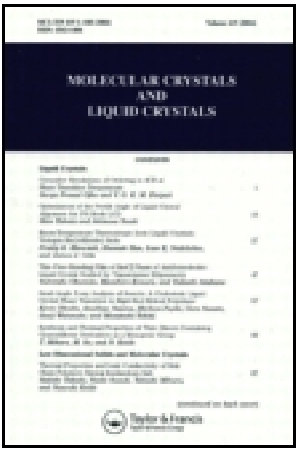
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 11:06
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Molecular Crystals and Liquid Crystals
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gmcl20

Extraordinary Field Sensitivity of Bent-Core Cybotactic Nematics

F. Vita [a], I. F. Placentino [a], E. T. Samulski [b] & O. Francescangeli [a]

[a] Dipartimento SIMAU and CNISM, Università Politecnica delle Marche, Ancona, Italy

[b] Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, USA

Published online: 02 Apr 2013.

To cite this article: F. Vita, I. F. Placentino, E. T. Samulski & O. Francescangeli (2013) Extraordinary Field Sensitivity of Bent-Core Cybotactic Nematics, Molecular Crystals and Liquid Crystals, 573:1, 46-53, DOI: 10.1080/15421406.2013.763336

To link to this article: http://dx.doi.org/10.1080/15421406.2013.763336

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the "Content") contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms & Conditions of access and use can be found at http://www.tandfonline.com/page/terms-and-conditions

Mol. Cryst. Liq. Cryst., Vol. 573: pp. 46–53, 2013
Copyright © Taylor & Francis Group, LLC
ISSN: 1542-1406 print/1563-5287 online
DOI: 10.1080/15421406.2013.763336

Extraordinary Field Sensitivity of Bent-Core Cybotactic Nematics

F. VITA,[1] I. F. PLACENTINO,[1] E. T. SAMULSKI,[2]
AND O. FRANCESCANGELI[1,*]

[1]Dipartimento SIMAU and CNISM, Università Politecnica delle Marche, Ancona, Italy
[2]Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, USA

Several experimental and theoretical studies conclude that the unconventional properties of bent-core nematics derive from cybotactic clusters, that is, very short-range correlation fluctuations of positional and orientational order. We show how X-ray diffraction from oxadiazole-based compounds strongly supports this model. Moreover, we recently reported an extraordinary magnetic-field-induced shift of both nematic-isotropic and smectic-C-nematic phase transition temperatures ($\Delta T = 4$ K for $B = 1$ T). We review this effect, which is orders of magnitude larger than previously reported data, in the framework of the cybotactic model of bent-core nematics.

Keywords Bent-core mesogens; Cybotaxis; Phase transitions

Introduction

In the recent past, the scientific interest in bent-core mesogens (BCMs) has been mainly focused on the spontaneous polar order exhibited by their smectic (Sm) phases [1,2]. Nowadays, growing attention is being focused on the odd properties of the nematic (N) phase of BCMs. Some of the extraordinary effects reported in the literature in the last few years include: biaxiality [3–5], ferroelectric-like behavior [6], giant flexoelectricity [7], unusual rheological properties [8], and large flow birefringence [9]. In particular, the claims of biaxiality [4,5], a property theoretically predicted but never experimentally observed in conventional (calamitic) nematics, soon fueled an intense scientific debate. The main controversial points concerned: (i) the correct interpretation of experimental data, in particular a characteristic *four-spot pattern* often observed in small-angle X-ray diffraction (XRD) measurements performed on aligned BCMs [10–15]; (ii) the fact that the observed *macroscopic* biaxiality might actually be induced in a *microscopically* (locally) biaxial sample by external effects, for example, surface interactions or magnetic/electric fields [16,17]. Eventually, a careful analysis of the experimental data led to the development of a molecular model of the BCMs' N phase, the cybotactic nematic (N_{cyb}) model, originally proposed in 2002 [18] and now widely embraced by the scientific community. According to this model, the N phase of BCMs is characterized by very short range positional and orientational order correlation fluctuations (*cybotactic clusters*) [17,19]. These clusters

---

[*] Address correspondence to O. Francescangeli, Dip. SIMAU and CNISM, Università Politecnica delle Marche, via Brecce Bianche, Ancona 60131, Italy. E-mail: o.francescangeli@univpm.it

