous paper.[19]

Homeotropic alignment was achieved by the combined effect of silane coating and a 3 kHz AC electric field (the dielectric anisotropy of the material being positive[19]). The sample was sandwiched between two cover slips (each of thickness ~ 100 μm), the *external* surfaces of which were coated with tin oxide, which served as electrodes, and the *internal* surfaces with silane. The alignment was checked by visual observation as well as by measuring the intensity of light transmitted by the sample between crossed polaroids under *orthoscopic* conditions using a He-Ne laser and a photo diode. For 'perfect' alignment there was almost complete extinction and the transmitted intensity was equal to that for the isotropic phase. The saturation voltage for perfect alignment was usually about 200 V across a film of thickness 125 μm. No electrohydrodynamic motion was seen in pure samples. There was evidence of some chemical decomposition on repeated heating of the material, and therefore only fresh samples were used for the experiments. All the conoscopic observations were found to be reproducible with well aligned samples in freshly prepared cells. The

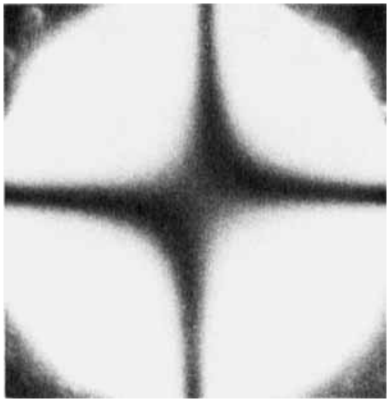


FIGURE 3 Conoscopic figure showing the biaxiality of the nematic phase of complex **A**. T_{NI}–T = 1.5°C. Film thickness ~125 μm, homeotropic alignment. Numerical aperture of the objective = 0.40.

conoscopic pattern was independent of the applied voltage for voltages greater than the saturation value.

Figure 3 gives the conoscopic figure for the nematic phase of complex **A**. The biaxiality can be seen quite clearly. In this case, the transition takes place directly from the isotropic phase to N_b.

Addition of even a very small quantity of the uniaxial nematogen 5CT (4″-*n*-pentyl-4-cyano-*p*-terphenyl) results in the appearance of an optically positive N_u phase between I and N_b, and the sequence of transition, on cooling, is then I → N_u → N_b. For 0.2% (by weight) of 5CT in **A** the temperature range of N_u ~ 1°C. The N_u–N_b transition occurs reversibly in both the heating and cooling modes, and the biaxiality increases as the temperature of the N_b phase is lowered. This is illustrated in the sequence of photographs shown in Figure 4.

Figure 5 gives the phase diagram for the binary mixture on an enlarged scale for the concentration range 0–1% of 5CT. The temperature range of N_u increases rapidly with increasing concentration of 5CT. For 1% 5CT, the mesophase remains uniaxial throughout till the sample crystallises.

CONCLUDING REMARKS

The method suggested a few years ago[17] of obtaining a low molecular weight thermotropic N_b phase has been demonstrated to be effica-

