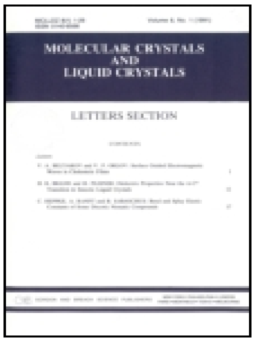

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Insights into Biaxial Ordering of Bent-Core Nematics: X-Ray Diffraction Evidence

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Recently we have reported the first X-ray diffraction evidence of biaxial order in the fluid cybotactic nematic phase of a pair of trimethylated bent-core mesogens. This evidence is based on the splitting of the wide-angle diffuse scattering in the plane normal to the nematic director. The additional experimental data presented here provide further insights into this unprecedented behavior observed over the entire nematic phase. Although we could not determine the spatial extent of biaxial order—intracluster or intercluster—our observations reveal an enhanced biaxial orientational correlation in the transverse molecular packing, possibly reflecting stronger anisotropic interactions between nearest-neighbor mesogens.

Keywords bent-core mesogens; biaxiality; cybotaxis; X-ray diffraction

Introduction

The experimental evidence of a biaxial nematic (N) phase has puzzled liquid crystal (LC) scientists since its first theoretical prediction in 1970 [1]. Whilst there is general consensus on the biaxiality of particular N systems (e.g., some lyotropic and polymeric LCs), the existence of such an unusual fluid phase in low molecular weight thermotropic nematics still remains controversial [2–5]. The problem is twofold. On the one hand, there is a fundamental issue described as the *vicious circle of molecular design* [5]: in order to get the three molecular axes aligned along individual directors requires mesogens with a large shape biaxiality coupled to strong supramolecular interactions. Both hamper rotational diffusion around the long molecular axis, and both either inhibit the formation of a N phase or affect its viscosity to such an extent that the directors cannot be switched, thus greatly

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reducing its technological interest. In fact, biaxiality in thermotropic nematics has often been reported for highly viscous systems on approaching the glass transition [6–8]. On the other hand, the experimental demonstration of biaxial N order is far from trivial, so much so that over the past years reports of biaxiality often precipitate fiery disputes within the scientific community. The potential and pitfalls of the most commonly used experimental approaches, namely optical techniques (conoscopy, defect inspection), nuclear magnetic resonance (NMR), and X-ray diffraction (XRD), have been reviewed in a number of papers [2–4]. Two basic problems connected with unequivocal demonstrations of biaxiality are: *i*) distinguishing between long-range (macroscopic) and short-range (local) biaxial order; *ii*) discriminating between spontaneous bulk biaxiality and induced biaxiality (e.g., by interactions with surfaces or applied fields). Both issues would be better tackled using monodomain samples in which all the molecular directors are uniformly aligned over the investigated volume. Unfortunately, extending the conventional alignment methods of uniaxial nematics to biaxial systems is still a technological challenge. As a consequence, unequivocal proof of *true* (i.e., spontaneous and macroscopic) biaxiality requires the use of several complementary experimental techniques and comparative studies of samples in different geometries.

In this context, XRD has usually been considered to be *blind* to N biaxiality [2,4]. In principle, biaxial order should manifest in the form of two distinct diffraction features related to different average intermolecular distances along two orthogonal directions in the transverse plane (i.e. the plane orthogonal to the long axis molecular director, the primary director **n**). However, since N positional order is very short range (liquid-like), diffraction features are very broad and hard to resolve in mesogens with a relatively small molecular shape anisotropy. In spite of this, we have recently reported the observation of a splitting in the wide-angle (WA) XRD pattern of a couple of laterally substituted bent-core nematics (BCNs), which represents the first direct proof of the mesogens' anisotropic ordering in the transversal plane [9]. In this paper we review this unprecedented finding, providing additional experimental data that leads to a deeper comprehension of this unconventional behavior.

Experimental

We have compared the WA-XRD patterns of a series of BCNs, all based on a 2,5-bis(*p*-hydroxyphenyl)-1,3,4-oxadiazole (ODBP) mesogenic core (Figure 1): the parent compound (**1**) [10], two monomethylated (**2**,**3**) and two trimethylated derivatives (**4**,**5**) [11]. All mesogens exhibit an enantiotropic N phase, with methylated compounds showing a reduced N onset temperature. This reduction is much stronger for trimethylated BCNs, whose N phase can also be supercooled down to room temperature in a highly viscous, metastable state [11].