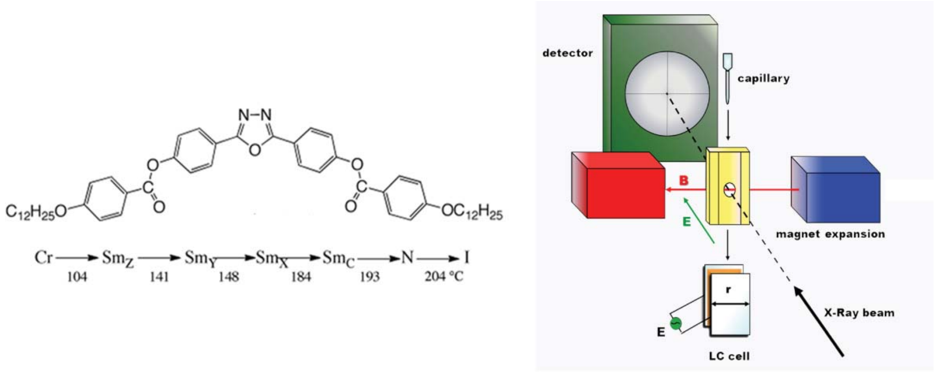
exhibit Sm-like positional order (usually a skewed SmC order), as well as biaxial (and possibly polar) orientational order. If no external effects align the clusters, the transverse, mesoscale orientational order is uncorrelated over macroscopic length scales and the N_{cyb} phase generally appears to be macroscopically uniaxial.

Very recently, we reported another extraordinary effect in an oxadiazole-based BCM: an extremely large (∼4 K) shift of both the SmC-N_{cyb} and the N_{cyb}-isotropic (N_{cyb}-I) transition temperatures upon application of a relatively weak magnetic field ($B = 1$ T, measured in air) [20]. Although the influence of electric and magnetic fields on the thermodynamic properties of liquid crystals is well known, such effects are usually very weak and require substantial fields to be observed [21–26]. In particular, both Landau-de Gennes (LdG) and Maier–Saupe theories predict a quadratic dependence of the N-I phase transition temperature on the field strength. A typical proportionality factor between the *B*-field-induced shift of the clearing point $\Delta T_{\text{N-I}}$ and the squared magnetic field B^2 was measured in 1981 by Rosenblatt, who found a value of 2.5×10^{-2} mK T^{-2}, corresponding to a shift of just a few microkelvin upon application of a 10 T *B*-field [23]. Since then, no other measurements appeared in the literature until 2008, when Ostapenko et al. reported the first observation of a *B*-field-induced first-order I-N phase transition in a thermotropic liquid crystal [27]. They measured a significantly larger shift $\Delta T_{\text{N-I}} = 0.7$ K by applying a magnetic field $B = 30$ T; $\Delta T_{\text{N-I}}$ followed only approximately the quadratic dependence on *B* anticipated by theory. In the authors' opinion, these results were related to the bent-core structure of their compound and to its very weakly first-order N-I phase transition. However, this result is orders of magnitude lower than our finding.

In this article, we provide a review of our recent XRD investigations and interpret them in the framework of the N_{cyb} model.

Experimental

We performed XRD measurements on several oxadiazole-based BCMs (for a comparison see reference [12]). Here, we only refer to the compound 4,4′(1,3,4-oxadiazole-2,5-diyl) di-*p*-dodecycloxybenzoate, usually indicated as ODBP-Ph-OC_{12}, whose structure and transition map is shown in Fig. 1(a). Its synthesis and physical properties have been described elsewhere [28,29].



(a) (b)

Figure 1. (a) Chemical structure and phase transition temperatures of ODBP-Ph-OC_{12}. (b) XRD experimental setup.

The experiments were carried out on the former BM16-CRG beamline at the European Syncrotron Radiation Facility (ESRF) in Grenoble, France. The beam wavelength was $\lambda = 0.9795$ Å and the sample-to-detector distance $l = 0.97$ m; overall, the setup provided a resolution better than $\Delta q = 3 \times 10^{-3}$ Å^{-1} (where q is the scattering wave vector). Samples were loaded either in capillaries (diameter 1 mm) or in 20-μm-thick glass cells (Fig. 1(b)). Rubbed polyimide layers on the inner cell surfaces provided antiparallel planar alignment. Both types of samples were mounted in a temperature-controlled hot stage, allowing a static magnetic field $B = 1$ T to be applied perpendicularly to the incident X-ray beam and parallel to the surface anchoring direction (horizontal in all figures). A digital temperature controller using a Pt100 thermal probe enabled a precision better than 0.1°C over the whole temperature range with an accuracy better than 0.5°C, confirmed by measuring the melting points of standard compounds.

