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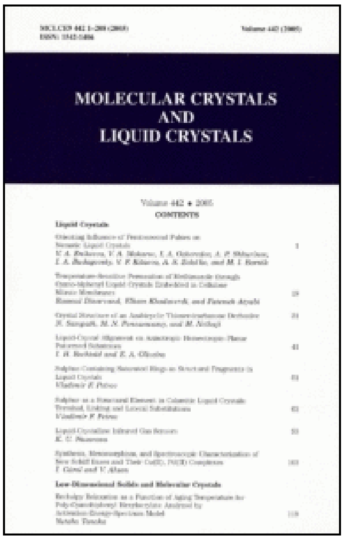

Molecular Crystals and Liquid Crystals

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First published on: 01 March 1994

To cite this Article Chandrasekhar, S.(1994) 'Biaxial Nematic Liquid Crystals in Low Molecular Weight Thermotropic Systems', Molecular Crystals and Liquid Crystals, 243: 1, 1 — 9
To link to this Article: DOI: 10.1080/10587259408037758
URL: http://dx.doi.org/10.1080/10587259408037758

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Mol. Cryst. Liq. Cryst., 1994, Vol. 243, pp. 1–9
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Printed in the United States of America

Biaxial Nematic Liquid Crystals in Low Molecular Weight Thermotropic Systems

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The evidence for the occurrence of the biaxial nematic phase in low molecular weight thermotropic systems is examined. The optical evidence for biaxility appears to be quite unambiguous for all the eleven cases discussed here. X-ray diffraction studies on magnetically aligned samples lend support to the optical evidence, but do not provide *independent* proof of long range biaxial orientational order. No X-ray studies on monodomain specimens have yet been reported. A noteworthy result, intriguing from the theoretical point of view, is that the isotropic phase transforms directly to the biaxial nematic phase in a first order transition for *all* the eleven compounds.

Keywords: biaxial nematic, conoscopic observations, X-ray studies

INTRODUCTION

The biaxial nematic (N_b) phase in low molecular weight thermotropic systems has been the subject of a number of studies in recent years. A convenient way of obtaining this phase is by "bridging the gap" between rod-like and disk-like molecules, i.e., by preparing a mesogen that combines the features of the rod and the disk.[1] Praefcke *et al.*[2] have discussed some molecular shapes that fulfill this criterion—the rod-disk-rod, disk-rod-disk, disk-rod and similar types of structures. To our knowledge, the following compounds have been reported to date to exhibit the N_b phase: (i) 4-[3′,4′,5′-tri(p-n-dodecyloxy benzyloxy)]-benzoyloxy, 4″-p-n-dodecyloxy benzoyloxy biphenyl[3]; (ii) bis[1-(p-n-decyl biphenyl) 3-(p-ethoxy phenyl) propane-1,3-dionato] copper (II)[4,5]; (iii) 2,3,4,-trialkoxy cinnamic acids[2,6]; (iv) nonyl and undecenyl pentakis [(4-pentyl phenyl) ethynyl] ethers[2,7]; (v) α,ω-bis{pentakis [(4-pentyl phenyl) ethynyl] phenoxy} alkanes.[2,7]

The view has been expressed that the characterization of the mesophase of compound (i) is not quite convincing and that it is probably smectic.[8] We shall not therefore discuss this compound but consider the other cases and examine the evidence presented for each of them.

Bis [1-(p-n-Decyl Biphenyl) 3-(p-Ethoxy Phenyl) Propane-1,3-Dionato] Copper (II)

This is a paramagnetic complex (hereafter referred to as complex A) that was prepared[4] and studied in some detail.[5] The structural formula of this complex is given in Figure 1(a). It is an 'elongated' version of the well known discotic complex

