

The elusive thermotropic biaxial nematic phase in rigid bent-core molecules

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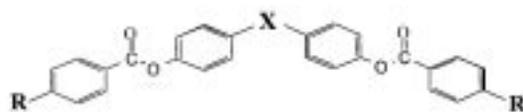
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Abstract. The biaxial nematic liquid crystalline phase was predicted several decades ago. Several vigorous attempts to find it in various systems resulted in mis-identifications. The results of X-ray diffraction and optical texture studies of the phases exhibited by rigid bent-core molecules derived from 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole reveal that the biaxial nematic phase is formed by three compounds of this type. X-ray diffraction studies reveal that the nematic phase of these compounds has the achiral symmetry D_{2h} , in which the overall long axes of the molecules are oriented parallel to each other to define the major axis of the biaxial phase. The apex of the bent-cores defines the minor axis of this phase along which the planes containing the bent-cores of neighboring molecules are oriented parallel to each other.

Keywords. Biaxial nematic phase; banana liquid crystals; X-ray diffraction; bent-core liquid crystals.

PACS Nos 42.70.Df; 61.30.Eb; 61.30.Gd; 83.80.Xz

Nematic liquid crystals (NLCs) possess long-range orientational order, along a spatial direction known as the director, and represented by the unit vector \mathbf{n} , but with no positional ordering [1]. An aligned NLC behaves as a uniaxial optical medium through which a beam of polarized light propagates along \mathbf{n} without a change in its polarization. Based on the symmetry considerations, the existence of a biaxial NLC phase, which possesses two orthogonal optic axes along which the polarization of propagating light remains unaffected, had been predicted [2] some time ago. One of the optic axes of the biaxial nematic phase is along the primary director \mathbf{n} along which the long axis of the molecules is oriented, and the second optic axis lies along the secondary director \mathbf{m} in the plane perpendicular to \mathbf{n} . To this day, only the existence of lyotropic biaxial nematic phases has been confirmed [3]. In spite of significant theoretical [4] work and several initial experimental [5,6] reports of its existence, the thermotropic biaxial nematic phase has remained elusive [7,8] and its existence unconfirmed. In one case [6], the nematic phase was found to have short-range fluctuations associated with the underlying SmC phase. These are commonly referred to as cybotactic clusters. In the second case [5], the uniaxial nematic phase composed of biaxial molecules gave rise to three X-ray reflections corresponding to the three molecular length scales. These were misconstrued as arising from a biaxial phase.



| Sample | X | - R |
|---|---|---------------------------------------|
| A | | C ₇ H ₁₅ |
| I - 222 - N - 173 - SmC - 166 - SmX - 141 - K | | |
| B | | - O - C ₁₂ H ₂₅ |
| I - 204 - N - 191 - SmC - (155 - 147) - SmX - 125 - | | |
| C | | - O - C ₁₂ H ₂₅ |
| I - 158 - N - 138 - SmC - 133 - SmX - 126 - K | | |

Figure 1. Molecular structures, phase sequence, and transition temperature in °C of the three bent-core molecules used in this study.

In recent years, the discovery of several novel mesophases formed by the bent-core molecules has engendered much scientific interest in them. The shape of these molecules has often been compared with bow and arrow, where the bent-core forms the body of the bow and a line parallel to molecule's overall long axis is parallel to the string. The direction of the arrow, along the apex of the core is used to define the direction of dipole moment, if present, for such molecules. The experimental [9,10] and theoretical [11,12] investigations of these systems reveal a new subclass of liquid crystals having unique structural and physical properties. Bent-core molecules had been suggested as good candidates to exhibit the biaxial nematic phase. Rigid bent-core compounds with large opening angle were considered suitable for the formation of such a phase. Dingemans and Samulski [13] have synthesized a series of such molecules that exhibit a nematic phase at higher temperatures, a smectic-C (SmC) phase and then a phase (which we denote as the SmX phase) that is very similar to the cubic phase, before crystallizing. In the nematic phase of these compounds, optical textures with two-brush disclinations were observed which are considered to be the hallmark of the biaxial nematic phase. Here, the results of X-ray diffraction (XRD) on this nematic phase in three compounds are reported. It is concluded that this phase is a biaxial nematic phase.

