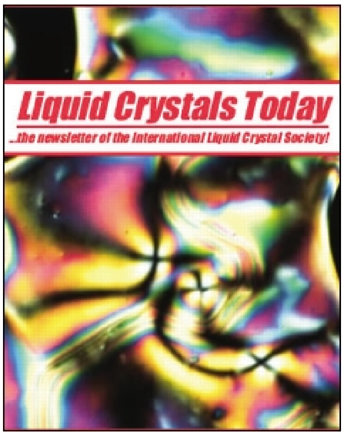

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Bharat R. Acharya[a]; Andrew Primak[a]; Satyendra Kumar[a]
[a] Department of Physics, Kent State University, Kent, Ohio 44242

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The Bent-Core Biaxial Nematic Phase

BHARAT R. ACHARYA*, ANDREW PRIMAK†
and SATYENDRA KUMAR#
Department of Physics, Kent State University, Kent, Ohio 44242

A biaxial nematic phase with D_{2h} symmetry has the mesogen's long and short transverse axes simultaneously aligned along the two orthogonal directors, **n** and **m**, respectively. Low-angle x-ray diffraction measurements in the nematic phase exhibited by three rigid bent-core mesogens clearly reveal its biaxiality. The diffraction results can be readily reproduced by *ab initio* calculations of molecular form factor assuming short-range positional correlations in the nematic phase with the apex of the core aligned along **m**.

The existence of a biaxial nematic liquid crystal phase, which possesses two orthogonal optic axes had been predicted [1] some time ago on the basis of symmetry considerations. To date, the existence of the biaxial nematic phase has been established only in complex three-component lyotropic mixtures [2]. Although there has been significant theoretical [3] work and several initial experimental [4] reports, its existence in *thermotropic* systems has not been confirmed [5]. Recent work [6–8] on bent-core mesogens has revealed a new subclass of liquid crystals having unique structural and physical properties. Computer simulations of "hard-boomerang fluids" suggested [9] that they could exhibit a stable biaxial nematic phase. A series of such boomerang-shaped molecules (see Fig. 1) with rigid cores [10] that exhibit a nematic phase was synthesized about three years ago. In their nematic phase, 2-brush disclinations were observed which indicated the possibility of a biaxial nematic phase [11]. Preliminary x-ray studies [12] of these nematic phases also suggested a biaxial nematic phase while ruling out cybotacticity. Recent experimental x-ray diffraction (XRD) results on this nematic phase under two different aligning (surface anchoring and electric) fields are in excellent agreement with calculations, which explicitly take into account the molecular bent-core shape, and confirm its biaxial nature.

Cells with sample thickness of 20 μm are prepared using plates of beryllium (Be) which are nearly transparent to x-rays. These plates are polished, insulated, and coated with polyimide (PI). The PI films are rubbed in an antiparallel direction (**R**) to achieve a homogeneous (i.e., **n** ∥ rubbing direction) orientation for sample ***B*** (Fig. 1). The sample thickness of ∼20 μm is

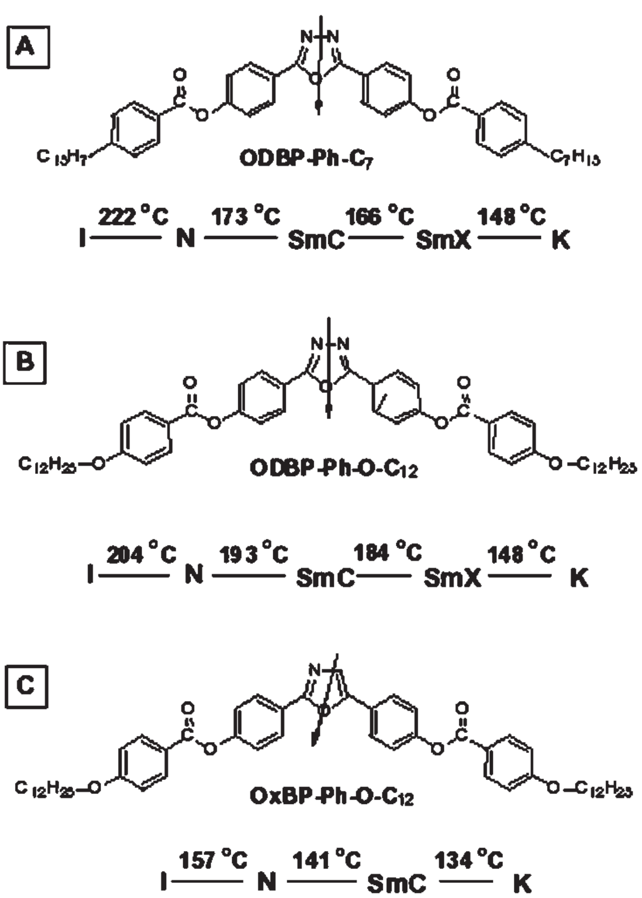

Figure 1. Molecular structures, phases, and transition temperature in °C of three rigid bent-core molecules. The arrows approximate the directions of the transverse dipole moments.

