

Biaxiality in a Cyclic Thermotropic Nematic Liquid Crystal.

JIAN-FENG LI(*), V. PERCEC(**), CH. ROSENBLATT(*)(**)([§]) and
O. D. LAVRENTOVICH(***)

(*) *Department of Physics, Case Western Reserve University
Cleveland, OH 44106, USA*

(**) *Department of Macromolecular Science, Case Western Reserve University
Cleveland, OH 44106, USA*

(***) *Liquid Crystal Institute, Kent State University - Kent, OH 44242, USA*

(received 22 September 1993; accepted in final form 22 November 1993)

PACS. 61.30E - Experimental determinations of smectic, nematic, cholesteric, and lyotropic structures.

PACS. 61.30G - Orientational order of liquid crystals in electric and magnetic fields.

PACS. 64.70M - Transitions in liquid crystals.

Abstract. - Birefringence and textural data are presented for a ring-shaped trimeric liquid crystal. The material apparently undergoes a uniaxial-to-biaxial nematic phase transition as a function of temperature.

In a recent paper [1] we showed that at least one member of a new class of cyclic thermotropic liquid crystals [2-9] exhibits a nearly second-order uniaxial nematic-isotropic (N_u -I) phase transition. Using a dynamic electric-field-induced birefringence method, we found that the quantity $T_{N_u-I} - T^* < 0.2$ K, where T_{N_u-I} is the first-order phase transition temperature and T^* is the supercooling limit of the isotropic phase. Such a weakly first-order N_u -I transition can be the signature of a nearby Landau point [10-13] on a temperature- Γ phase diagram, where Γ corresponds to an experimentally adjustable parameter such as concentration or molecular architecture. The Landau point is an isolated critical point which separates a high-temperature isotropic phase from three lower-temperature nematic phases: one uniaxial phase at large Γ and another at small Γ , with a biaxial nematic phase (N_b) in between [13-15]. Thus, if one decreases temperature along an «iso- Γ » line, one expects to encounter, respectively, an isotropic phase, a uniaxial nematic phase, and a biaxial nematic phase.

For the cyclic molecule we also observed the onset of textures at $T \approx T_{N_u-I} - 25$ K in what had been a homeotropically oriented uniaxial nematic phase at higher temperatures [1]. These observations are consistent with a low-temperature nematic biaxial phase. Such a biaxial phase was first discovered in lyotropic systems by Yu and Saupe in 1980 [16], and later in a thermotropic liquid crystal [17] by Malthête *et al.* Since that time there have been numerous reports of thermotropic biaxiality [18-24], many of which have since been called into question [25]. In this paper we report on several investigations below what we believe is

([§]) e-mail address: cxr@po.cwru.edu.

an N_u - N_b phase transition in the cyclic trimer TPB-(c)9(3). Again, these results are consistent with a uniaxial-biaxial nematic phase transition.

The cyclic trimer TPB-(c)9(3) is based on the general structure shown in fig. 1, with $n=9$ and $X=3$. Details of the syntheses and thermal characterization of this compound are described elsewhere [5, 7]. As TPB-(c)9(3) and related molecules are synthesized in minute quantities, a single sample was prepared in such a manner as to be used in several different experiments. Two glass slides coated with semi-transparent indium-tin-oxide (ITO) were in turn coated with the surfactant hexadecyltrimethyl ammonium bromide to induce homeotropic alignment. The slides were separated by Mylar spacers of nominal thickness $3\ \mu\text{m}$, and the cell was adjusted for excellent parallelism under monochromatic light. Since the two regions of ITO had a well-defined overlap area $A = (0.20 \pm 0.01)\ \text{cm}^2$, we found from a measurement of the empty-cell capacitance that the cell thickness $d = (3.3 \pm 0.1) \cdot 10^{-4}\ \text{cm}$. (Errors in d arising from this technique will be proportionally represented in the birefringence results.) The cell was placed in a small oven, temperature controlled to approximately 50 mK, and the oven was in turn mounted on a rotation stage. TPB-(c)9(3) was introduced into the cell in the isotropic phase, and was oriented homeotropically in the uniaxial nematic phase by the surfactant. The birefringence apparatus was based upon a modulated Pockels cell and is described in detail elsewhere [26]. In this experiment the laser beam was focused to a spot size of order $50\ \mu\text{m}$ in order to probe a small region of the sample.