The three liquid crystal compounds (denoted as samples A, B, and C) investigated are derived from 2,5-bis-(*p*-hydroxyphenyl)-1,3,4-oxadiazole (see figure 1). Their synthesis has been described elsewhere [13]. They possess a rigid core with $\sim 140^\circ$ apex angle and a large dipole moment (~ 4 D). All compounds exhibit the same phase sequence (shown in figure 1), i.e., nematic (N), SmC, and an unknown SmX phase. Their optical textures were examined under polarizing microscopy at different temperatures. Two-dimensional XRD patterns were recorded using two different systems: (i) Siemens polymer powder

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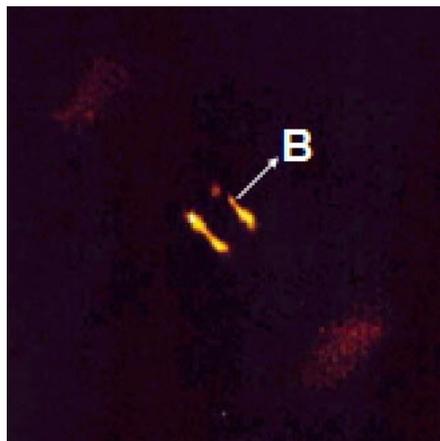


Figure 2. The two-dimensional diffraction pattern in the nematic phase of sample A aligned in a magnetic field. B shows four diffuse peaks at small angle.

diffractometer which uses the area detector X-1000 system. An *in situ* magnetic field of ~ 2.5 kG was used to orient the nematic director \mathbf{n} and (ii) high-resolution X-ray diffraction measurements which were made using an instrument based on an 18 kW Rigaku rotating anode X-ray source and a Huber four-circle goniometer. The $\text{CuK}\alpha$ line was selected using a pair of Si(111) single crystals as monochromator and analyzer. Samples were aligned in a strong magnetic field of ~ 50 kG produced by a superconducting magnet and placed in an oven with a temperature stability of ± 0.1 K.

In the N phase, all three samples exhibit typical nematic microscopic optical textures. Sample A shows a Schlieren texture with disclination lines of strength $S = 1/2$ [13,14]. The Schlieren texture of sample B shows both two and four brushes. Sample C, on the other hand, exhibits the marble texture.

The two-dimensional XRD patterns from the N phase have two pairs of diffuse but well-defined peaks at small angle (~ 44.2 Å) unlike a standard uniaxial nematic phase in which only one pair of diffuse peaks along the director (i.e., the magnetic field) is observed. The azimuthal angular separation between the diffused peaks is $\sim 80^\circ$. At large diffraction angles, two diffuse crescents are observed at ~ 4.65 Å arising from liquid-like structure factor in the direction perpendicular to the magnetic field. The line connecting the two large-angle diffuse peaks are oblique with respect to the lines connecting the opposite small-angle peaks in each pair. This is in contrast to the diffraction pattern of a uniaxial nematic phase in which the large-angle and small-angle peaks are always orthogonal to each other.

The possibility that the observed X-ray peaks may be arising due to the presence of the cybotactic groups, i.e., pre-transitional SmC-like fluctuations pertaining to the underlying phase, can be completely ruled out on the basis of the following: (a) Cybotacticity should be observed only in a narrow temperature range above the smectic phase. But the four small-angle peaks shown in figure 2 persist over the entire temperature nematic range which is as wide as 50 K (!) for sample A; (b) the positional order correlations in the nematic phase exists over a length scale that can be estimated from the half-width of the 2θ scans. It is found to be comparable to the molecular length (~ 44 Å). Moreover, it is



Figure 3. Two-dimensional diffraction pattern from sample B aligned between two PI coated and rubbed Be plates, at zero electric field. The pattern shows four diffuse peaks at small angle. R represents the rubbing direction.