The experiments were carried out at the BM16-CRG beamline of the European Synchrotron Radiation Facility (ESRF), France. Samples were placed in capillaries (1 mm diameter) and mounted in a hot stage allowing a static magnetic field **B** ($B = 1$ T, horizontal in all figures) to be applied orthogonally to the capillary and to the beam direction, so as to align the **n** molecular director, i.e. the average orientation of the long molecular axes. Measurements were taken on cooling from the isotropic melt, after allowing the sample to equilibrate at each set point. The beam size was 0.1×0.1 mm^2, the wavelength $\lambda = 0.980$ Å, and the sample-to-detector distance $l = 0.222$ m for compound **1** and $l = 0.243$ m for compounds **2-5**. The resolution, estimated from the full width at half maximum (FWHM) of

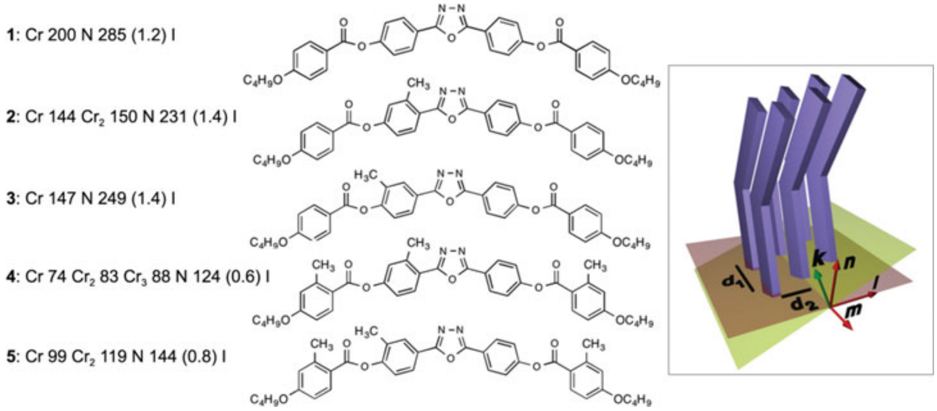

Figure 1. Chemical structures, transition temperatures (°C, measured on heating), and isotropization enthalpies (kJ/mol) of investigated BCNs. In the inset, a schematic drawing of the molecular ordering within a cybotactic cluster: **k** indicates the normal to the smectic plane (green), **n**, **m** and **l** are the three orthogonal molecular directors; d_1 and d_2 are the intermolecular distances in the plane normal to **n** (purple).

the intrinsic Gaussian instrumental broadening, was better than $\Delta q = 3 \times 10^{-3}$ Å^{-1} in the investigated range.

Results

The mesomorphic behavior of BCNs **1-5** was previously studied by means of small-angle (SA) XRD [10,11]. All samples exhibit a characteristic *four-spot* SA diffraction pattern over the entire N range. Such a pattern was first observed in an asymmetric oxadiazole BCN [12,13] and later in a longer-alkoxy-tail homologue of BCN **1** where its change into the conventional *two-spot* pattern upon application of an electric field was interpreted as the proof of biaxial order [14]. After a decade of experimental investigations, it is now widely recognized that the four-spot pattern is instead the signature of a cybotactic N phase, i.e., a N phase consisting of nano-sized molecular aggregates (the cybotactic clusters) characterized by tilted layered (i.e., smectic-C-like) positional order [10,15–21]. In addition, cybotactic clusters are usually assumed to be inherently biaxial (and possibly polar [15,22–24]), with cluster transverse axes randomly oriented with respect to neighboring clusters [25]. Hence, the cybotactic N phase is macroscopically uniaxial with a single common director, unless steps are taken to coherently align the biaxial clusters over large spatial scales with an external agent (e.g. the interaction with a field or a surface). Although this assumption was supported by several experimental findings [15,21–24,26–29] and molecular simulations [15,30,31], there was in the past no *direct* experimental evidence of cluster biaxiality. In particular, XRD has long been considered unfit to probe biaxial order due to the inherently small molecular biaxiality of bent-core mesogens coupled with the typical broadness of X-ray scattering from nematics [2,4].

