Biaxial Nematic Phase in Bent-Core Thermotropic Mesogens

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(Received 10 October 2003; published 9 April 2004)

A biaxial nematic phase had been predicted with D_{2h} symmetry, wherein the mesogen's long and short transverse axes are simultaneously aligned along the two orthogonal, primary and secondary directors, **n** and **m**, respectively. The unique low-angle x-ray diffraction patterns in the nematic phases exhibited by three rigid bent-core mesogens clearly reveal their biaxiality. The results of x-ray diffraction can be readily reproduced by *ab initio* calculations that explicitly include the bent-core shape in the form factor and assume short-range positional correlations.

DOI: 10.1103/PhysRevLett.92.145506 PACS numbers: 61.30.–v, 61.30.Eb, 61.30.Gd

The existence of a biaxial nematic liquid crystal phase, which possesses two orthogonal optic axes had been predicted [1] from symmetry considerations. To date, the existence of the biaxial nematic phase has been confirmed [2] only in complex lyotropic mixtures comprised of micellar aggregates. Although there has been significant theoretical [3] work and several initial experimental [4] reports, its existence in a low-molar-mass thermotropic system has not been confirmed [5]. In recent years, the discovery [6–9] of novel mesophases formed by the bent-core molecules has engendered much scientific interest in the possibility of the biaxial nematic phase. The bent-core shape of these molecules has often been compared with a bow, the molecule's overall long axis with the string (wingspan), and the apex of the core which defines the direction of the ''bend'' (or, dipole moment, if present) with the direction of the arrow. Computer simulations of ''hard-boomerang fluids'' previously suggested [10] that the bent-core shape could exhibit a stable biaxial nematic phase. Dingemans and Samulski synthesized a series of bent-core molecules with a rigid core that exhibit a nematic phase only with 2-brush [11,12] disclinations in their optical textures. In the uniaxial nematic (N) phase, the planar 4-brush singularity can be avoided by the director's escape in the third dimension. However, in the biaxial N phase there are three mutually perpendicular directions (or, directors). If one of the directors escapes, then a 4-brush disclination can only be formed by another director at a high cost in energy [12]. The absence of 4-brush defects [11] is, therefore, suggestive of the biaxial N phase.

X-ray diffraction (XRD) patterns of uniaxial N phases normally exhibit one pair of diffuse spots at small angle and a second pair at large angle along orthogonal directions due to short-range positional correlations associated with molecular length and width, respectively. However, preliminary x-ray studies [13] of these nematic phases showed splitting of the small angle reflections into two pairs suggesting a biaxial N phase. In this Letter, we present the results of XRD experiments that are in excellent agreement with the calculated diffraction pattern explicitly taking into account the bent-core shape of the mesogens and, thus, confirm their biaxial nature.

Primary differences between the three bent-core mesogens (samples ***A***, ***B***, and ***C***) investigated [11,14], Fig. 1, lie in their cores and in the nature of the terminal units. Sample ***C*** has the oxazole heterocycle core which shifts the dipole moment away from the bisector of the bent-core apex. They possess a rigid bent core with ~140° apex angle and a large dipole moment (~4D). Two dimensional XRD patterns were recorded using the Siemens polymer powder diffractometer which uses the area detector X-1000 system. An *in situ* magnetic field of ~2.5 kG was used to successfully orient the nematic

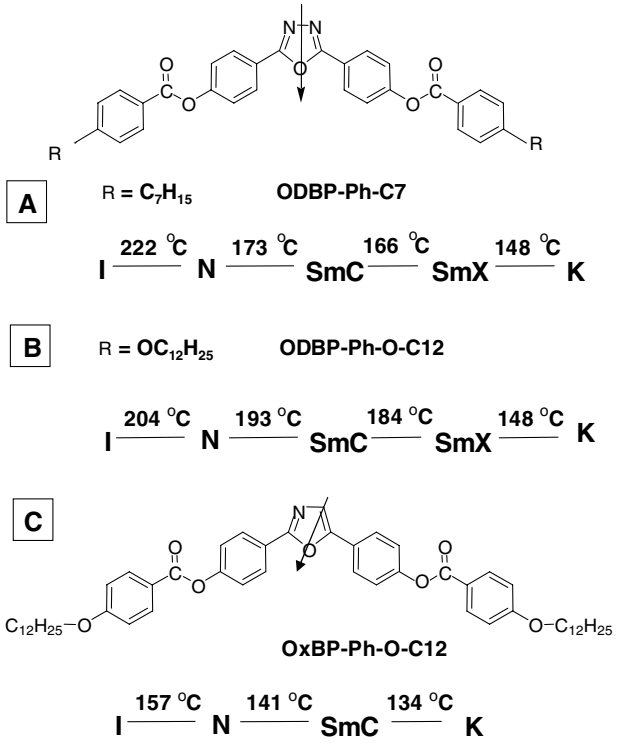

FIG. 1. Molecular structure, phase sequence, and transition temperatures of samples ***A***, ***B***, and ***C***. The arrows show the direction of the large (~4D) transverse dipole moment.