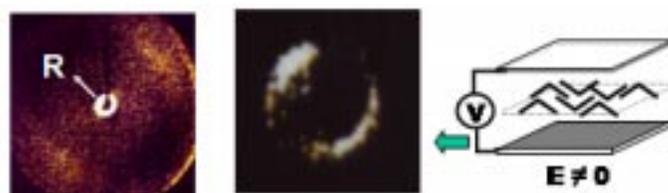


Figure 4. The small angle pattern changes into two diffuse arcs along R at small angle when the applied field is perpendicular to the substrate. The large-angle reflections remain unchanged indicating that the molecular long axes are still parallel to R. The middle column shows small-angle scattering on a magnified scale. Schematic on the right represent the experimental situation and the molecular orientation.

temperature independent; (c) the length scales calculated from the four diffuse peaks correspond to the molecular length ruling out any tilt which accompanies the formation of the cybotactic clusters; and (d) we were able to occasionally obtain single domains of the SmC phase by cooling the sample in a high magnetic field. These samples exhibit only one pair of small-angle X-ray reflections. However, such domains always reversibly melt into the N phase giving rise to four reflections, indicating that the structure of the nematic phase is unrelated to the underlying SmC phase.

The presence of the four small-angle X-ray peaks and the existence of only two brush disclinations in the optical texture [13] of sample A, strongly suggest a biaxial character for the N phase. In order to confirm the biaxial nature of the nematic phase of these materials, XRD measurements were performed while orienting both \mathbf{n} and \mathbf{m} . Sample cells of $20\ \mu\text{m}$ thickness were prepared using beryllium (Be) plates which are nearly transparent to X-rays. These plates were polished, insulated, and coated with polyimide (PI). The PI films were rubbed in antiparallel directions to achieve a homogeneous nematic (i.e., $\mathbf{n} \parallel$ rubbing direction) alignment for sample B. It should be pointed out that the sample size of $\sim 20\ \mu\text{m}$ is one order of magnitude larger than the value of smectic correlation lengths (typically $\leq 1\ \mu\text{m}$) of a highly ordered bulk smectic phase [15]. Hence, for all practical purposes, it is a bulk sample. A square wave voltage with variable amplitude was applied to create varying electric field perpendicular to the Be plates to reorient \mathbf{m} . XRD patterns were recorded for different field strengths. The resultant X-ray diffraction patterns are shown in figures 3 and 4.

In the absence of applied field, the diffraction pattern shows four diffuse peaks (figure 3) very similar to those obtained for the magnetic field aligned samples. This confirms that the bent-core molecules are aligned with \mathbf{n} parallel to the PI's rubbing direction and the

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four peaks arise from intrinsic structure of this nematic phase. As will be shown below, the secondary director \mathbf{m} , which most naturally lies along the molecular dipoles and in the plane containing the bent-core of the molecules, is oriented parallel to the substrate and the four peaks arise from a single domain of this biaxial nematic phase. Upon application of the electric field, no changes occur until the field strength exceeds a minimum value of 6×10^6 V/m at 500 Hz. Above this threshold, the applied electric field succeeds, in a manner similar to Frederick's transitions, in reorienting \mathbf{m} perpendicular to the substrates. Consequently, the two pairs of reflections at small angle change to one pair of (weaker) reflections at the angle (figure 4), which lie along the rubbing direction. The orientation of the large-angle (19.1°) peaks remains essentially unchanged confirming that \mathbf{n} still remains parallel to the rubbing direction. The two reflections are weaker due to non-uniformity of the local electric field and microscopic variations in the anchoring energy of the rubbed PI surface. These factors cause the diffracted X-rays to be distributed over a larger volume of reciprocal space, and hence lower intensity. Relatively higher intensity of the four reflections in the absence of the applied field was, evidently, due to uniform alignment of \mathbf{n} parallel to the substrate. The two distinct diffraction patterns, with and without applied field, clearly result from different orientations of \mathbf{m} associated with the same orientation of \mathbf{n} ruling out the possibility of this being a uniaxial nematic or a cybotactic nematic phase. In a uniaxial N phase with rotational symmetry about \mathbf{n} , all directions orthogonal to \mathbf{n} are equivalent and it is not possible to reorient the molecular planes. For a cybotactic nematic, it will not be possible to change four reflections into two with the application of electric field.