Apparently, this belief is confirmed by the XRD patterns of BCNs **1-3**. As the behaviors of these mesogens are very similar, in Figure 2a–b we just report the representative patterns of BCN **2** measured at the two extremes of the N range (under an aligning magnetic field **B**). Besides the characteristic four-spot pattern in the SA region, the sample exhibits one single

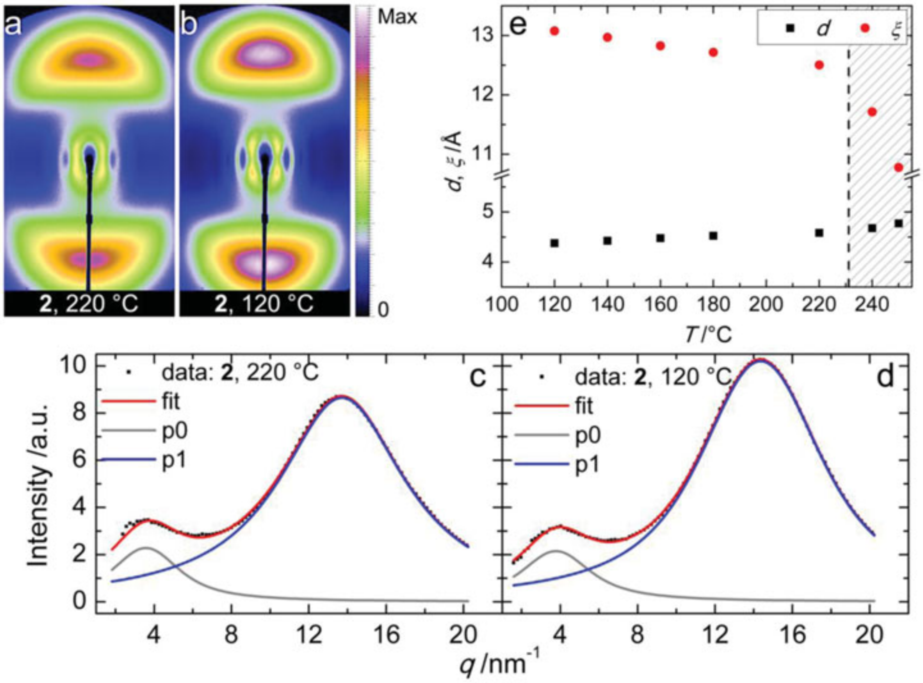

Figure 2. XRD patterns of BCN **2** recorded on cooling from the isotropic melt under **B** field: (a) 220°C and (b) 120°C. (c,d) Fit of the corresponding q-scans along the equatorial axis by two Voigt lineshapes (note that p0, the low hump in the SA region, is just peripheral scattering from the four-spot feature). (e) Temperature dependence of the resulting transverse intermolecular distance d and correlation length ξ (the shaded area indicates the isotropic phase).

pair of diffuse WA diffraction features centered on the equatorial axis (i.e. perpendicular to **n**). At any temperature in the N range, the equatorial intensity profiles of the WA features can be fitted very well by a single Voigt lineshape, as shown in Figure 2c–d. The peak position in the q-space, q_0, gives the average intermolecular distance $d = 2\pi/q_0$ in the plane orthogonal to **n** (the transverse plane): it ranges between 4.4 and 4.8 Å, smoothly increasing throughout the N range up to the isotropic phase (Figure 2e). The FWHM Δq is inversely proportional to the spatial extent of positional order: following Leadbetter *et al.* [32], a quantitative evaluation of the correlation length ξ can be obtained as $\xi = 9.92/\Delta q$, where the factor at the numerator is derived from the Hosemann's paracrystalline model. It is found that ξ decreases only slightly with the temperature in the N phase, but it exhibits an abrupt reduction on entering the isotropic phase (Figure 2e). The described behavior is common to most BCNs and is similar to that of conventional calamitic nematics described by Leadbetter *et al.* [32]. With reference to the latter, the main difference is in the ξ/d ratio, being $\sim$5 in ref.[32] (with $d \approx 5$ Å), while being ≤ 3 in our case. This range reduction is probably related to the nonlinear shape of the ODBP mesogens, which unfavorably impacts the range of positional order.

By contrast, the WA-XRD patterns of BCNs **4-5** are quite unconventional, consisting of two partially superimposed diffraction peaks, as shown in Figure 3a–c for BCN **4** (the behavior of BCN **5** is very similar). Fitting the WA intensity profiles measured along the equatorial direction with two Voigt lineshapes allows resolving the two peaks, indicated as