On entering the biaxial phase, the twofold degeneracy of the smaller refractive index (the ordinary index n^{ord}) is broken into n_1^{ord} and n_2^{ord} , and there is an apparent birefringence $\Delta n = n_1^{\text{ord}} - n_2^{\text{ord}}$ in the plane of the sample. In order to measure this birefringence, one ideally would like to orient all three eigenvectors of the optical dielectric tensor along appropriate directions in the laboratory frame. In many materials this can be accomplished by the combined action of the surface treatment and orthogonal electric and/or magnetic fields [14, 27]. However, for TPB-(c)9(3) this is not possible, as is apparent from fig. 1, and light and dark regions are visible when the sample is viewed under a polarizing microscope. Thus we needed to choose a different tack. At each equilibrated temperature the sample was rotated to achieve a maximum birefringence. Since the orientation of the sample does not, in principle, affect the measured optical retardation (only the signal-to-noise ratio), this method provides the correct Δn [26]. There are, however, several sources of error endemic to this approach. If the beam does not precisely sample the center of the rotation stage, different parts of the cell will be probed as the cell is rotated. This creates two problems. First, any strain-induced birefringence in the glass cell or oven windows will vary as the cell is rotated

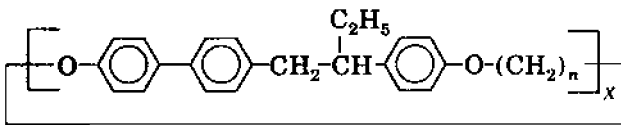


Fig. 1.

Fig. 1. - The monomer that constitutes TPB-(c)9(3). ($X=3$, $n=9$.)

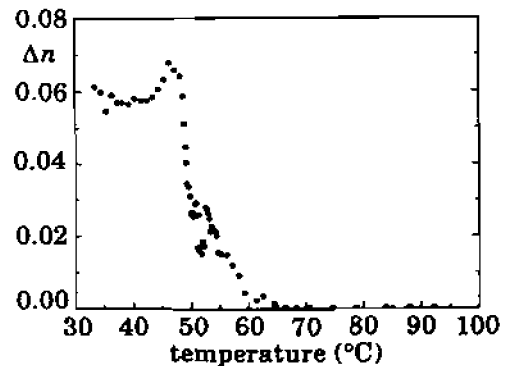


Fig. 2.

Fig. 2. - Measured in-plane birefringence $\Delta n = n_1^{\text{ord}} - n_2^{\text{ord}}$ vs. temperature.

