

Structure of Liquid Crystalline Phases of a Novel Class of Achiral Bent-core Mesogens

S.-W. Kang,¹ Veena Prasad,² and Satyendra Kumar¹

¹Department of Physics, Kent State University, Kent, OH 44242, USA

²Center for Liquid Crystal Research, P.B.No.1329, Jalahalli, Bangalore – 560 013, India

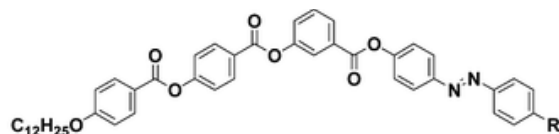
Introduction

Achiral bent-core mesogens [1] are new and an exciting area of research in the field of ferro-/antiferro-electric liquid crystals [2-6]. Although the constituent molecules here are achiral, phases exhibited by such compounds are often chiral with potential for use in practical applications [5]. Recently, we have synthesized [7] bent-core compounds with an azo (-N=N-) linkage. The azo linkage undergoes *trans-cis* isomerisation in under UV illumination making these materials photoresponsive.

The results of our investigations to determine the nature and structure of the mesophases using optical microscopy and x-ray diffraction techniques are summarized here.

Methods and Materials

We synthesized a new series of bent-core azo compounds **1a-e** and **2a-e** shown in Fig. 1. The details of chemical synthesis and characterization of these compounds can be found in the reference [8]. We selected three representative compounds, **1c**, **1e**, and **2e** for investigations.



1a-e: R = OC₄H₉, OC₆H₁₃, OC₈H₁₇, OC₁₀H₂₁, OC₁₂H₂₅

2a-e: R = C₄H₉, C₆H₁₃, C₈H₁₇, C₁₀H₂₁, C₁₂H₂₅

Fig. 1: Molecular structures of the liquid crystalline azo compounds of the two series **2a-e** and **1a-e**.

The samples were sealed in 1mm diameter Lindeman capillaries with 10 μm thick walls. They were heated above the clearing point and cooled in the presence of a magnetic field of ~ 2.5 kG to the first liquid crystalline phase to obtain well aligned samples. X-ray studies were performed at the Advanced Photon Source of Argonne National Laboratory using the Midwestern Universities Collaborative Team's spectrometer on Sector 6. X-ray wavelength of 1.26515 \AA was used. The diffraction patterns were collected using a high-resolution MAR3450 area detector placed at a distance of 362.9 mm from the sample. The data was calibrated against Silicon powder. Sample temperature was controllable with a precision of $\pm 0.1\text{K}$ using a home made oven and temperature controller.

Results and Discussion

Optical Textures

The compound **1c**, on cooling from the isotropic phase, forms a fan-shaped texture along with mosaic pattern in some regions. This characteristic texture of the **B₁** phase is shown in Fig. 2(a). On further cooling, the **B₁** phase transforms in to an unknown **B_x** phase, Fig. 2(b). The appearance of striations over the texture of the **B₁** phase upon cooling in to the **B_x** phase is similar to the changes seen at the Crystal-B to Crystal E phase transition [9] of calamitic liquid crystals. It is indicative of the

freezing of rotational diffusional motion about the molecules' long axis. On cooling from the isotropic phase, compounds **1e** and **2e** form textures characteristic of the **B₂** phase, shown in Fig. 2(c) and (d), respectively.

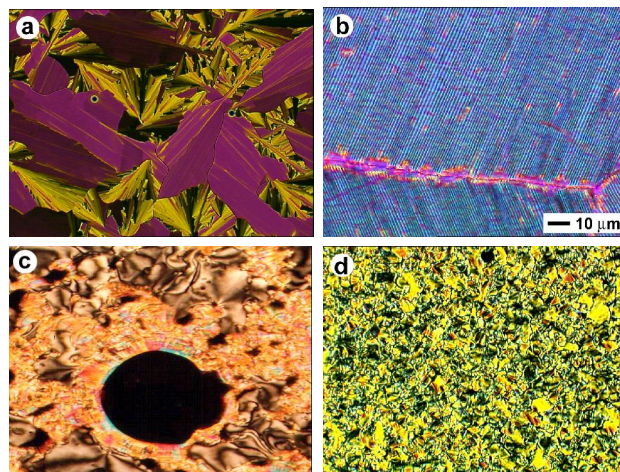


Fig. 2: (a) The texture of **B₁** phase of **1c** at 119.0°C. Further cooling yields the phase **B_x**, shown in (b). (c) The unspecified texture of **B₂** phase along with the schlieren texture in some regions) exhibited by **1e** at 114.5°C and (d) schlieren texture of the **B₂** phase of **2e**.