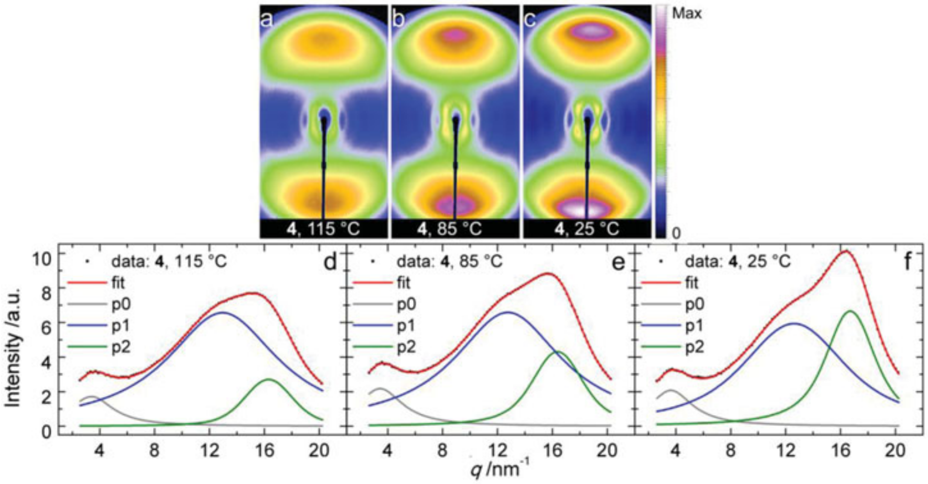

Figure 3. XRD patterns of BCN **4** measured on cooling from the isotropic melt under **B** field at selected temperatures in the N range: (a) 115°C, (b) 85°C, and (c) 25°C. (d–f) Fit of the corresponding *q*-scans along the equatorial axis by means of three Voigt lineshapes.

p1 and p2 in Figure 3d–f: their maxima correspond to distinct transverse intermolecular distances, $d_1 \approx 4.9$ Å and $d_2 \approx 3.8$ Å, respectively. In our view such a splitting represents undisputable proof of the mesogens' biaxial packing (see the scheme in Figure 1). In fact, d_2 is typical of the face-to-face distance between stacked π-systems, while d_1 is closer to the width of a planar aromatic ring and comparable to the typical intermolecular distance normally observed in uniaxial nematics (both bent-core and calamitic) [6,7,16,32]. These values exhibit a weak temperature dependence, with their difference being higher at room temperature, but still larger than 1.0 Å just below the clearing point (Figure 4a).

The correlation lengths ξ_1 and ξ_2 of peaks p1 and p2 are reported in Figure 4b as a function of the temperature: these values stay approximately constant up to the clearing point, with $\xi_1 \approx 10.5$ Å $\approx 2d_1$ and $\xi_2 \approx 22.6$ Å $\approx 6d_2$ (ξ_2 is lower, $\sim 4d_2$, for BCN **5**). Apparently, close packing constraints favor the face-to-face stacking of aromatic cores more strongly than their in-plane arrangement. However, while the amplitude A_1 of peak p1 is almost constant, with just a slight increase at higher temperatures, the amplitude A_2 of peak p2 changes from being larger than A_1 close to room temperature, to being significantly lower on approaching the clearing point (Figure 4c). This latter effect reflects a reduced

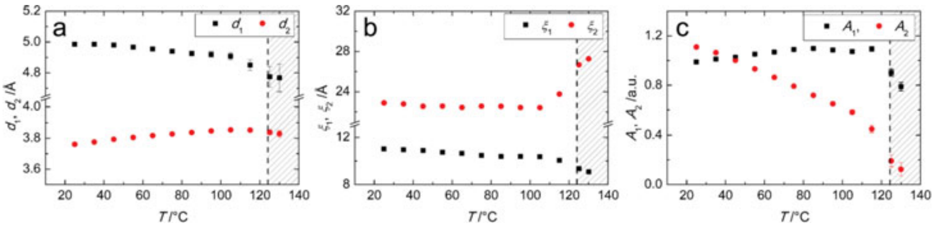

Figure 4. Temperature dependence of various structural parameters of BCN **4** obtained by fitting peaks p1 and p2: (a) transverse intermolecular distances; (b) corresponding correlations lengths; (c) peak amplitudes. The shaded areas indicate the isotropic phase.