Results and Discussion

Small-angle XRD measurements performed on the N phase of aligned BCMs exhibit a characteristic *four-spot pattern*, very different from that observed in conventional calamitic nematics. A comparison between two typical patterns is presented in Fig. 2. While the wide-angle signal is similar in the two cases (two wide diffuse crescents, orthogonal to **n** and related to transversal nearest neighbor separations, i.e., the molecular diameter D), the small-angle signal is strikingly different: two diffuse crescents centered on the meridional line (parallel to **n**) and related to the molecular length L for calamitic nematics; four symmetric diffuse spots for BCMs. It was the observation of the latter pattern that first prompted the claim of biaxiality in the N phase of BCMs [3,4]. However, it is now widely accepted that the four-spot pattern rather reflects the peculiar *cybotactic* order of BCMs'

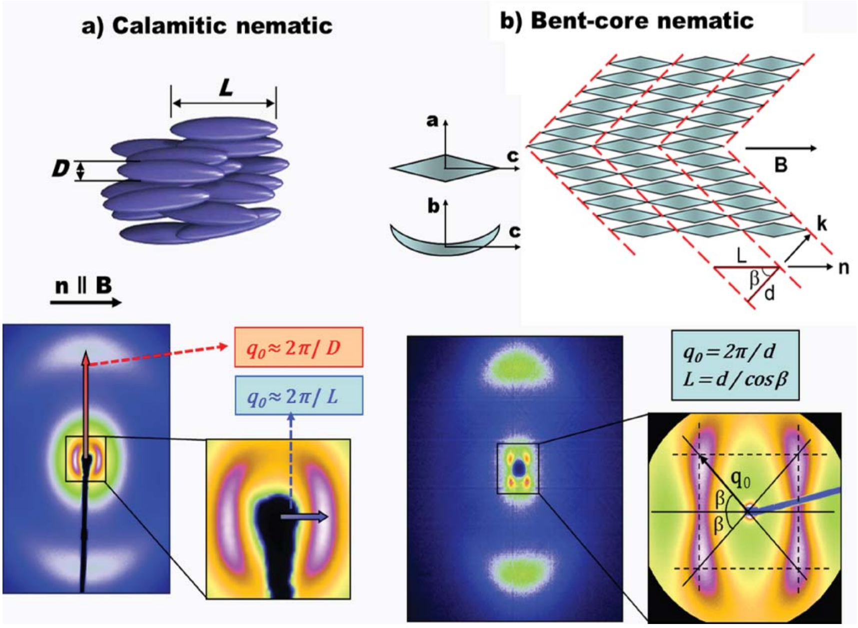


Figure 2. Molecular arrangement and XRD diffraction pattern in the N phase of calamitic (a) and bent-core liquid crystals (b).

N phase. According to this model, the N_{cyb} phase consists of nanometer-sized cybotactic clusters, dynamic aggregates comprising a number of molecules of the order of 10^2 and characterized by a higher degree of positional and orientational order. In fact, on a very short length scale, BCMs adopt a layered (and usually skewed) Sm structure, with their short axes aligned along a direction orthogonal both to **n**, the long axis molecular director, and **k**, the normal to the Sm layers (Fig. 2(b)). This short-range order, imposed by close packing the nonlinear BCM shape, differs from that found in conventional cybotactic nematics [30] as it is not a pretransition effect related to an underlying Sm phase, but rather a characteristic feature over the entire N range.

The cybotactic order results in a four-spot small-angle XRD pattern in which:

(i) the modulus of the scattering vector $\mathbf{q_0}$ associated to the maxima of the four spots is related to the spacing d of the Sm layers, that is, $q_0 = 2\pi/d$;

(ii) the four-spot split angle β, that is, the angle between $\mathbf{q_0}$ and **n**, corresponds to the tilt angle of the Sm layers with respect to the long axis alignment direction;

(iii) the molecular length L is related to the projection of $\mathbf{q_0}$ over **n**, that is, $L = 2\pi/(q_0 \cos\beta) = d/\cos\beta$;

(iv) the full width at half maximum of the spots measured along cuts parallel and orthogonal to **n**, $\Delta q_{\parallel,\perp}$, provides an estimate of the correlation lengths in the two directions, $\xi_{\parallel,\perp} = 2\pi/\Delta q_{\parallel,\perp}$ (typically of the order of the molecular length and a few molecular diameters, respectively), and hence of the cluster size [10].