In order to correlate the observed X-ray diffraction pattern with the molecular structure, we use a simple model to calculate X-ray scattering from these bent-core molecules. X-ray scattering intensity from a large ensemble of molecules is simply a product of the molecular form factor and the structure factor of the corresponding phase averaged over the ensemble. Molecular form factor is the Fourier transform of the electron density distribution of the molecule and reflects the molecular symmetry, while a structure factor originates from the density-density correlation function and is related to the macroscopic structure of the ensemble.

As a simple approximation, a boomerang molecule is assumed to be composed of two solid cylindrical segments of length l and radius R , at an angle φ between them. The electron density is considered to be distributed uniformly over the molecular volume. The coordinate system is chosen such that the z -axis is parallel to the molecular long axis (i.e., the string of the bow) and the short axis (the arrow) is along the x -axis. The form factor for the boomerang is given by the sum of two similar Fourier transforms of electron density, one for each segment, i.e., $f(\mathbf{q}) \propto [\int_{\text{seg1}} e^{i\mathbf{q}\cdot\mathbf{r}} d^3r + \int_{\text{seg2}} e^{i\mathbf{q}\cdot\mathbf{r}} d^3r]$ where \mathbf{q} is the reciprocal lattice vector, and the integration is performed over each segment of the molecule. These integrals are evaluated in the respective segment coordinate systems and then transformed to laboratory frame to obtain an analytical expression for $f(\mathbf{q})$.

For an ensemble of boomerang molecules with their long molecular axes aligned along z -direction in the nematic phase, the structure factor for small \mathbf{q} values can be approximated by the well-known [16] Lorentzian-like structure factor for the short range (liquid-like) positional order with correlation lengths of the orders of the molecular dimensions as

$$S(\mathbf{q}) = \frac{1}{1 + \xi_z^2(q_z - q_0)^2 + \xi_x^2 q_x^2 + \xi_y^2 q_y^2},$$

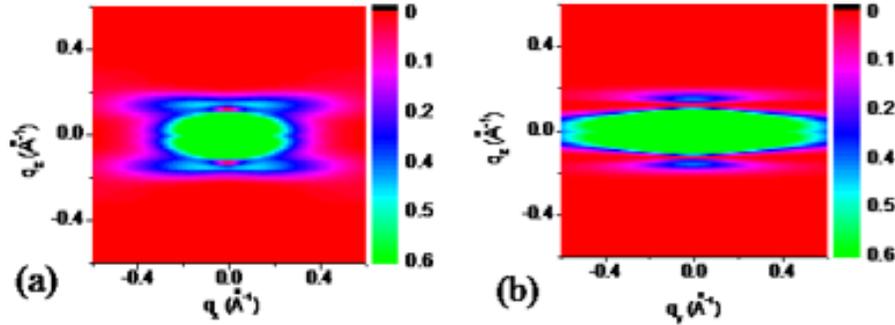


Figure 5. The X-ray scattering intensity in the reciprocal space calculated for perfect biaxial order of boomerang molecules with $l = 27 \text{ \AA}$, $R = 2.5 \text{ \AA}$, $\phi = 140^\circ$, $\xi_z = 53.6 \text{ \AA}$, $\xi_x = 16.5 \text{ \AA}$, and $\xi_y = 8 \text{ \AA}$ (a) in q_x - q_z plane and (b) in q_y - q_z plane small-angle reflections at an enlarged scale.

where ξ s are the correlation lengths along the respective directions and $q_0 = 2\pi/l$ is the smectic order wave vector.