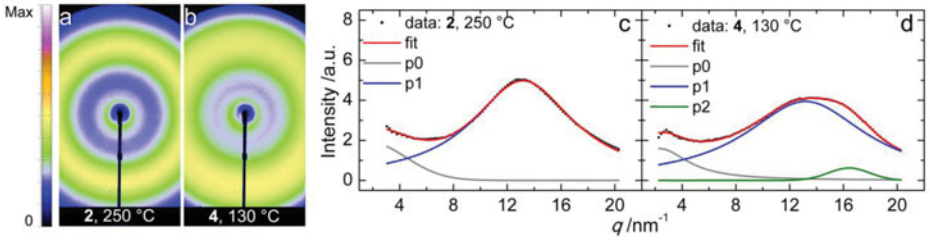

Figure 5. XRD patterns and fit of the corresponding q-scans in the isotropic phase: (a,c) BCN **2** at 250°C; (b,d) BCN **4** at 130°C.

fraction of mesogens stacked face-to-face as the temperature increases, hence a reduction of the overall biaxial order. On the other hand, the negligible effect of the temperature on A_1 is not surprising, as a disruption of biaxial order results in a transverse intermolecular distance which is, on average, still close to d_1. Nevertheless, it is remarkable that the WA splitting remains visible even beyond the clearing point. This is shown in Figure 5, where the XRD patterns and the corresponding intensity profiles of BCNs **2** and **4** are compared in the isotropic phase: the WA feature of BCN **4** is clearly broader than in BCN **2** and, contrary to the latter, requires two Voigt lineshapes to be properly fitted. Although this unconventional behavior deserves further investigation, it could be related to the persistence of cybotactic clusters in the isotropic phase, an effect suggested by several authors [17,29,33].

Finally, we performed a comparative data analysis to rule out the possibility that the WA splitting observed in the N phase was generated by the applied (relatively strong) magnetic field **B**. In fact, it is known that magnetic and electric fields can strongly affect the N order of bent-core mesogens [28,34]. In Figure 6 we compare the XRD patterns and corresponding intensity profiles of BCNs **3** and **5** under a 1 T magnetic field (**B** on) and under a very weak (practically null) 12 mT magnetic field (**B** off). Regardless of the magnitude of **B**, no radial

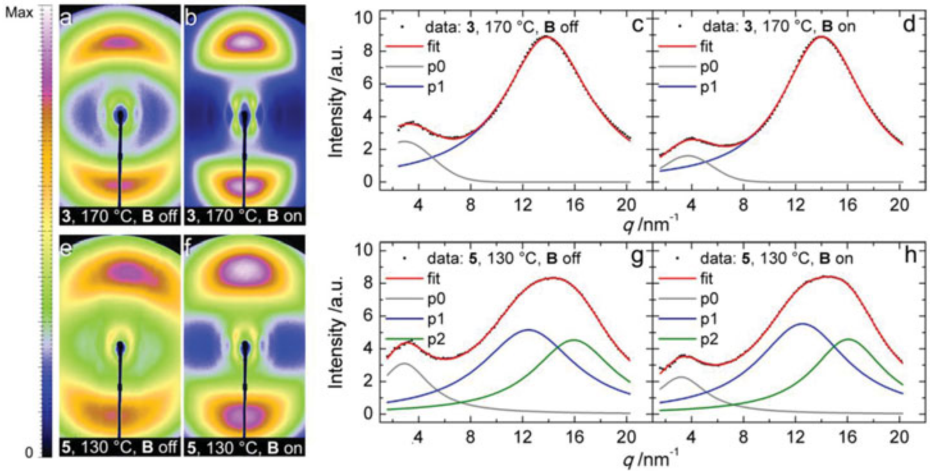

Figure 6. XRD diffraction patterns and fit of the corresponding equatorial q-scans with **B** field switched off and on: (a,c) BCN **3**, field off; (b,d) BCN **3**, field on; (e,g) BCN **5**, field off; (f,h) BCN **5**, field on.

splitting is observed in the monomethylated compound (**3**) whereas the WA splitting is well evident in the trimethylated mesogen (**5**). This confirms the expectation that the applied **B** field only affects the ordering of the long molecular axes (as indicated by the azimuthal broadening of the patterns when **B** is switched off), while having only a marginal (if any) effect on the transverse ordering of the mesogens' short axes.

Discussion

The experimental data summarized above provide unequivocal proof of the (unique) biaxial packing of trimethylated BCNs **4**-**5**. In particular, the low value of d_2 is only compatible with the piling-up of the mesogens' aromatic cores. However, there are a few subtle issues that deserve more careful consideration. The most obvious one regards the spatial extent of transverse biaxial order. The measured correlation lengths are of the same order of magnitude as the transverse size of cybotactic clusters, as estimated by the broadening of the SA four-spot pattern [10,11,15–21]. However, it should be pointed out that ξ_1 and ξ_2 reflect the mesogens *positional* order, which is only indirectly related to the mesogen *orientational* order via considering the close-packing constraints. Actually, the range of orientational and positional order could be completely different—e.g., in a conventional (uniaxial) calamitic nematic positional order is very short-ranged (liquid-like) even though orientational order extends to macroscopic length scales [32].