This model fits very well the experimental data and in particular the four-spot pattern evolution with temperature. Figure 3 shows a sequence of small-angle XRD diffraction patterns taken on our sample while lowering the temperature from the isotropic melt by steps of 1 K, each time waiting for the sample to reach thermal equilibrium. Four spots are clearly visible over the greatest part of the N range: they are quite broad just below the clearing point, but soon become very well-defined and persist until the N-Sm phase transition, when much sharper features appear. Figure 4 shows the temperature dependence of the main structural parameters, the Sm layer spacing d and the tilt angle β, calculated from the position of the four-spot maxima as explained above. Over most of the N range d increases with temperature, but its value always remains much lower than the expected molecular length (~50 Å [11]). In contrast, β decreases on approaching the melting point, that is, the maxima move toward the alignment direction at higher temperatures. Within the cybotactic model, this means that the molecular tilt in the Sm layers decreases on increasing temperature. These trends are common to oxadiazole-based BCMs and typically persist over the entire N range [6,10–12]; however, ODBP-Ph-OC_{12} and other homologous compounds

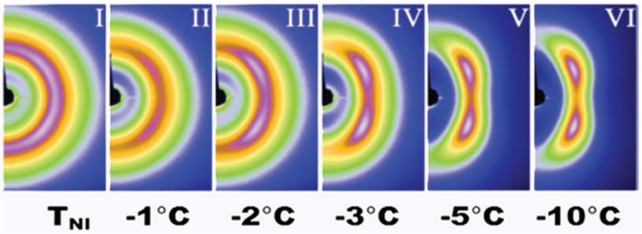


Figure 3. Evolution of the small-angle XRD diffraction pattern of ODBP-Ph-OC_{12} at different temperatures below the clearing point T_{N-I}. Because of the pattern symmetry, only the right half is shown.

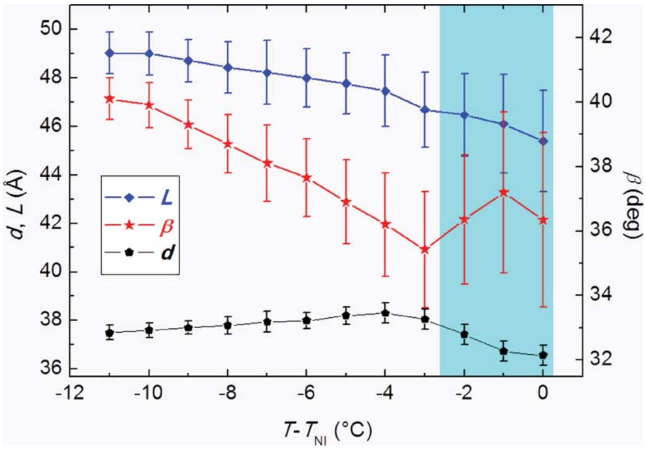


Figure 4. Values of relevant structure parameters for different temperatures T below the clearing point $T_{\text{N-I}}$: d is the Sm layer spacing, β the tilt angle, and $L = d/\cos\beta$ the calculated molecular length.

with long terminal chains show an inverted behavior a few degrees below isotropization (the shaded area in Fig. 4), probably related to pretransition effects. More important, the value of $L = d/\cos\beta$ remains reasonably constant with temperature and in good agreement with the expected value. The possibility of simply explaining the dependence of the structural parameters on the temperature is a strong point in favor of the cybotactic model. This model was also confirmed by molecular dynamics simulations [6], and a detailed statistical theory has been developed to describe it [17].