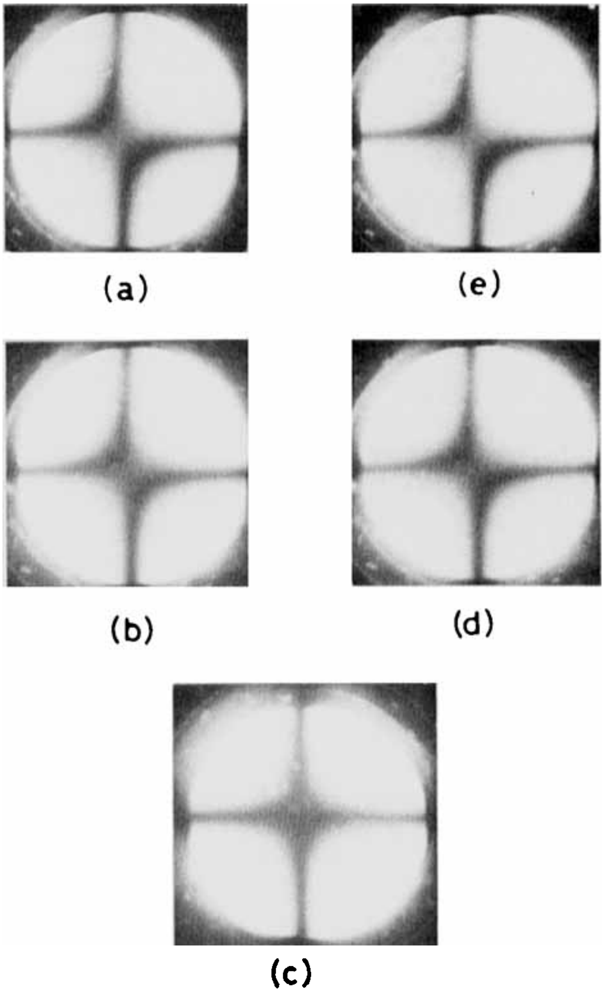


FIGURE 4 Sequence of photographs showing the reversibility of the N_b–N_u transition on heating and cooling in a binary mixture of 0.25% (by weight) of 5CT in **A**. Heating mode: (a) N_b at 165.8°C, (b) N_b at 167.0°C, (c) N_u at 167.8°C; Cooling mode: (d) N_b at 167.2°C, (e) N_b at 166.3°C. The biaxiality of N_b can be seen to decrease on approaching the N_b–N_u transition at 167.5°C. Film thickness ~125 μm, homeotropic alignment.

cious in a practical case. Such a phase offers a much more convenient system for investigating the physics of the biaxial nematic liquid crystal and verifying some important theoretical predictions that have been made concerning phase transitions,[21–28,30–33] hydrodynamics,[34–40] topological defects,[41–46] etc. Further studies are in progress.

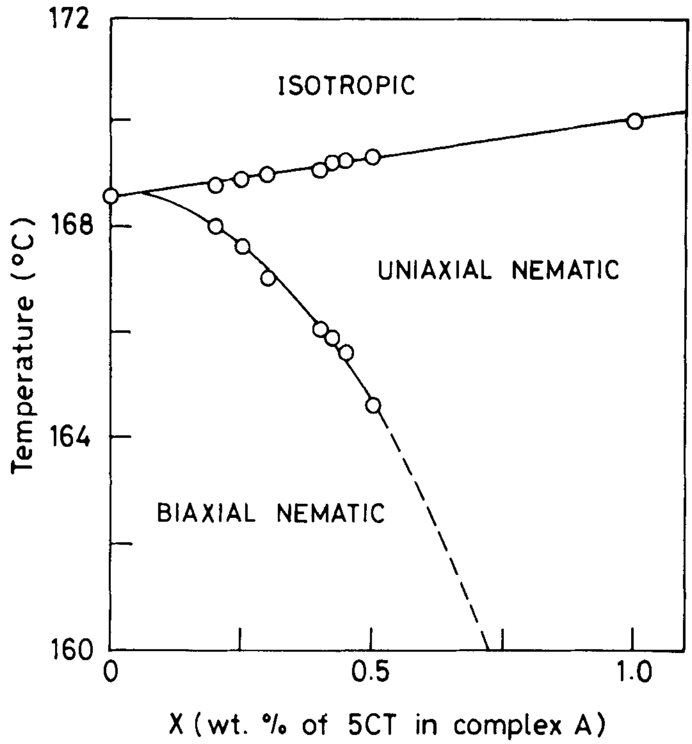


FIGURE 5 Partial phase diagram of the binary mixture of **A** and 5CT in the concentration range 0–1% 5CT, showing the I–N_u and N_u–N_b phase boundaries. The dashed portion of the curve represents an extrapolation.

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