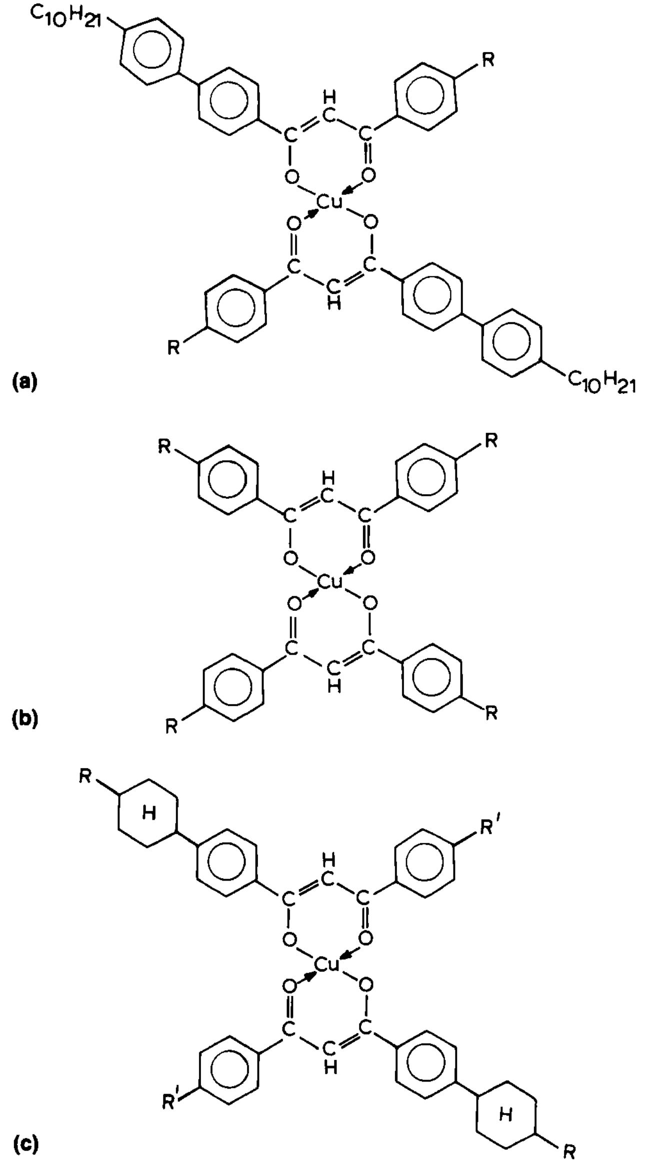

FIGURE 1 Structural formulas of (a) bis [1-(p-n-decylbiphenyl)3-(p-ethoxy phenyl) propane-1, 3-dionato] copper (II) (Chandrasekhar *et al.*[4]); (b) discotic complex bis (p-n-decylbenzoyl) methanato copper (II) (Giroud-Godquin and Billard[14]); (c) nematogenic complex bis [1-{4-trans-(4-alkyl cyclohexyl) phenyl} alkyl propane-1, 3-dionato] copper (II) (Mühlberger and Haase[9]).

shown in Figure 1(b). Another nematogenic copper complex, somewhat similar to *A*, was prepared subsequently by Mühlberger and Haase[9] (Figure 1(c)), but no studies have been made to check whether the nematic phase is biaxial.

Complex *A* exhibits a monotropic nematic phase. The transition temperatures are[5(b)]: melting transition 186.6°C and isotropic-nematic transition 168.5°C. Since the identification of the N_b phase involved delicate experiments, it is perhaps worthwhile summarizing them here. All the observations described below were made only on samples of the highest purity.

The mesophase showed the typical nematic schlieren textures when viewed under the polarizing microscope, except that often the pattern consisted entirely of disclinations of strength $|s| = \frac{1}{2}$. This is almost certainly an indication of biaxiality. Since the escape mechanism for $|s| = 1$ does not, in principle, eliminate the singularity in a biaxial nematic,[10,11] as it does in the uniaxial case, $|s| = 1$ probably becomes energetically unfavorable. Some samples showed zig-zag disclinations,[12] but they made their appearance only very rarely. We did not consider this as conclusive evidence of biaxiality.