Small-angle XRD measurements allow a straightforward determination of the BCM phase transition temperatures in aligned samples: a diffuse diffraction ring identifies the isotropic phase; the four-spot pattern discussed above characterizes the N_{cyb} phase; and sharp diffraction peaks are the signature of a Sm phase. If the sample is not aligned, the four-spot pattern becomes a circle very similar to the diffuse ring in the I phase, so that it is difficult, or even impossible, to distinguish the clearing point. When studying planar cells, we first tried to get alignment just by surface rubbing; although the alignment quality was not particularly good, probably because of the degradation of the polyimide layer at the high working temperatures, we could still infer both the I-N_{cyb} and N_{cyb}-SmC transitions in a temperature scan starting from the isotropic melt. Subsequently, we repeated the measurements with the alignment reinforced by a magnetic field parallel to the rubbing direction. While the transition temperatures found with the former set of measurements ($T_{\text{N-I}} = 204 \pm 0.5°\text{C}$, $T_{\text{SmC-N}} = 193 \pm 0.5°\text{C}$) were in agreement with differential scanning calorimetry and polarization microscopy values, the results in the presence of the field showed an unexpectedly large shift of both the I-N_{cybC} and N_{cybC}-SmC phase transitions temperatures. With the B-field present, the two phase transitions occurred at $T_{\text{N-I}} = 208 \pm 0.5°\text{C}$ and $T_{\text{SmC-N}} = 197 \pm 0.5°\text{C}$, that is, 4°C above the corresponding transition temperatures measured without a field (see the phase diagram shown in Fig. 5) [20]. This result is extremely surprising if one considers that a shift of such magnitude, never observed before, was obtained with a B-field of only 1 T.

Looking at the two-dimensional (T,B) phase diagram in Fig. 5, it is clear that a shift of the phase transition temperatures should also allow the observation of field-induced phase transitions. The experiment we performed to verify this effect followed the ABC and DE "thermodynamic paths" indicated in Fig. 5: with no field applied, we cooled the sample

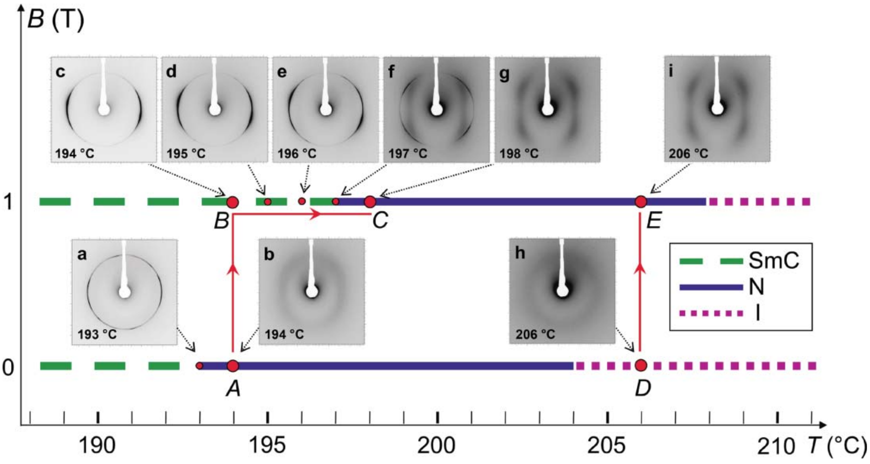


Figure 5. Sketch of the phase diagram of ODBP-Ph-OC$_{12}$ in the two-dimensional (T,B) space. The insets show the XRD patterns measured at selected points in the paths across the phase boundaries (after reference [20]).

until we found the SmC-N$_{\mathrm{cyb}}$ phase transition at $T = 193°\mathrm{C}$ (Fig. 5(a)); after verifying that no supercooling effect was taking place, we heated the sample by 1°C and, as expected, observed the cybotactic four-spot pattern shown in Fig. 5(b) (the surface alignment was rather weak and the four spots were not so well-defined; however, the pattern was still clearly anisotropic); holding the sample at $T = 194°\mathrm{C}$, we applied a 1 T B-field and recorded the effect we were looking for, a B-field-induced transition to the Sm phase (Fig. 5(c)); finally, maintaining $B = 1$ T, we heated the sample again observing the SmC-N$_{\mathrm{cyb}}$ transition at $T = 197°\mathrm{C}$, that is, 4°C above that at $B = 0$ (Figs 5(c)–(g)). Similarly, we observed a B-field-induced transition from the I phase (Fig. 5(h)) to the N$_{\mathrm{cyb}}$ phase (Fig. 5(i)) at $T =$ 206°C.