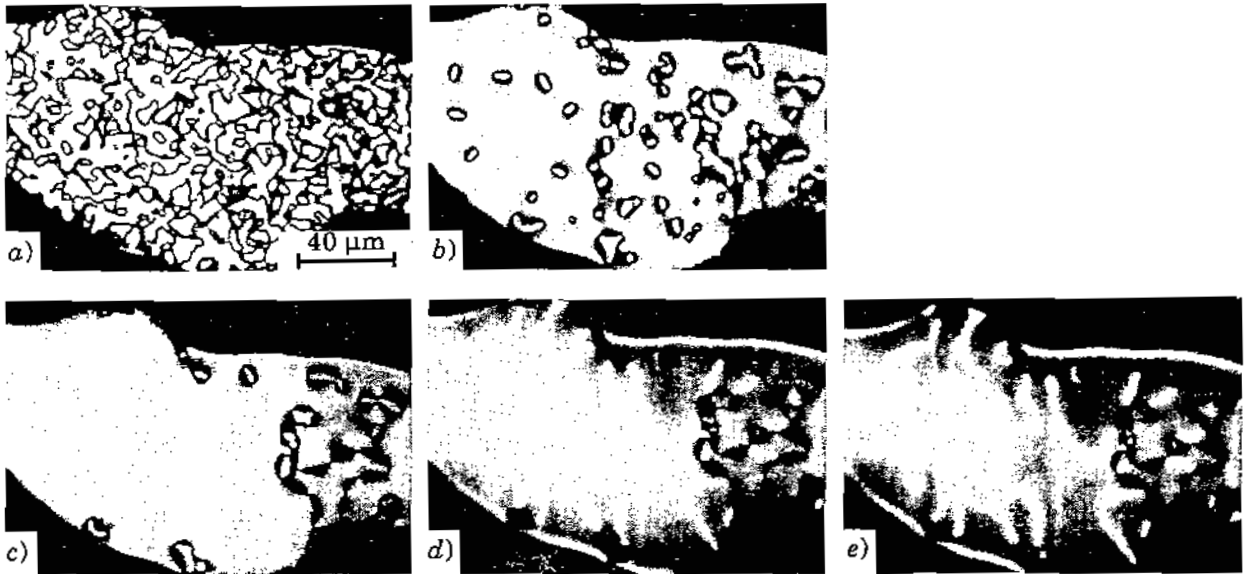


Fig. 3. – Polarizing microscope texture at several different temperature: a) 75 °C, b) 70 °C, c) 65 °C, d) 60 °C, e) 55 °C.

and the temperature is changed. This can give rise, of course, to substantial noise for large cell rotations, or systematic deviations if a small rotation is needed for each new temperature. Second, as different parts of the sample may be probed as the cell is rotated, small variations in cell thickness give rise to variations in optical retardation and apparent Δn . Finally, the physical rotation of the sample itself introduces an additional noise factor.

The experiment was performed three times, and data from one such run is shown in fig. 2. The cell was translated slightly for each data run so as to sample different parts of the cell. All three experiments gave similar results, with a transition from a zero in-plane birefringence state above approximately $T_{N_u-N_b} \approx 62$ °C, to a $\Delta n \neq 0$ state below. In all cases the rise in Δn with decreasing temperature exhibited linear or slightly concave downward curvature below $T_{N_u-N_b}$, behavior which is a bit disturbing [13,14]. Although this might indicate an order parameter exponent $\beta \geq 1$, it is clear that a precise exponent cannot be extracted from the data. The observed curvature of Δn vs. temperature may be due in part to the onset of the glass transition. Calorimetry measurements [5] indicate a glass transition approximately 42 °C below $T_{N_u-I} \approx 90$ °C. This behavior is seen in our data by a peak in Δn , and subsequent leveling out below approximately 47 °C⁽¹⁾. We observed this behavior in all three data sets, where the glass transition has effectively frozen in the biaxial order parameter.

A measurement of the birefringence is not, in and of itself, sufficient to prove biaxiality. The observed birefringence may also arise from other effects, such as a uniaxial nematic-smectic C transition, or from a surface tilt transition in the nematic phase [28-30]. To check for these possibilities, we mounted the oven in an electromagnet, such that the magnetic field was in the plane of the cell. Laser light passed sequentially through a polarizer, the cell, an analyzer, a light chopper, and into a detector. The detector signal was

⁽¹⁾ In ref.[1] we indicated a glass transition at approximately 36 °C, based upon differential scanning calorimetry (DSC) measurements. As DSC-determined transition temperatures correspond to nonequilibrium values, and the birefringence measurements reported herein correspond to a measurement made in equilibrium, it is not surprising that the glass transition temperature reported herein differs from that of ref.[1].

input to a lock-in amplifier, which was referenced to the light chopper frequency. In the homeotropic N_u phase no light reached the detector, even at the highest field of 7.7 kG. (The field needed to induce a Freedericksz transition is greater than 10 kG for a sample of thickness 3.3 μm .) In the N_b phase a significant amount of light reached the detector. On ramping the field to 7.7 kG the intensity change was under 1%, not much above the noise. This measurement was performed at several different temperatures, at each temperature with the beam passing through the sample at several different locations. Additionally, the beam was focused to approximately 50 μm and again passed through the sample at several different spots. In all cases the results were similar: no reproducible intensity change. Had the birefringence been due to the onset of a smectic C phase or tilt transition at the nematic-substrate surface, the field would have caused a torque on the director throughout the sample. In consequence, one would have expected significant changes in the transmitted intensity (even with strong azimuthal surface anchoring), which were not observed.