The optical texture of these phases changes with the brightness of the microscope lamp. In order to determine this effect, the temperature at which the characteristic texture of the **B₂** phase appears upon cooling is recorded under different levels of illumination. The transition temperature drops, Fig. 3, by more than 4K as the incident power is increased from 0 to ~ 0.85 mW/cm^2 . The biggest change in transition temperature was obtained in sample **2e** [8]. The presence of *cis* isomers formed under illumination appears to act as an impurity in reducing the transition temperature [10, 11].

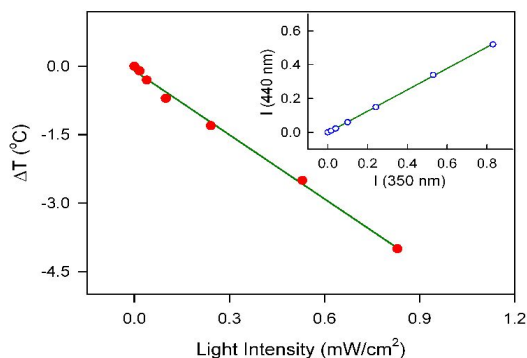


Fig. 3: The isotropic to the **B₂** transition temperature for **2e** as a function of light intensity of 350 nm. Inset shows the relative intensity of the 350 and 440 nm lines in the lamp's spectrum.

Structure of Phases

The x-ray results in the two phases of **1c** are shown in Fig. 4. The sample melts into the B_1 phase that exhibits a liquid like diffraction ring at 4.57 Å and two rings at 36.4±0.2 Å and 23.6±0.1 Å, which are typically observed in the B_1 phase. Upon cooling slowly from the isotropic phase, the presence of a weak magnetic field aligns it well, Fig. 4(a). This diffraction pattern has its origin in a two dimensional rectangular cell with dimensions of 36.4±0.2 and 30.4±0.2 Å, and is very similar to the previously reported results [5].

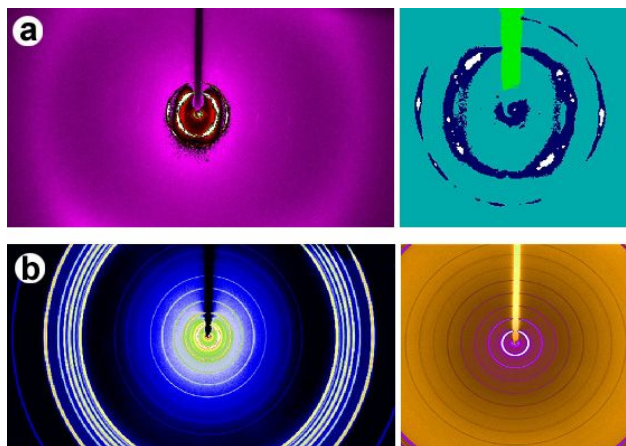


Fig. 4: X-ray diffraction patterns of sample **1c**. The panels at right show the small angle scattering at high magnification. (a) B_1 phase at 115°C. (b) In the B_x phase at ~1.5 K below the transition, 9 harmonics of the reflection at 54.2 Å are seen at small angle.

Upon further cooling the sample **1c** below 111°C, it undergoes a transition to the B_x phase with the diffraction pattern shown in Fig. 4(b). The first small angle reflection corresponds to 54.2±1 Å. Up to 9 harmonics of this primary reflection corresponding to lattice dimensions of 54.2/ n , where $n = 1, 2, \dots, 9$, are observed. Several reflections are observed in the range from 4.79 to 3.22 Å from the in-plane crystalline order. However, this phase does not have a true three-dimensional order as evident from the absence of any intervening reflections, i.e., in between the peaks corresponding to the in-plane structure and small angle peaks arising from smectic layers. Based on these data, we conclude that this phase consists of extremely well defined bilayers with crystalline in-plane order but no inter-layer positional correlations. One expects the layers in such a phase to be able