For a calamitic (uniaxial) N phase, the LdG theory predicts a quadratic dependence of the shift of the clearing point, $\Delta T_{\text{N-I}}(B)$, on the magnetic field B:

$$\Delta T_{\text{N-I}}(B) = \frac{1}{3} T_{\mathrm{cp}} \frac{S_{\mathrm{cp}} \Delta \chi_0}{|Q|\, \mu_0} B^2, \tag{1}$$

where T_{cp} is the zero field clearing point temperature, S_{cp} the order parameter at $T = T_{\mathrm{cp}}$, $\Delta\chi_0$ the saturated diamagnetic anisotropy, μ_0 the vacuum permeability, and Q the latent heat (per unit volume) associated to the N-I phase transition [21]. Therefore, a larger shift is expected for weakly first-order (i.e., low Q) phase transitions. In fact, Ostapenko et al. attributed the large shift reported in their work to the weakly first-order N-I phase transition characterizing their BCM [27]. However, this explanation appears unsatisfactory for our BCM, whose N-I phase transition is characterized by a molar latent heat $|Q_{\mathrm{mol}}| = 0.9$ kJ/mol [28], a value quite comparable to that of calamitic nematics.

We believe instead that the real explanation for this odd effect should reside in the peculiar cluster nature of the BCM N$_{\mathrm{cyb}}$ phase [20]. In fact, in the N$_{\mathrm{cyb}}$ phase, an external field would couple with the (anisotropic) cybotactic clusters rather than with individual molecules, leading to a response amplification factor of the order of the average number of molecules per cluster. Vanakaras and Photinos have developed a theoretical description for this particular mesophase, providing a more formal foundation for this idea [17].

In particular, their calculations clearly indicate a much enhanced field sensitivity of the cybotactic cluster phase with respect to a conventional (molecular) N phase. Even though Vanakaras and Photinos only treated the case of an electric field, their work should be readily extendable to the magnetic case.

Finally, we notice that we also observed a field-induced shift of the phase transition temperatures upon application of a low-frequency electric field. In that case, the shift was negative, as a consequence of the negative dielectric anisotropy of our compound. These latter results require a more careful analysis to exclude undesired effects, such as electric heating and electrodynamic instabilities, and will be reported in detail in a forthcoming paper.

Conclusions

Several studies have shown how the nonlinear shape of BCMs leads to a N phase which is drastically different from the classical N phase of calamitic liquid crystals. A careful analysis of XRD data, in agreement with other recent theoretical and experimental works, clearly point to a cluster N phase, namely, a N_{cyb} phase, characterized by short-range correlation fluctuations of positional (layered) and orientational (biaxial) order. In contrast to calamitic nematics, BCM cybotaxis is not a pretransition phenomenon. Rather, it should be considered as a new type of masophase, characteristic of BCMs throughout their entire N range, even when no underlying Sm phase occurs. This microscopic structure explains many unconventional macroscopic properties observed in BCM nematics. In particular, it can explain the extraordinary sensitivity of these materials to magnetic and electric fields, which leads to unexpectedly large modifications of the phase diagram in presence of relatively low external fields. Beyond its fundamental relevance, the exceptional sensitivity of this state of matter is important from a practical point of view: when working with BCMs, external fields cannot be regarded as a mere tool to control the alignment of the molecular director(s), but their effect on the thermodynamic properties of the materials must always be considered in the framework of a two-dimensional, field strength-temperature phase diagram.

Acknowledgments

We acknowledge C. Ferrero, F. Fauth, J. Gorini, E. Di Cola, and T. Narayanan from ESRF for their support in XRD measurements.

References

[1] Takezoe, H., & Takanishi, Y. (2006). *Jpn. J. Appl. Phys.*, *45*, 597.
[2] Pelzl, G., Diele, S., & Weissflog, W. (1999). *Adv. Mater.*, *11*, 707.
[3] Acharya, B. R., Primak, A., Dingemans, T. J., Samulski, E. T., & Kumar, S. (2003). *Pramana*, *61*, 231.
[4] Acharya, B. R., Primak, A., & Kumar, S. (2004). *Phys. Rev. Lett.*, *92*, 145506.
[5] Madsen, L. A., Dingemans, T. J., Nakata, M., & Samulski, E. T. (2004). *Phys. Rev. Lett.*, *92*, 145505.
[6] Francescangeli, O., Stanic, V., Torgova, S. I., Strigazzi, A., Scaramuzza, N., Ferrero, C., Dolbnya, I. P., Weiss, T. M., Berardi, R., Muccioli, L., Orlandi, S., & Zannoni, C. (2009). *Adv. Funct. Mater.*, *19*, 2592.
[7] Harden, J., Mbanga, B., Eber, N., Fodor-Csorba, K., Sprunt, S., Gleeson, J. T., & Jakli, A. (2006). *Phys. Rev. Lett.*, *97*, 157802.