We therefore resorted to conoscopic observations on thick films (~125 μm). Homeotropic alignment was achieved by the combined effect of silane coating on the *inner* surfaces of the cover slips and a 3 kHz A.C. electric field applied to tin oxide electrodes coated on the *outer* surfaces. (It was verified previously that the material is dielectrically positive. The tin oxide being coated on the external surfaces excluded the possibility of director distortion by charge injection.) The alignment was checked by visual observation as well as by measuring the intensity of light transmitted by the material between crossed polaroids under orthoscopic conditions using a He-Ne laser and a photodiode. For 'perfect' alignment there was almost complete extinction and the transmitted intensity was equal to that through the isotropic phase. The saturation voltage for perfect alignment was about 200 V for 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. On switching from the orthoscopic to the conoscopic condition, the biaxiality was clearly visible. This implied, of course, that there were large enough areas of uniform orientation in the film, as was confirmed by rotating the sample. The conoscopic pattern was independent of the applied voltage for voltages greater than the saturation value. All the observations were reproducible with well aligned samples in freshly prepared cells. We were able to demonstrate (a) the biaxiality of the nematic phase of the pure complex; and a *discontinuous* transition from the isotropic phase to the N_b phase, (b) a continuous, reversible uniaxial-biaxial (N_u-N_b) transition with change of temperature in a binary mixture of complex A with very small quantities, less than 1% by weight, of the uniaxial nematogen 4″-n-pentyl-4-cyano-p-terphenyl; and (c) the temperature variation of the biaxiality near the (N_u-N_b) transition. We were also able to obtain the I-N_u-N_b phase diagram for this binary system in the temperature-concentration plane.

X-ray diffraction photographs were taken of the sample contained in a 0.5 mm diameter Lindemann glass capillary. The sample was aligned by means of a magnetic field of 1.8 T, but the orientation was random in a plane perpendicular to the field. Intensity scans of the diffraction peaks were obtained with a Joyce-Loebl microdensitometer. As compared with the diffraction pattern from a uniaxial nematic, there was an additional pair of diffuse (liquid-like) peaks in the equatorial scans, as would be expected from an orthorhombic fluid. Though this provides evidence in support of biaxiality, strictly speaking, it cannot be regarded as conclusive proof of *long-range* biaxial nematic orientational order. A complete investigation requires X-ray studies on monodomain specimens obtained by the application of crossed electric and magnetic fields. Nevertheless, taken along with the optical evidence described earlier, it would seem justified to conclude that the nematic phase of complex *A* is biaxial.

The three principal spacings as determined from the X-ray photographs were 31 Å along the meridional axis, and 24 Å and 4.7 Å in the lateral direction. In the absence of any molecular association, these spacings should correspond approximately to the three principal dimensions of the molecule. However, the intensities of the low angle peaks indicate a considerable degree of molecular association (or cybotacticity), and as is well known in such a case the mean repeat distances as determined by X-rays may be quite different from the dimensions of the free molecule. Moreover, the true molecular shape itself may be different from that depicted schematically in Figure 1(a). For example, Mühlberger and Haase[9] have