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* Present address: Platypus Technologies, 505 S. Rosa Road, Madison, WI 53 719

† Present Address: Pacific Northwest National Lab, P.O. Box 999/MS K8-98, Richland, WA 99 352

\# satyen@xray.kent.edu

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one order of magnitude larger than the value of smectic correlation lengths (typically≈1 μm) in a highly ordered and nearly single domain bulk smectic phase [13]. Hence, for all practical purposes, it is a *bulk* sample. The large transverse dipole moment (∼4D) bisecting the oxadiazole bent-core mesogen apex dominates the anticipated negative dielectric anisotropy of the mesophase. A square wave electric field was applied normal to the Be plates, to align **m** (i.e., apex bisectors) along the field.

With no applied electric field, the diffraction pattern taken at 195°C shows four diffuse small-angle peaks (Fig. 2(a)) of intensity about one order of magnitude higher than in the bulk sample with no alignment of **m**. The higher intensity arises from the alignment of the long axis of mesogens, or **n**, parallel to **R** and spontaneous orientation of **m** perpendicularly to **n** and parallel to the substrate. The four peaks have their origin in the intrinsic structure of this nematic phase, as we show below.

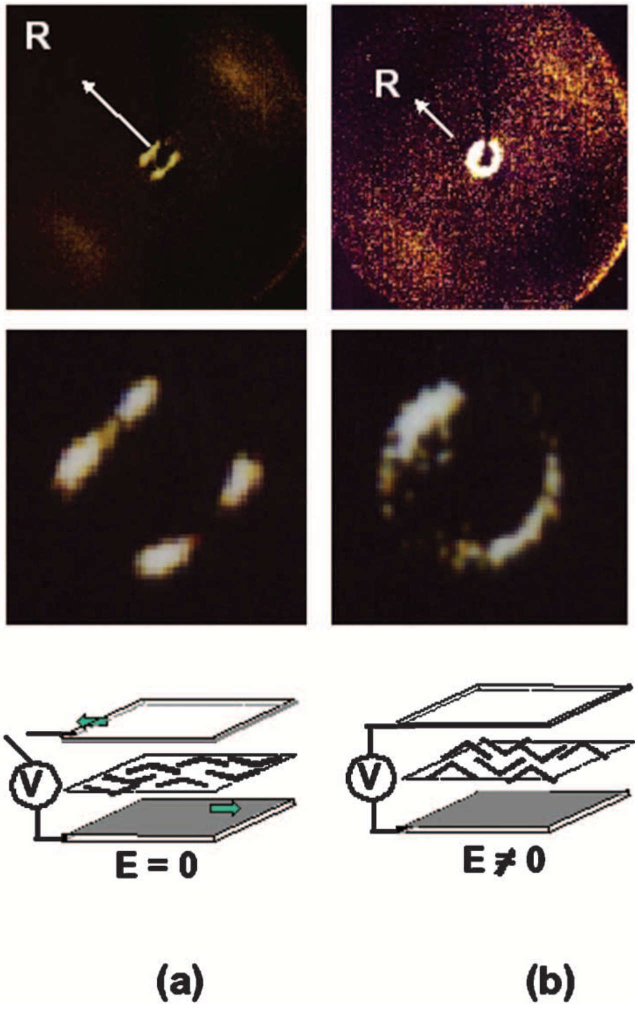

Figure 2. Two-dimensional nematic diffraction patterns from sample ***B*** aligned between two rubbed PI coated Be plates, (a) at zero electric field, **R** represents the rubbing direction; (b) at a field of 6×10^6V/m, the small-angle pattern changes into two diffuse arcs along **R**. The large-angle reflections remain unchanged as **n** is still parallel to **R**. The middle panels show small-angle scattering on expanded scale. Schematics at the bottom represent the molecular orientation.

When an electric field is applied, no changes occur until the field strength exceeds a threshold value of 6×10^6 V/m at 500 Hz when it succeeds in reorienting **m** perpendicular to the substrates. Consequently, the two pairs of reflections at small angle change to one pair of (weaker) reflections (Fig. 2(b)), which lie along the rubbing direction. The large-angle reflections at 19.1° remain essentially unchanged confirming that **n** is still parallel to the rubbing direction. The two small-angle reflections become weaker due to non-uniformity of the local electric field and microscopic variations in the anchoring energy of the rubbed PI surface causing the x-ray intensity to be distributed over a larger volume of the reciprocal space. The two distinct diffraction patterns, with and without applied field, clearly result from different orientations of **m** associated with the same orientation of **n**. The energy of interaction of molecular dipole moment of ∼4D in the applied field of 6×10^6 V/m is two orders of magnitude smaller than $K_B T$ ruling out the possibility of the observed effects being a field-induced phenomenon.

We use a simple model to calculate the average, over an ensemble of bent-core molecules, of the product of the molecular form factor $f(\mathbf{q})$ and the structure factor $S(\mathbf{q})$ to obtain the observed diffraction pattern. The form factor $f(\mathbf{q})$ is the Fourier transform of the molecular electron density function and reflects the molecular symmetry, while $S(\mathbf{q})$ originates from the density-density correlations and is related to the macroscopic structure of the phase.