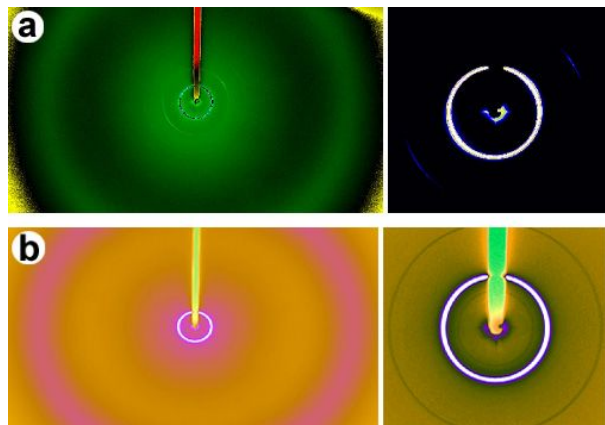


Fig. 5: Diffraction patterns in the partially aligned B_2 phase of (a) **1e** at 111.4°C and (b) **2e** at 111.5°C. The panels at right show the small angle region on an expanded scale.

to freely slide relative to each other and act like a highly lubricating medium. This expectation was qualitatively confirmed by shearing the phase between two glass plates.

The x-ray diffraction patterns, Fig. 5, of compounds **1e** and **2e**, were taken at 111.4 and 111.5°C, respectively, after cooling from the isotropic phase. Fig. 6 shows the x-ray intensity vs. 2θ for the three samples in their B_1 or B_2 phases. For sample **1e**, diffraction peaks appear at 41.7±0.8 Å, 20.42±0.1 Å, 13.51±0.05 Å and 4.57 Å. For sample **2e**, the reflections correspond to 42.8±0.8 Å, 21.06±0.1 Å, 13.95±0.05 Å, and 4.70 Å. For both samples, the first peak is the brightest and the ratio of the lattice spacings corresponding to the three reflections is 1:2:3 indicating a lamellae or smectic type ordering.

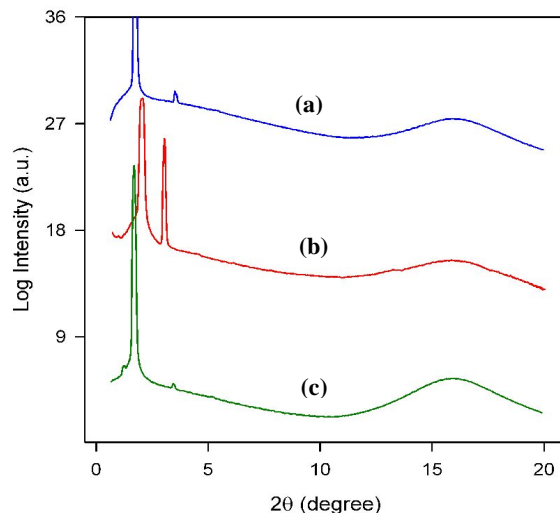


Fig. 6: Intensity vs 2θ for samples: (a) **1e** at 120°C, (b) **1c** at 139°C, and (c) **2e** at 98°C. The curves have been shifted vertically for clarity.

Acknowledgments

This research was supported by the US National Science Foundation grant DMR-0312792. The use of the Advanced Photon Source (APS) was supported by the U.S. DOE, Basic Energy Sciences, Office of Science, under Contract No. W-31-109-Eng-38. The Midwest Universities Collaborative Access Team's sector is supported by the U.S. DOE, Basic Energy Sciences, Office of Science, through the Ames Laboratory under Contract No. W-7405-Eng-82.

References

- [1] T. Niori, et al., *J. Mater. Chem.*, 1996, **6**, 1231; J. Watanabe, et al., *Jpn. J. Appl. Phys.*, 1998, **37**, L139.
- [2] D. Shen, et al., *J. Mater. Chem.*, 1999, **9**, 661.
- [3] G. Pelzl, et al., *Liq. Cryst.*, 1999, **26**, 135.
- [4] D. Shen, et al., *J. Am. Chem. Soc.*, 2000, **122**, 1593.
- [5] G. Pelzl, S. Diele and W. Weissflog, *Adv. Mater.*, 1999, **11**, 707 and the references therein.
- [6] D.M. Walba, et al., *Science*, 2000, **288**, 2181.
- [7] V. Prasad, D. S. S. Rao and S. K. Prasad, *Liq. Cryst.*, 2001, **28**, 643; V. Prasad, *Mol. Cryst. Liq. Cryst.*, 2001, **363**, 167.
- [8] V. Prasad, et al., *J. Mater. Chem.*, 2004, **14**, 1495.
- [9] D. Demus and L. Richter, *Textures of Liquid Crystals*, Verlag Chemie: New York (1978).
- [10] T. A. Krentsel, O. D. Lavrentovich, and S. Kumar, *Mol. Cryst. Liq. Cryst.*, 1997, **304**, 463.
- [11] Y. Lansac, et al., *Nature*, 1999, **398**, 54.