The observed X-ray scattering intensity is then the product $f(\mathbf{q}) \times S(\mathbf{q})$ averaged over all possible director orientations in the different domains of the nematic phase. Note that, besides imposing the nematic ordering and asymmetry (or, inequality) in the correlation lengths along x - and y -directions, we have not made any explicit assumption regarding the biaxial order. The symmetry of the scattered X-ray intensity depends upon the molecular architecture of the boomerang. The contribution from the form factor for small \mathbf{q} values in the q_x - q_z plane gives rise to four diffuse peaks and reflects the molecular symmetry. The angular separation between these peaks depends on the molecular parameters l , R , and ϕ . On the other hand, the contribution from the structure factor for small q values exhibits only two peaks corresponding to the wave vector $\pm q_0$ along the director. In order to simplify things even further, let us impose a perfect biaxial symmetry in a mono-domain nematic system by assuming that all the strings of the boomerang (i.e., \mathbf{n}) are aligned along z -axis and the arrows (i.e., \mathbf{m}) aligned along x -axis. Then the scattered X-ray intensity $I(\mathbf{q}) = f(\mathbf{q}) \times S(\mathbf{q})$.

Figure 5a shows the plot of the intensity $I(q_x, q_z)$ calculated for the molecules used in the experiment with $l = 27 \text{ \AA}$, $R = 2.5 \text{ \AA}$, $\phi = 140^\circ$, $\xi_z = 2l \sin(\phi/2) = 53.6 \text{ \AA}$, and $\xi_x = 16.5 \text{ \AA}$. The pattern features four diffused peaks as observed in the experiment and a central (near $\mathbf{q} = 0$) bright spot where the form factor naturally has a maximum. The angular separation between the diffuse peaks is ($\sim 80^\circ$) in close agreement with the experimentally measured 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 corresponding plot for $I(q_z, q_y)$ calculated using the same parameters as in figure 5a and $\xi_y = 8 \text{ \AA}$ is depicted in figure 5b.

If the boomerang molecules have only uniaxial order, i.e., the second axis of the biaxial nematic phase is not aligned, then we have to average the product $f(\mathbf{q}) \times S(\mathbf{q})$ over a random distribution of \mathbf{m} to obtain the intensity. In this case, both the $I(q_x, q_z)$ and $I(q_z, q_y)$ plots would be identical and each would feature four diffuse spots, though less pronounced compared to the system with biaxial order as the total scattered intensity will then be distributed over a circle. Clearly, the existence of four diffuse peaks is not a suf-

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ficient condition for the biaxial ordering. However, the observation of two distinct X-ray patterns similar to the patterns shown in figures 4a and 4b in two orthogonal planes in the reciprocal space unambiguously proves that this nematic phase possesses biaxial symmetry, i.e., a phase in which both the primary and secondary directors are aligned.

To summarize, the observation of two distinct XRD patterns and two brushes in the Schlieren texture suggest the existence of a biaxial nematic phase in these bent-core molecules. We believe that the biaxiality arises from the spontaneous antiparallel arrangement of the molecular dipoles. The observation of a biaxial nematic phase in these thermotropic liquid crystals is further supported by the agreement between experimentally observed diffraction pattern and calculations based on the form factor of boomerang molecules and the structure factors for the nematic phase.

Acknowledgements

This work was supported by the NSF Science and Technology Center ALCOM Grant DMR-89-20147 (Kent State University) and the NSF DMR-94-12701 (University of North Carolina). The authors are grateful to J Luckhurst, P Heiney and P Toledano for very helpful discussions and help.

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