We now turn to our observations of textures. Figure 3 represents the textures observed under a polarizing microscope in a small area near the *edge* of the cell as a function of temperature. Note that in this region homeotropic alignment does *not* obtain and the molecules are oriented tangentially. On cooling the sample from the isotropic phase we observed a typical N_u texture (fig. 3a) with numerous singular points from which two or four dark brushes emanate. The brushes arise wherever the optical axis is directed either parallel or perpendicular to the polarization of the light [31,32]. Moreover, the brushes indicate that the director is not twisting along the sample normal direction [32]. The points associated with two brushes correspond to line disclinations of half-strength [31,32], as shown in fig. 4a). The points associated with four brushes correspond to escape linear defects that leave point defects (boojums) at the surfaces [33]. The observation of the half-strength disclinations implies that the director is oriented tangentially to the sample plates. At constant temperature in the N_u phase some of the points and lines of opposite strength were observed to approach and annihilate each other (fig. 4b, c).

The texture changes principally when the temperature decreases below $T_{N_u-N_b}$ and new topological defects—walls connecting the points with two brushes or forming closed loops (fig. 4d, e)—appear. As boojums remain isolated, the walls do not contain point defects associated with four brushes. In addition, the contrast between the walls and their surrounding regions increases with decreasing temperature. By rotating the microscope stage it is possible to find an orientation where the wall becomes dark and indistinguishable from the background. This observation implies that the walls do not involve deformations in the plane of the cell, but are rather due to vertical deformations. In consequence we can identify these as Bloch walls [32], or equivalently as type-II inversion walls according to Nehring and Saupe [31]. As pointed out in ref. [31], Bloch walls have never been observed in a smectic C phase, which supports the magneto-optic observations that the behavior observed in TPB-(c)9(3) below $T_{N_u-N_b}$ is *not* caused by a uniaxial nematic-to-smectic C phase transition. Thus, the reason for the textural alterations must be connected with the very nature of the nematic phase(s).

Another possible mechanism for the wall's appearance is an anchoring transition in the director field n : the walls become unavoidable when n tilts away from the cell [31,32,34]. Earlier we noted that a tilt transition is inconsistent with the absence of magnetically induced changes in the optical transmission. We now discuss the textural issues. The geometry of the classical Bloch walls [31] implies the existence of twist deformations; this is because the corresponding twist elastic constant in a uniaxial nematic is smaller than that of the bend. Although this elasticity difference for the cyclic molecule in the N_u phase may not be quite so large as for a rod-shaped molecule, this general relationship is expected to be valid. For biaxial nematics the difference between twist and bend elastic moduli is likely to be even

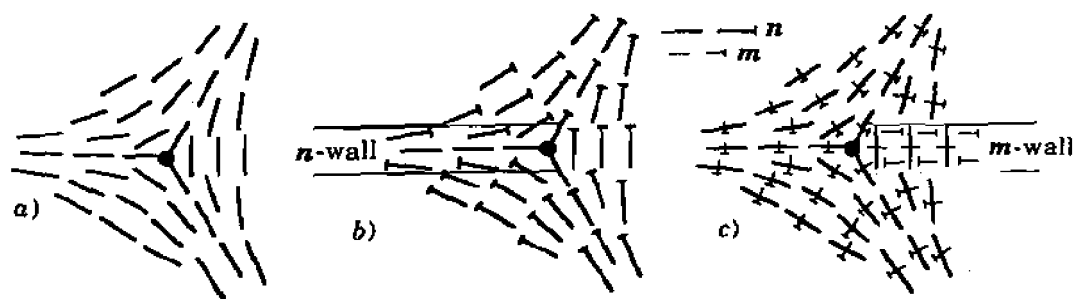


Fig. 4. - Structure of the $-1/2$ disclinations: a) uniaxial nematic with tangential anchoring; b) uniaxial nematic with tilted anchoring such that the twist n -wall appears; c) biaxial nematic with tangential anchoring for n and tilted anchoring for m ; the m -wall is perpendicular to the direction of n .