director **n** parallel to the field. In addition, high-resolution x-ray diffraction measurements were made using an 18 kW Rigaku rotating anode x-ray source, a Huber four-circle goniometer, and a pair of Si(111) single crystals as monochromator and analyzer to select the CuK_α line. Two types of sample cells were used. Samples filled in capillaries of 1 mm diameter were aligned in a strong magnetic field of ~50 kG. Thin cells with sample thickness of 20 μm were prepared using insulated beryllium (Be) plates which are nearly transparent to x rays. They were coated with polyimide (PI) films and rubbed in antiparallel directions to achieve homogeneous director orientation (i.e., **n** ∥ rubbing direction) for sample ***B***. This cell was used to apply an electric field between the plates and study the response of the director. The sample cells were placed in a homemade oven with temperature stability of ±0.1 K and then mounted onto the x-ray spectrometer.

In the *N* phase of all samples, XRD patterns, Fig. 2, show two pairs of diffuse peaks at small angle (~2.2°) unlike a uniaxial *N* phase in which only one pair of diffuse peaks along the primary director is observed. The diamagnetic anisotropy of these all-aromatic bent-core mesogens is positive and their bent-core shape aligns with its wingspans, i.e., **n**, along the field. The azimuthal angular separation between the pairs of diffuse peaks is ~80°. The large angle XRD pattern consists of two diffuse crescents at ~19.1°arising from a liquid-like structure factor in the direction perpendicular to **n**.

One can completely rule out the possibility of the four small angle peaks being due to the presence of the cybotactic groups, i.e., pretransitional fluctuations pertaining to the underlying smectic-*C* (Sm*C*) phase, on the basis of the following four results: (i) cybotacticity, being a temperature dependent pretransitional phenomenon, should be observed only in a narrow temperature range above the Sm*C* phase. However, these four peaks (Fig. 2) persist essentially over the entire range of the *N* phases (50 K for sample ***A***, 10 K for ***B***, and 16 K for ***C***); (ii) the positional order correlation length along **n** in the *N* phase, estimated from the half-width of the high-resolution 2θ scans, is comparable to the molecular length (~44 Å) and is temperature independent; (iii) the position of these peaks corresponds to the molecular length, ruling out any tilt which accompanies the formation of the cybotactic clusters; and (iv) the single domain Sm*C* phase, occasionally (and fortunately) obtained by aligning in a 50 kG field, exhibits only one pair of small angle x-ray reflections and always reversibly melts into the *N* phase with four reflections. This indicates that the alignment of the nematic phase is unrelated to the underlying phase.

In order to confirm the biaxial nature of the *N* phase, XRD measurements using the Be cell were performed while orienting both **n** and **m**, the latter defined as the mean orientation of the molecular (dipole or) apex bisectors. Since the sample thickness of ~20 μm in Be cells is 1 order of magnitude larger than the value of smectic

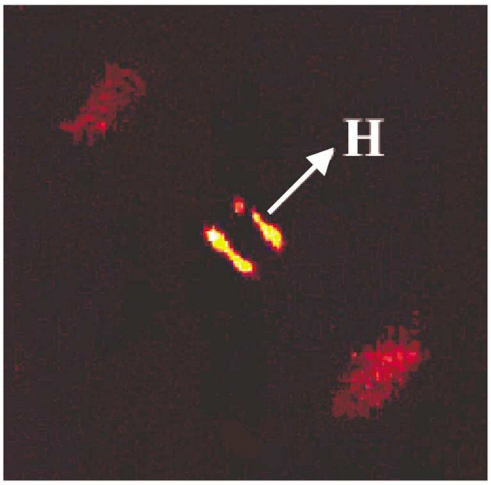

FIG. 2 (color). The two dimensional XRD pattern in magnetic field (**H**) aligned biaxial *N* phase of sample ***A*** at 195 °C.

correlation lengths (typically ≈1 μm) in a highly ordered and nearly single domain bulk smectic phase [15], for all practical purposes, it is a bulk sample. The large transverse dipole moment (~4*D*) bisecting the oxadiazole bent-core mesogen apex will dominate the anticipated negative dielectric anisotropy of the mesophase. A square wave electric field of different strengths is applied perpendicular to the Be plates to reorient **m** during XRD measurements.