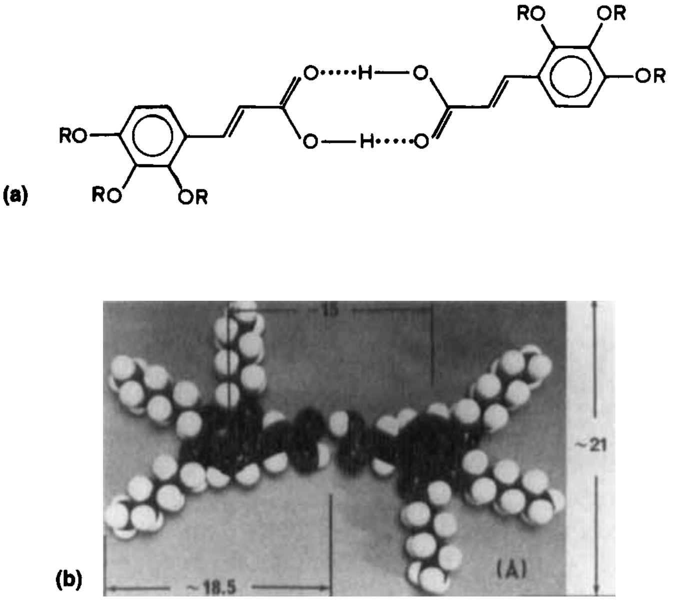

FIGURE 2 (a) Structural formula of the dimeric form of 2,3,4-trialkoxy cinnamic acids (Praefcke *et al.*[2,6]) and (b) space filling model of 2,3,4-trihexyloxy cinnamic acid dimer (Praefcke *et al.*[6]).

TABLE I

Temperatures (°C) and heats of transition (kJ/mol in parentheses) for 2,3,4-trialkoxy cinnamic acid dimers[2] (Figure 2(a))

R	Crystal	N_b	I
CH_3	● 173.2 (32.2)	—	●
C_4H_9	● 75.8 (18.6)	{● 67.9 (0.8)}	●
C_6H_{13}	● 51.2 (14.1)	● 59.6 (0.9)	●
C_8H_{17}	● 54.2 (48.7)	{● 50.9 (0.5)}	●

{ }Signify monotropic transitions.

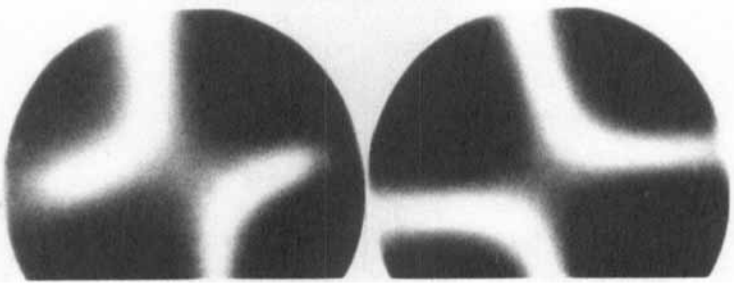

FIGURE 3 Conoscopic patterns of an aligned nematic sample of 2,3,4-trihexyloxy cinnamic acid dimer for two settings of the sample (Praefcke *et al.*[6]).

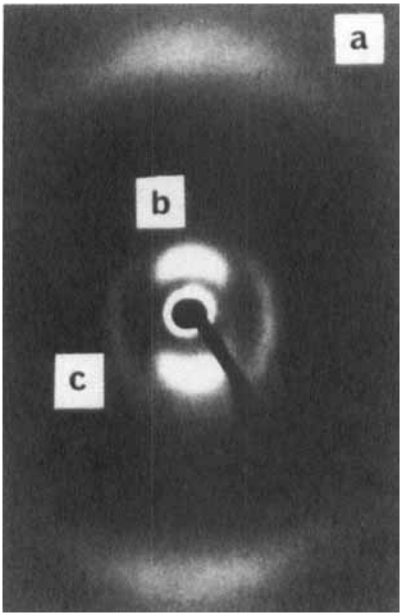

FIGURE 4 X-ray diffraction photograph of a magnetically aligned nematic sample of 2,3,4-trihexyloxy cinnamic acid dimer (Praefcke *et al.*[2,6]).

TABLE II

Principal spacings in the biaxial nematic phase of 2,3,4-trihexyloxy cinnamic acid dimer as determined from X-ray diffraction[2] (Figure 4)

R	a (Å)	b (Å)	c (Å)
C_4H_9	4.3	17.5	12.5
C_6H_{13}	4.4	19.5	14.0
C_8H_{17}	4.3	20.5	14.7