smaller [31-33]. Now, if the textures were due to a surface tilt transition in an otherwise N_u phase, the elasticity anisotropy would imply that the wall axis would preferentially emanate from the point defect along the axis (parallel to n) shown in fig. 4b). On the other hand, if the liquid crystal were biaxial, then owing to the relative isotropy of the elastic moduli, the wall could emanate at *any* angle (parallel to the plane of the cell) from the defect. Observations of textures using a red plate I (gypsum plate) revealed that the walls, in fact, emanate in apparently random directions from the defect, lending further evidence to the existence of biaxiality rather than a tilt transition.

An additional observation suggests the absence of a surface tilt transition. Polarizing microscopy showed textural changes in both the central homeotropic region and the planar regions near the edge of the cell occurring *simultaneously* as the temperature was decreased below $T_{N_u-N_b}$. It is highly unlikely that a surface tilt transition would occur at the same temperature in both regions, one planar and one homeotropic, given the very different interactions associated with the two alignments.

The textural changes near the edge of the cell (in the tangentially aligned region) might, on the other hand, be explained by a N_u-N_b transition in the following manner. Biaxiality requires the appearance of a second director field m (fig. 4c)), as measured in the birefringence experiments above. One may imagine a scenario in which m tilts with respect to the cell plane. (The principal director field n , which characterizes order in both the N_u and N_b phases, remains tangentially anchored.) Because of this nonzero m tilt ($\theta \neq 0$), a vector projection m_{xy} of m onto the cell plane does not satisfy the condition $m_{xy} = -m_{xy}$. With $m_{xy} \neq -m_{xy}$, isolated lines of half-strength are topologically prohibited (see, e.g., ref. [33]). A wall, as observed in fig. 4d) and e), provides a mechanism which permits the existence of nonisolated half-strength line disclinations in a biaxial phase. From the definition of a half-strength disclination, the director field undergoes an azimuthal rotation through $\pm \pi$ in one circuit around the disclination (fig. 4). For tangential anchoring of m , a $\pm \pi$ rotation of the director n transforms m into $-m$, which are equivalent to each other. However, for a tilted orientation, $m_{xy} \neq -m_{xy}$ and a $\pm \pi$ rotation of n must result in a plane of discontinuity where m_{xy} and $-m_{xy}$ meet each other. The half-strength line disclination is no longer isolated and represents the edge of the plane (fig. 4c)). In practice, the singular plane spreads out and forms the observed wall, providing a continuous reorientation of m_{xy} into $-m_{xy}$ through the region where the tilt is zero and m lies in the cell plane (fig. 4c)). Thus, the observation of these walls is consistent with the existence of biaxiality. At higher temperatures the biaxiality disappears, causing the disappearance of the walls.

To summarize, we have presented evidence that the cyclic thermotropic molecule TPB-(3)9(c) exhibits a uniaxial-biaxial nematic phase transition.

* * *

We are grateful to Drs. M. NEUBERT and A. SAUPE for useful discussions. This work was supported by the National Science Foundation under grants DMR-9122227 (J-FL, VP and CR), DMR-9206781 (VP), and DMR-8920147 (ODL).