With no applied field, the diffraction pattern shows four diffuse peaks [Fig. 3(a)] very similar to the magnetic field aligned capillary samples. Their integrated intensity was ~1 order of magnitude higher than in the capillary sample, after correcting for the difference in sample thickness. This increase in intensity is consistent with the alignment of **n** parallel to the PI's rubbing direction and spontaneous orientation of **m** parallel to the substrate and perpendicularly to **n**. The four peaks arise from the intrinsic structure of this *N* phase in the **n**-**m** (or, *z*-*x*) plane, as discussed later in this Letter. The intensity of the four peaks increases gradually with decreasing temperature, suggesting that either the biaxiality order was increasing or the alignment of **m** was improving. When an electric field is applied, no changes occur until the field strength exceeds a (Frederick's transition) threshold value of 6×10^6 V/m at 500 Hz and reorients **m** perpendicular to the Be substrates. Consequently, the two pairs of reflections at small angle change to one pair of (weaker) reflections [Fig. 3(b)] 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 are weaker due to the nonuniformity of the local electric field and variations in local anchoring energy. These factors cause the diffracted x rays to be distributed over a larger volume of the reciprocal space resulting in lower intensity. The two distinct diffraction patterns, with and without applied field, clearly result from different

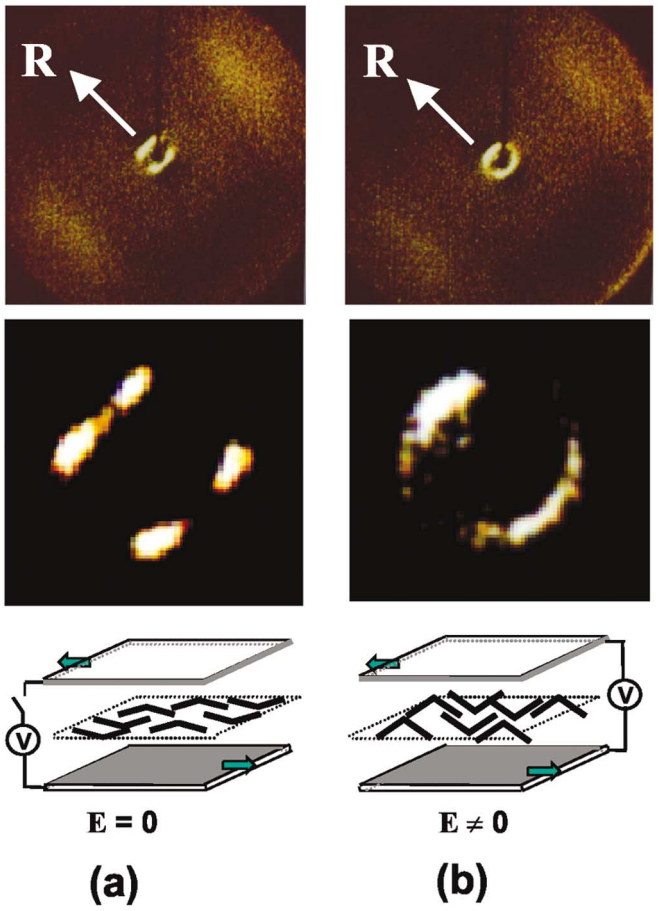

FIG. 3 (color). Two dimensional XRD patterns of sample ***B*** aligned between two Be plates along the rubbing direction represented by **R** and the green arrows (a) at zero electric field and (b) with field applied perpendicular to the substrate. Small angle (shown magnified in middle panels) pattern changes to two diffuse arcs along **R** while large angle reflections remain unchanged. Intensity difference in the two arcs in (b) arises due to slight instrument misalignment. Schematics at the bottom represent the corresponding experimental situation and molecular orientation.

orientations of **m** associated with the same orientation of **n** ruling out the possibility of this being a uniaxial nematic. In a uniaxial phase, all directions orthogonal to **n** are equivalent. The energy of interaction of the molecular dipole moment of $\sim 4D$ in a field of 6×10^6 V/m is 2 orders of magnitude smaller than $K_B T$. This rules out the possibility of the observed reorientation of **m** being a field induced phenomenon.