[8] Bailey, C., Fodor-Csorba, K., Gleeson, J. T., Sprunt, S. N., & Jakli, A. (2009). *Soft Matter*, *5*, 3618.

[9] Bailey, C., Fodor-Csorba, K., Verduzco, R., Gleeson, J. T., Sprunt, S., & Jakli, A. (2009). *Phys. Rev. Lett.*, *103*, 237803.

[10] Francescangeli, O., & Samulski, E. T. (2010). *Soft Matter*, *6*, 2413.

[11] Francescangeli, O., Vita, F., Ferrero, C., Dingemans, T., & Samulski, E. T. (2011). *Soft Matter*, *7*, 895.

[12] Vita, F., Placentino, I. F., & Francescangeli, O. (2011). *J. Nonlinear Opt. Phys. Mater.*, *20*, 485.

[13] Vaupotič, N., Szydlowska, J., Salamonczyk, M., Kovarova, A., Svoboda, J., Osipov, M., Pociecha, M., & Gorecka, E. (2009). *Phys. Rev. E*, *80*, 030701.

[14] Keith, C., Lehmann, A., Baumeister, U., Prehm, M., & Tschierske, C. (2010). *Soft Matter*, *6*, 1704.

[15] Hong, S. H., Verduzco, R., Williams, J. C., Twieg, R. J., DiMasi, E., Pindak, R., Jákli, A., Gleeson, J. T., & Sprunt, S. (2010). *Soft Matter*, *6*, 4819.

[16] Tschierske, C., & Photinos, D. J. (2010). *J. Mater. Chem.*, *20*, 4263.

[17] Vanakaras, A. G., & Photinos, D. J. (2008). *J. Chem. Phys.*, *128*, 154512.

[18] Francescangeli, O., Torgova, S. I., Karamysheva, L. A., Geivandova, T. A., Strigazzi, A., Stanic, V., Ferrero, C., & Dolbnya, I. (2002). *19th International Liquid Crystal Conference*, Edinburgh, UK, Book of Abstracts, p. 137.

[19] Samulski, E. T. (2010). *Liq. Cryst.*, *37*, 669.

[20] Francescangeli, O., Vita, F., Fauth, F., & Samulski, E. T. (2011). *Phys. Rev. Lett.*, *107*, 207801.

[21] Gramsbergen, E. F., Longa, L., & de Jeu, W. H. (1986). *Phys. Rep.*, *135*, 195.

[22] Dunmur, D. A., & Palffy-Muhoray, P. (1988). *J. Phys. Chem.*, *92*, 1406.

[23] Rosenblatt, C. (1981). *Phys. Rev. A*, *24*, 2236.

[24] Sakamoto, A., Yoshino, K., Kubo, U., & Inuishi, Y. (1976). *Jpn. J. Appl. Phys.*, *15*, 545.

[25] Helfrich, W. (1970). *Phys. Rev. Lett.*, *24*, 201.

[26] Lelidis, I., & Durand, G. (1993). *Phys. Rev. E*, *48*, 3822.

[27] Ostapenko, T., Wiant, D. B., Sprunt, S. N., Jákli, A., & Gleeson, J. T. (2008). *Phys. Rev. Lett.*, *101*, 247801.

[28] Dingemans, T. J., & Samulski, E. T. (2000). *Liq. Cryst.*, *27*, 131.

[29] Senyuk, B., Kim, Y.-K., Tortora, L., Shin, S.-T., Shiyanovskii, S. V., & Lavrentovich, O. D. (2011). *Mol. Cryst. Liq. Cryst.*, *540*, 20.

[30] De Vries, A. (1970). *Mol. Cryst. Liq. Cryst.*, *10*, 219.