REFERENCES

- [1] LI J.-F., PERCEC V. and ROSENBLATT C., *Phys. Rev. E*, 38 (1993) R1.
- [2] PERCEC V., KAWASUMI M., RINALDI P. L. and LITMAN V. E., *Macromolecules*, 25 (1992) 3851.
- [3] PERCEC V. and KAWASUMI M., *Adv. Mater.*, 4 (1992) 572.
- [4] PERCEC V. and KAWASUMI M., *Liq. Cryst.*, 13 (1993) 83.
- [5] PERCEC V. and KAWASUMI M., *Chem. Mater.*, 5 (1993) 826.
- [6] PERCEC V. and KAWASUMI M., *J. Mater. Chem.*, 3 (1993) 725.
- [7] PERCEC V. and KAWASUMI M., *J. Chem. Soc. Perkins Trans.*, 1 (1993) 1319.
- [8] PERCEC V. and KAWASUMI M., *Macromolecules*, 26 (1993) 3663.
- [9] PERCEC V. and KAWASUMI M., *Macromolecules*, 26 (1993) 3917.
- [10] PRIEST R. G. and LUBENSKY T. C., *Phys. Rev. B*, 13 (1976) 4159.
- [11] ALBEN R., *Phys. Rev. Lett.*, 30 (1973) 778.
- [12] SIH C. S. and ALBEN R., *J. Chem. Phys.*, 57 (1972) 3055.
- [13] MELNIK G., PHOTINOS P. and SAUPE A., *J. Chem. Phys.*, 88 (1988) 4046.
- [14] BOONBRAHM P. and SAUPE A., *J. Chem. Phys.*, 81 (1984) 2076.
- [15] ROSENBLATT C., *J. Phys. (Paris)*, 47 (1986) 1097.
- [16] YU L. J. and SAUPE A., *Phys. Rev. Lett.*, 45 (1980) 1000.
- [17] MALTHÊTE J., LIEBERT L., LEVELUT A.-M. and GALERNE Y., *C. R. Acad. Sci. Paris II*, 303 (1986) 1073.
- [18] CHANDRASEKHAR S., SADASIVA B. K., RATNA B. R. and RAJA N. V., *Pramāna*, 30 (1988) L-491.
- [19] PRAEFCKE K., KOHNE B., GÜNDOGAN B., DEMUS D., DIELE S. and PELZL G., *Mol. Cryst. Liq. Cryst. Lett.*, 7 (1990) 27.
- [20] PRAEFCKE K., KOHNE B., SINGER D., DEMUS D., PELZL G. and DIELE S., *Liq. Cryst.*, 7 (1990) 589.
- [21] PRAEFCKE K., KOHNE B., GÜNDOGAN B., SINGER D., DEMUS D., DIELE S., PELZL G. and BAKOWSKY U., *Mol. Cryst. Liq. Cryst.*, 198 (1991) 393.
- [22] HESSEL F. and FINKELMANN H., *Polym. Bull.*, 15 (1986) 349.
- [23] HESSEL F., HERR R.-P. and FINKELMANN H., *Makromol. Chem.*, 188 (1987) 1597.
- [24] EBERT M., HERRMANN-SCHÖNHERR O., WENDORFF J. H., RINGSDORF H. and TSCHIRNER P., *Makromol. Chem. Rapid Commun.*, 9 (1988) 445.
- [25] FAN S. M., FLETCHER I. D., GÜNDOGAN B., HEATON N. J., KOTHE G., LUCKHURST G. R. and PRAEFCKE K., *Chem. Phys. Lett.*, 204 (1993) 517.
- [26] ROSENBLATT C., *J. Phys. (Paris)*, 45 (1984) 1087.
- [27] GALERNE Y. and MARECEROU J. P., *Phys. Rev. Lett.*, 51 (1983) 2109.
- [28] CHIARELLI P., FAETTI S. and FRONZONI L., *J. Phys. (Paris)*, 44 (1983) 1061.
- [29] CHIARELLI P., FAETTI S. and FRONZONI L., *Phys. Lett. A*, 101 (1984) 31.
- [30] DI LISI G. A., ROSENBLATT C., GRIFFIN A. C. and HARI U., *Liq. Cryst.*, 7 (1990) 353.
- [31] NEHRING J. and SAUPE A., *J. Chem. Soc. Faraday Trans. 2*, 68 (1972) 1.
- [32] RYSCHENKOW G. and KLÉMAN M., *J. Chem. Phys.*, 64 (1976) 404.
- [33] KURIK M. V. and LAVRENTOVICH O. D., *Usp. Fiz. Nauk*, 154 (1988) 381 (*Sov. Phys. Usp.*, 31 (1988) 196).
- [34] PATEL J. S. and YOKOYAMA H., *Nature*, 362 (1993) 525.