We use a simple model to calculate x-ray scattering intensity for a large ensemble of such bent-core molecules. The product of the molecular form factor (i.e., Fourier transform of molecular electron density), $f(\mathbf{q})$, and the structure factor (i.e., density-density correlations), $S(\mathbf{q})$, gives the observed diffraction pattern. We assume the bent-core molecules to be composed of two solid cylindrical segments of length l and radius R, forming an apex angle φ between them. The electron density is taken to be uniform over the segment volumes. The coordinate system is chosen such that the z axis is parallel to the molecular long axis (i.e., string) and the apex bisector along the x axis. The form factor for the bent cylinder is a sum of two Fourier transforms of electron density, one for each segment, i.e., $f(\mathbf{q}) = |\int_{\text{seg1}} e^{i\mathbf{q}\cdot\mathbf{r}} d^3r + \int_{\text{seg2}} e^{i\mathbf{q}\cdot\mathbf{r}} d^3r|^2$ where $\mathbf{q}$ is the momentum transfer vector. Each of these integrals is evaluated in the respective segment coordinate systems and then transformed back to the laboratory frame to obtain an analytical expression for $f(\mathbf{q})$.

For bent-core molecules with their long axis aligned along the z direction in the N phase, the structure factor for small $\mathbf{q}$ values can be approximated by a [16] Lorentzian for short-range positional (liquid-like) order correlation lengths of the order of the molecular dimensions, $S(\mathbf{q}) = [1 + \xi_z^2(q_z - q_0)^2 + \xi_x^2 q_x^2 + \xi_y^2 q_y^2]^{-1}$ where, ξ's are the correlation lengths in the respective spatial directions and $q_0 = 2\pi/L$, L being the molecular length.

Note that, other than imposing the nematic ordering and asymmetry, i.e., inequality in the correlation lengths along the x and y directions, we have so far not made any explicit assumption regarding the biaxial order. 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, as shown in Fig. 4(a). The angular separation between these peaks, $\varphi = 140°$, arises from the molecular structure, i.e., the angle between two cylindrical segments. On the other hand, the structure factor [Fig. 4(b)] for small $\mathbf{q}$ exhibits only two peaks at $\pm q_0$ along $\mathbf{n}$. Now if a perfect biaxial order is imposed by assuming that $\mathbf{n} \parallel \hat{z}$ and $\mathbf{m} \parallel \hat{x}$, the observed x-ray scattering intensity is $I(\mathbf{q}) = f(\mathbf{q}) \times S(\mathbf{q})$.

Figure 4(c) shows the plot of the intensity $I(q_x, q_z)$ calculated for $l = 27$ Å, $R = 2.5$ Å, $\varphi = 140°$, $\xi_z = 2l \sin(\varphi/2) = 50.7$ Å, and $\xi_x = 16.5$ Å. It features 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 two pairs of 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 peaks, 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 for $I(q_x, q_z)$ and $\xi_y = 8$ Å, is depicted in Fig. 4(d).

If the bent-core molecules have only uniaxial order or the second axis 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 $\mathbf{m}$. In that case, both the $I(q_x, q_z)$ and $I(q_y, q_z)$ plots would be identical and each would feature four diffuse peaks, though less pronounced 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, while the existence of four diffuse peaks is not a sufficient

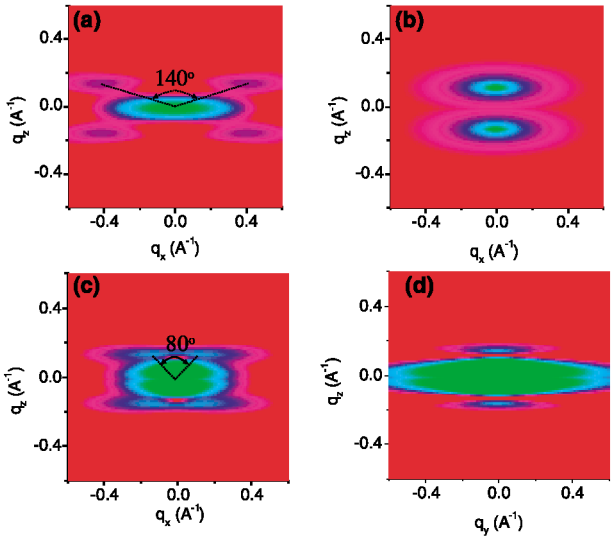

FIG. 4 (color). (a) Form factor calculated for a bent-cylindrical shape molecule. (b) Structure factor for the small angle reflection. The small angle x-ray pattern calculated from $f(\mathbf{q}) \times S(\mathbf{q})$ in (c) the q_x-q_z plane and (d) the q_y-q_z plane for perfect biaxial order.

condition for biaxiality, the observation of two distinct x-ray patterns—similar to Figs. 4(c) and 4(d)—in two orthogonal planes of the reciprocal space unambiguously proves that this nematic phase possesses biaxial symmetry. Recent optical measurements [17] on a similarly prepared and aligned (i.e., with rubbed substrates and electric field) N phase of sample ***A*** revealed that the two indices of refraction in the plane perpendicular to $\mathbf{n}$ are different suggesting biaxiality. Furthermore, 2D powder NMR spectra [17] yield a biaxiality parameter of ~ 0.11 and support the inferences drawn here.