The *bent-core* molecules are assumed to be composed of two solid cylindrical segments of length l and radius R, forming an apex angle φ (140°) between them. The electron density is considered to be distributed uniformly over the molecular volume. For an ensemble of boomerang molecules with their wingspans aligned along the z-direction in the N phase, the structure factor for small **q** values can be approximated by the well-known [14] Lorentzian form for the short-range (liquid-like) positional order with correlation lengths (ξ_x, ξ_y, and ξ_z in the three spatial directions) of the order of the molecular dimensions.

The contribution from $f(\mathbf{q})$ for small q in the $q_x - q_z$ plane of the experimental geometry, gives rise to four diffuse maxima and reflects the molecular symmetry. For a mono-domain biaxial nematic system, all the

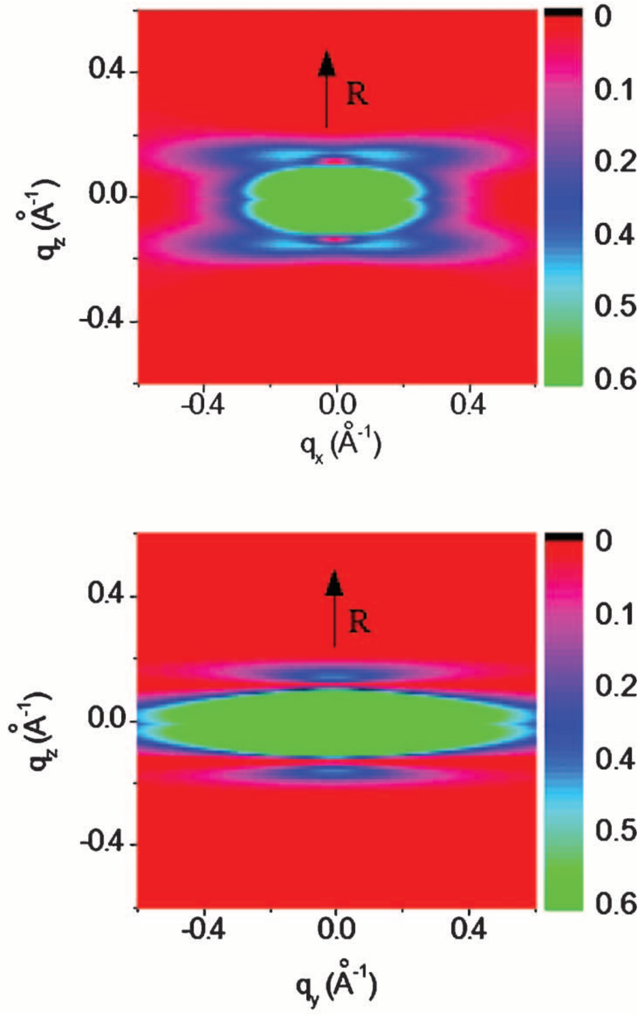

Figure 3. The small-angle x-ray reflections calculated for perfect biaxial order of bent-core molecules (a) in q_x-q_z plane and (b) in q_y-q_z plane.

boomerang wingspans (i.e., **n**) are assumed to align along the z-axis and the apex bisectors (i.e., **m**) are aligned along the x-axis. The angular separation between these peaks depends on the molecular parameters l, R, and φ. On the other hand, the contribution of S(**q**) for small q exhibits only two maxima corresponding to the wave vector $\pm q_0$ along the director. The observed x-ray scattering intensity is then the product $f(\mathbf{q}) \times S(\mathbf{q})$.

Figure 3(a) shows the plot of the intensity $I(q_x, q_z)$ calculated for the molecules of the sample ***B*** experiment with $l = 27$ Å, $R = 2.5$ Å, $\varphi = 140°$, $\xi_z = 2l\sin(\varphi/2) = 50.7$ $\mathring{A}$, and $\xi_x = 16.5$ $\mathring{A}$. The calculated pattern has four diffuse peaks as observed in the experiment, and a central bright spot (near $\mathbf{q} = 0$) where the form factor naturally has a maximum. The angular separation between the diffuse peaks is $\sim 80°$, in excellent agreement with the experimental value. It is important to note that the molecular form factor in the q_y-q_z plane does not show four spots, since the projection of molecular electron density onto the y−z plane is rod-like. The intensity $I(q_y, q_z)$ calculated using the same parameters as in Fig. 3(a) and $\xi_y = 8$ Å is depicted in Fig. 3(b).

If the boomerang molecules have only uniaxial order or if the director **m** of the biaxial nematic phase is not aligned, we have to average the product $f(\mathbf{q}) \times S(\mathbf{q})$ over a random distribution of **m**. In that case, both the I (q_x, q_z) and $I(q_y, q_z)$ plots would be identical and each would exhibit four diffuse spots. Peak intensities will be lower compared to the system with monodomain biaxial order, as the total scattered intensity will then be distributed over a circle in the reciprocal space. Clearly, the observation of two distinct x-ray patterns, similar to the patterns shown in Figs. 3(a) and 3(b), in two orthogonal planes of reciprocal space unambiguously proves that the nematic phase under study possesses the biaxial symmetry.

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