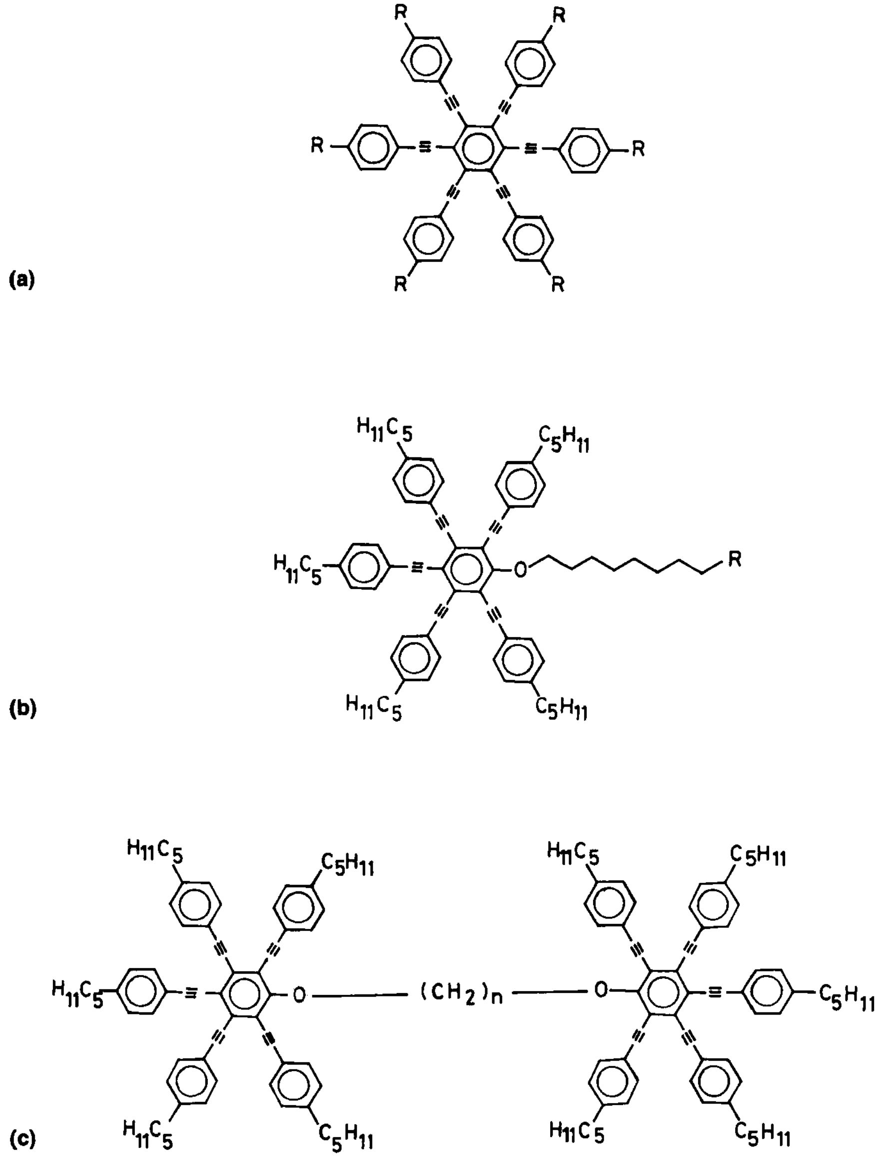

FIGURE 5 (a) Structural formula of discotic hexakis [(4-octyl phenyl)ethynyl] benzene (Praefcke *et al.*[7]); (b) nonyl and undecenyl pentakis [(4-pentyl phenyl) ethynyl] phenyl ether (Praefcke *et al.*[2,6]); (c) α, ω-bis{penta (4-pentyl phenyl ethynyl) phenoxy} alkanes (Praefcke *et al.*[2,7]).

analyzed the crystal and molecular structures of the complex of Figure 1(c) by X-ray methods. The molecular shape, especially the disposition of the end chains, turns out to be significantly different from that represented schematically in Figure 1(c). It would therefore be premature at this stage to speculate on the nature of the molecular association in the N_b phase of this complex. As emphasized earlier, a more complete X-ray study using monodomain specimens, aligned in crossed

TABLE III

Temperatures (°C) and heats of transition (kJ/mol in parentheses)

Nonyl and undecenyl pentakis [(4-pentyl phenyl)ethynyl] phenyl ether[2] (Figure 5(b))