In our case an additional problem arises from the lack of a monodomain sample with the transverse molecular directors uniformly aligned over the probed sample volume. The simultaneous observation of two transverse d-spacings points to biaxial domains whose transverse axes are isotropically distributed around the common direction of the primary director **n**. However this consideration does *not* exclude macroscopic biaxial order. In fact, in the liquid crystal context *short-range* (local) and *long-range* (macroscopic) refer to molecular length scales, not to the sample size. Unless some external aligning mechanism is applied, the orientational order of fluid LC phases spontaneously extends over domains which are typically micron-sized. As this length scale is still much larger than the molecular length scale, these micro-domains are considered macroscopic even though they are much smaller than the typical sample size.

In the case of cybotactic nematics the situation is complicated by an additional characteristic length, intermediate between the molecular length scale and the scale of micro-domains, namely, the average size of cybotactic clusters. In this situation, biaxial order can be considered "local" if limited to the length scale of the cybotactic cluster dimensions (i.e. a few nanometers), and "macroscopic" if extending to the size of micro-domains. In any case, biaxial order is not expected to extend over the entire volume of the probed region of the sample ($\sim$mm^3) unless the sample is very viscous and/or some external interaction is used to get a monodomain biaxial sample. Therefore, the simultaneous observation of two d-spacings in our experiment could be equally explained either in term of *i*) biaxial cybotactic clusters having an isotropic orientational distribution of their transverse axes around **n**, i.e., local biaxial order, or, *ii*) biaxial micro-domains with transverse directors isotropically distributed about **n**, i.e., macroscopic biaxial order. Of course, intermediate situations could be possible, too, with biaxial order ranging between these two extremes.

A second relevant issue concerns the nature of the unique behavior of our trimethylated compounds compared to ordinary cybotactic BCNs (including mesogens **1**-**3**), where such a splitting has never been observed despite the well-supported belief that they are all locally (i.e., on the cluster scale) biaxial. This paradox was previously explained by the inability to resolve (within the broad WA feature of nematics) two different *d*-spacings which are very close to each other [2,4], but this explanation now appears to be moot based upon our findings. This is particularly significant because the molecular shape anisotropy of our trimethylated BCNs does not differ significantly from that of mesogens **1**-**3** and other BCNs (as confirmed by the small value of the WA splitting, with $|d_1\text{-}d_2| \approx 1$ Å). Therefore, our ability to resolve such a subtle difference in the transverse intermolecular distances can only be ascribed to a higher degree of biaxial orientational correlations in mesogens **4**-**5** compared to other BCNs, although our data do not allow a quantitative evaluation of the magnitude and range of such biaxial order. These increased orientational correlations are somehow related to the two additional methyl groups present on the outer aromatic rings of trimethylated compounds. This in turn must influence molecular packing enabling BCNs **4**-**5** to be supercooled down to room temperature in a highly viscous N phase, as noticed in other LC systems [5–8]. However, contrary to previous reports, herein biaxial order persists into the high temperature fluid N phase (with no sign of a biaxial-uniaxial N transition); in fact, the cluster biaxiality is detectable even above the clearing point. The phenomenon is spontaneous and is not influenced by surfaces (we studied bulk samples in capillaries, with no aligning treatment) nor by external fields (as demonstrated by Figure 6).

Conclusions

We have reported the first direct (XRD) experimental evidence of biaxial order *at least* on a short-range (local) spatial scale for a pair of trimethylated cybotactic BCNs. Even though we could not determine whether biaxiality extends beyond the size of cybotactic clusters to the macroscopic scale, our result is particularly significant as it pertains to the fluid N phase of a class of mesogens, namely the cybotactic BCNs, whose biaxial properties have been deeply debated in the recent past. Furthermore, as the molecular shape biaxiality of our trimethylated compounds does not differ significantly from that of most BCNs, we must infer that the WA splitting uniquely observed in our samples reflects a higher degree of local biaxial order compared to other related compounds. This implies enhanced orientational correlations in the transverse molecular packing, possibly promoted by stronger anisotropic interactions between nearest-neighbor mesogens. For this reason, our trimethylated compounds are of particular relevance and can be considered as prime candidates in the search for proper, i.e. spontaneous and macroscopic, biaxiality.

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