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A biaxial nematic liquid crystal

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Abstract. We report a biaxial nematic liquid crystal in a simple thermotropic system.

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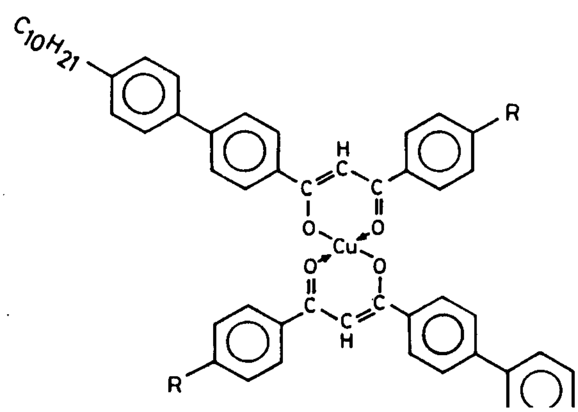
The suggestion was made a few years ago (Chandrasekhar 1984) that a convenient way of obtaining the biaxial nematic phase in a simple (low molecular weight) thermotropic system would be by 'bridging the gap' between rod-like and disc-like molecules, i.e. by preparing a mesogen that combines the features of the rod and the disc. We succeeded in producing such molecules—nematogenic copper complexes—and reported preliminary studies on them (Chandrasekhar *et al* 1986, 1987). We have since made careful conoscopic observations which reveal the occurrence of the biaxial nematic phase (N_b). Independently, Malthete *et al* (1986) reported the N_b phase in another compound, 4-[3′, 4′, 5′-tri(*p*-*n*-dodecyloxybenzyloxy)]-benzoyloxy, 4″-*p*-*n*-dodecyloxybenzoyloxybiphenyl, which again combines the features of the rod and the disc. Surprisingly, however, in this case they find an *inverted* sequence of transitions, i.e., N_b occurs at a higher temperature relative to N_u, the uniaxial phase.

We describe our observations on one complex (hereafter referred to as **A**):



The transition temperatures of A are: melting transition 186·6°C, isotropic-nematic transition 168·5°C (for further details, see Chandrasekhar *et al* 1987).

The optical textures of N_u and N_b are virtually indistinguishable. Some samples did occasionally show zig-zag disclinations (Galerne and Liebert 1984) but as these lines made their appearance unpredictably, we did not regard this as conclusive evidence of biaxiality. We therefore resorted to conoscopic observations using thick films ($\sim 100\,\mu$m). 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, Chandrasekhar *et al* 1987). No electrohydrodynamic motion was seen in pure

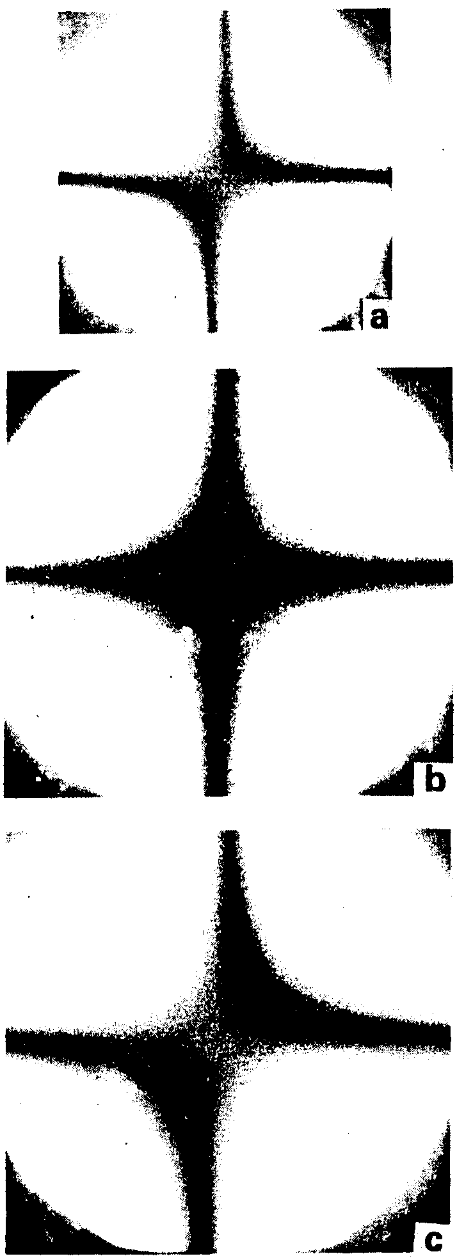


Figure 1. Conoscopic figures: **(a)** Biaxial nematic phase of the pure complex A at $T_{NI} - T$

samples. There was evidence of some chemical decomposition on repeated heating of the material, and therefore only fresh samples were used for the observations.

Figure 1(a) gives the conoscopic figure obtained for **A**. The biaxiality can be seen very clearly. (This result was announced briefly at a recent conference (Chandrasekhar 1987).) In the pure complex the transition takes place directly from the isotropic phase to N_b. Addition of a small quantity of the uniaxial nematogen 5CT (4″-*n*-pentyl-4-cyano-*p*-terphenyl) results in the appearance of N_u between the isotropic and N_b phases, and the sequence of transition on cooling is then as follows: isotropic $\rightarrow N_u \rightarrow N_b$. The temperature range of N_u increases with increasing concentration of 5CT, as expected; for 0·2% 5CT (by weight) N_u exists for $\sim 1°C$, for 0·4% 5CT it exists for $\sim 3°C$. Figures 1(b) and (c) show the conoscopic figures for the uniaxial and biaxial phases of a mixture with 0·2% 5CT. The $N_u - N_b$ transition occurs reversibly in both the cooling and heating modes, and the biaxial angle is seen to increase as the temperature of the N_b phase is lowered. For 1% 5CT, the range of N_u becomes large and persists till the sample crystallizes. All the observations were found to be reproducible with freshly prepared cells. Further work, e.g., precise determinations of the transition temperatures, phase diagrams, biaxial angles, etc., is in progress.

The occurrence of the N_b phase in amphiphilic systems has been known since it was first observed by Yu and Saupe (1980) in potassium laurate + 1-decanol + D_2O. Subsequently, evidence has been presented of biaxiality in certain nematic polymers (Hessel and Finkelmann 1986; Windle *et al* 1985). A number of important ideas concerning the N_b phase have been discussed—statistical theories, continuum theories, topological theories of defects, etc. (for a full list of references see Chandrasekhar 1984; Chandrasekhar and Ranganath 1986; Ranganath 1988). For example, Saupe (1981) and Kini (1984), who used different theoretical approaches, have both concluded that the orthorhombic N_b has 15 curvature elastic and 15 viscous constants. Again, a remarkable conclusion of the homotopy theory is that the usual law of coalescence of two defects breaks down in the N_b phase. The combination rule is now non-Abelian. Moreover, there can arise an entanglement of disclination lines, which may lead to what Toulouse describes as 'topological rigidity' (Toulouse 1977; Poenaru and Toulouse 1977; Mermin 1979; Trebin 1982; Kleman 1983). These and other ideas have yet to be investigated experimentally. The availability of a simple thermotropic biaxial nematic phase makes it conveniently possible to carry out physical studies and to test some of these predictions.

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