R	Crystal	N_{db}	I
H	● 86.4 (42.9)	● 109.9 (0.3)	●
CH=CH_2	● 76.7 (26.2)	● 101.4 (0.2)	●

α,ω-bis{pentakis [(4-pentyl phenyl)ethynyl] phenoxy} alkanes[2] (Figure 5(c))

n	Crystal	N_{db}	I
8	● 127.0 (61.8)	● 127.8[a]	●
9	● 131.0 (67.5)	{● 112.5[a]}	●
10	● 129.1 (57.0)	● 153.5 (0.3)	●
11	● 118.2 (62.2)	● 140.8 (0.3)	●
12	● 121.4 (67.9)	● 155.0 (0.4)	●

[a] The enthalpies could not be determined for these two cases. { } signifies monotropic transition. The I-N_{db} transition temperatures exhibit an odd-even effect.

electric and magnetic fields, should lead to a better understanding of the structure of the N_b phase.

2,3,4,-Trialkoxycinnamic Acids

The structural formula and a space-filling model of the dimeric form of 2,3,4-trialkoxycinnamic acids are shown in Figure 2, and the temperatures and latent heats of transition for the homologs are listed in Table I. It is worth noting that for all the three homologs (R = C_4H_9, C_6H_{13} and C_8H_{17}) that show the N_b phase, the I-N_b transition is of first order.

Optical observations were made using samples of thickness about 20 μm sandwiched between glass plates, the inside surfaces of which were coated with tin oxide. The mesophase exhibited the usual nematic schlieren texture. With planar orientation (obtained by oblique deposition) a Freedericksz transition was observed when the applied electric field exceeded a certain critical value. At fields much higher than the critical value, the sample was well aligned homeotropically. Conoscopic observation under these conditions clearly revealed the biaxiality of the phase (Figure 3). The biaxial angle was independent of the temperature and dropped abruptly to zero at the transition to the isotropic phase.

X-ray diffraction photographs were obtained in the same way as described in the previous section for complex A. The sample was aligned by means of a magnetic field (1.5T) but randomly oriented in a plane perpendicular to the field. As expected, three pairs of diffuse (liquid-like) maxima were seen (Figure 4). The principal spacings are given in Table II for three homologs. Again, as for complex A, the correlation between these spacings and the dimensions of the dimer is not so obvious. Praefcke *et al.*[7] have tentatively suggested a possible arrangement of the molecules in the N_b phase, but clearly a more detailed study using monodomain specimens is necessary to elucidate the structure.

Multiethyne Compounds

Hexakis [(4-octylphenyl) ethynyl] benzene (Figure 5(a)) is a symmetric disc-shaped compound which exhibits an optically negative discotic nematic (N_d) phase. Asymmetric modifications of this structure (Figures 5(b) and 5(c)) exhibit a 'negative' biaxial nematic (N_{db}) phase. Interestingly, the I-N_{db} transition in all cases is of first order (Table III).

The biaxiality was established by conoscopic observations on samples of thickness 23 μm, homogeneously aligned by unidirectional rubbing of the glass surfaces. The sign of the biaxiality was proven by standard optical methods. No X-ray studies have yet been reported.

CONCLUSIONS

1) The occurrence of the biaxial nematic phase in low molecular weight thermotropic systems appears to be conclusively established by optical observations.

2) X-ray diffraction studies on magnetically aligned samples offer supporting evidence, but do not provide *independent*, unambiguous proof of long range biaxial orientational order. This requires X-ray studies on monodomain samples, obtained, for example, by the application of crossed electric and magnetic fields, but such studies have yet to be carried out.

3) The optical observations indicate that for the pure compounds the biaxiality is practically temperature independent and drops abruptly to zero at the transition to the isotropic phase. Calorimetric studies confirm that this transition is first order. This result may have interesting implications in regard to the theory of the biaxial nematic phase.[13]

Acknowledgment

The valuable cooperation of Dr. B. R. Ratna and Dr. V. N. Raja in the experimental work on complex *A* is gratefully acknowledged.

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