In conclusion, the observation of two distinct XRD patterns with and without applied electric field show that the N phase of these bent-core mesogens is a biaxial phase. Orientational correlations transverse to the primary director are probably driven by excluded volume interactions and supplemented by electrostatic interactions associated with their large transverse dipole moments. The existence of the biaxial nematic phase is confirmed by excellent agreement between the experimentally observed diffraction pattern and calculations based on the form factor of bent-core shaped molecules and the structure factor for the N phase. Although previous investigations [11] suggest only one nematic phase which we show here to be biaxial, the existence of a narrow uniaxial nematic phase in these compounds cannot be completely ruled out.

This work was supported by the National Science Foundation Grants No. DMR-03-12792 and No. DMR-87-20147. The authors are grateful to Professor G. Luckhurst, Professor T. Lubensky, Professor P. Heiney, and Professor P. Toledano for extremely helpful discussions. The authors thank Professor E. T. Samulski and Professor T. Dingeman for providing the materials.

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[1] M. J. Freiser, Phys. Rev. Lett. **24**, 1041 (1970).
[2] L. J. Yu and A. Saupe, Phys. Rev. Lett. **45**, 1000 (1980); A. Saupe, P. Boonbrahm, and L. J. Yu, J. Chem. Phys. **80**, 7 (1983).
[3] R. Alben, J. Chem. Phys. **59**, 4299 (1973); Phys. Rev. Lett. **30**, 778 (1973); D.W. Allender, M. A. Lee, and N. Hafiz, Mol. Cryst. Liq. Cryst. **124**, 45 (1985).
[4] S. Chandrasekhar, V. N. Raja, and B. K. Sadashiva, Mol. Cryst. Liq. Cryst. Lett. **7**, 65 (1990); J. Malthele *et al.*, C.R. Acad. Sci. Paris **303**, 1073 (1986).
[5] I. G. Shenouda, Y. Shi, and M. Neubert, Mol. Cryst. Liq. Cryst. **257**, 209 (1994); J. Hughes *et al.*, J. Chem. Phys. **107**, 9252 (1997).
[6] D. Coleman *et al.*, Science **301**, 1204 (2003); D. M. Walba *et al.*, Science **288**, 2181 (2000); R. Macdonald *et al.*, Phys. Rev. Lett. **81**, 4408 (1998); M. Nakata *et al.*, Liq. Cryst. **28**, 1301 (2001).
[7] T. Niori *et al.*, J. Mater. Chem. **6**, 1231 (1996); D. R. Link *et al.*, Science **278**, 1924 (1997); G. Heppke *et al.*, Phys. Rev. E **60**, 5575 (1999).
[8] T. C. Lubensky and L. Radzihovsky, Phys. Rev. E **66**, 031704 (2002); V. L. Lorman and B. Mettout, Phys. Rev. Lett. **82**, 940 (1999); P. Tolédano *et al.*, Phys. Rev. E **62**, 5143 (2000); A. Roy *et al.*, Phys. Rev. Lett. **82**, 1466 (1999).
[9] G. Pelzl, S. Diele, and W. Weissflog, Adv. Mater. **11**, 707 (1999); W. Wiessflog *et al.*, Liq. Cryst. **11**, 1603 (2001).
[10] P. I. C. Teixeira, A. J. Masters, and B. M. Mulder, Mol. Cryst. Liq. Cryst. **323**, 167 (1998); G. R. Luckhurst, Thin Solid Films **393**, 40 (2000).
[11] T. J. Dingemans and E. T. Samulski, Liq. Cryst. **27**, 131 (2000).
[12] C. Chiccoli *et al.*, Phys. Rev. E **66**, 030701(R) (2002).
[13] B. R. Acharya and S. Kumar, Bull. Am. Phys. Soc. **45**, 101 (2000); B. R. Acharya *et al.*, Pramana **61**, 231 (2003).
[14] Other smectic phases of sample ***B*** reported [11] appear to be coexistence of different phases.
[15] A. Primak, M. Fisch, and S. Kumar, Phys. Rev. Lett. **88**, 035701 (2002).
[16] W. L. McMillan, Phys. Rev. A **5**, 1673 (1973).
[17] J. A. Olivares *et al.*, Phys. Rev. E **68**, 041704 (2003); L. A. Madsen *et al.*, Phys. Rev. Lett. **92**, 145505 (2004).