ESRF	**Experiment title:** X-RAY DIFFRACTION STUDY OF THE BIAXIAL NEMATIC PHASE IN BENT-CORE THERMOTROPIC MESOGENS	**Experiment number**: SC-2854
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The biaxial nematic (N_b) liquid crystal (LC) phase, which possesses two orthogonal optic axes (i.e. the director axis **n** and the additional *biaxial* or *short* axis **m**), was predicted in 1970 on the basis of symmetry considerations [1]. Since the theoretical prediction, however, the N_b has been a constant challenge in LC research and, in spite of the relevant theoretical and simulation work, it has eluded experimentalists until 2004 when it was reported [2-3] evidence of its existence in a bent-core (or *banana-shaped*) thermotropic mesogen. The announcement has created considerable excitement, for it opened new areas of both fundamental and applied research, as highlighted in *Nature* (**2004**, *430*, 413) and *AngewandteChemie* (**2005**, *44*, 2834). From a fundamental point of view, existence of the N_b raises the question of the mechanism underlying its formation. So far, this has been attributed to molecular shape, but for these boomerang-shaped (V-shaped) molecules this seems unlikely because their apex angle of around 140°C is far from the predicted optimum value of 109° [5]. Indeed, Madsen *et al.* [2] have recognized this, suggesting that strong electrostatic forces should be crucial in stabilizing the N_b. This would be especially intriguing for it could be related to another much sought after feature: ferroelectricity. In fact, a ferroelectric response has been recently demonstrated for the first time in the nematic (N) phase of a class of banana-shaped (BS) mesogens with asymmetric 1,2,4-oxadiazoles cores [6]. In spite of the great resonance of the claim of refs.[2-3], some questions concerning the *true* nature of this N remain still unsolved. Firstly, serious doubts have been raised [4,6] about the correct interpretation of the XRD data of ref.[3] in support of the biaxiality of the N. Secondly, a debate has opened concerning the *spontaneous* or *field-stabilized* nature of the N biaxiality in BS mesogens. In addition, the connections between N biaxiality and ferroelectric response are still essentially unexplored. Finally, in some cases the literature data from different experimental techniques seem to provide

contradictory results. The main drawback connected with most of these experiments is the lack of simultaneous control of the orientations of the two molecular axes (**m**,**n**).

In a previous experiment at BM16 (SC-2441) we have carried out a detailed X-ray diffraction (XRD) study of three thermptropic oxadiazole-based bent-core (BS) mesogens, **I** (ODBP-Ph-OC_4), **II** (9BPO), and **III** (OC_8-F), which were well representative of a new class of *potentially* N_b mesogens. The results have definitively confirmed the *cybotactic* nature of the N mesophase, which was originally conjectured on the basis of previous experiments at ID02 (SC-2042, SC-1939), and have ruled out the intrinsic molecular V-shape as the cause of the peculiar SAXS pattern, thus calling into question the still widely diffuse interpretation of Acharya *et al*. [3] on similar bent-core mesogens. The XRD results (in combination with molecular dynamics simulations) have also highlighted the field-induced nature of the N biaxiality and have further suggested a connection between the N biaxiality and the ferroelectric response observed for some of these compounds in previous repolarization current measurements [6].

In this experiment we have extended the above study to the four homologous series of N_b mesogens shown in Fig.1. These compounds are representative of the two most relevant series of BS mesogens with oxadiazole-cores (including either symmetric or asymmetric core) presently under consideration for N biaxiality [2] and ferroelectricity [6]. The primary aim of this experiment was to provide firm and definitive evidence of the cybotactic nature of the N phases of these compounds.

Sample planar cells of 20 μm thickness were prepared using two ultra-thin (100 μm) glass plates coated with a conductive ITO-film (50 μm). These glass plates were further coated with a thin film of SiO_x deposited under vacuum at 60° evaporation angle in order to achieve strong planar anchoring and homogeneous in plane orientation of the nematic director **n** parallel to a reference direction **r**. The cells were then assembled with the glass plates facing their coated sides in a antiparallel-plane configuration and separated by high precision spacers. Finally, the cell (13 mm x 7 mm) was filled by capillary with the LC in the fluid phase and then slowly cooled down to room temperature. The cell was mounted on a special temperature controlled (± 0.1°C) hot stage allowing the insertion of a static magnetic field of variable intensity (up to 1.1 T) perpendicular to the incident X-ray beam. This cell was used to apply a low frequency (0-1 KHz) electric field E (up to 10^5 V/m) across the conductive plates and parallel to the X-ray beam. The XRD analysis was carried out on samples aligned under the combined actions of **B**, **E** and the surface anchoring field. As our molecules exhibit positive diamagnetic- and negative dielectric-anisotropy, **B** and **E** could orient the two molecular axes **n**,**m**, respectively, along mutually orthogonal directions. Time-resolved experiments were carried out to follow the dynamics of the structural changes following the axes reorientations upon applying or removing the fields (the kinetics of the reorientation processes involve times of a few tenths of second). We have study the mesomorphic behavior of the samples over the entire mesophasic range as a function of the temperature. XRD diffraction patterns were collected in the q range 0.1 $Å^{-1}$ - 2 $Å^{-1}$ covering the overall SAXS-WAXS range relevant to these materials. 2D diffraction patterns were recorded using a MAR CCD detector.

To answer the main questions to which the experiment wa addressed, we probed the in-plane (normal to **n**) short-range molecular ordering along the two directions parallel and orthogonal to the short-axis **m**, in the monodomain cell samples where the orientations of the two axes **n**, **m** were individually and simultaneously controlled by external magnetic and electric field, respectively. To this purpose, 2D simultaneous SAXS and WAXS data acquisition was performed along with use of a special home-made T-controlled sample holder allowing simultaneous insertion of **E** and **B**.

The XRD data have clearly shown that all the investigated samples show the cybotactic N phase: the N phase intrinsically exhibits microscopic (i.e. within the cybotactic domain) biaxial and polar (hence ferroelectric) ordering. An example of the four-spot pattern typical of the cybotactic N mesophase for one of the investigated samples is shown in Fig. 2. In addition, we have discovered [7] the first example of a thermotropic bent-core mesogen, ODBP-Ph-O-$C_4H_{9,}$, that displays the four-spot signature of a cybotactic *N* phase (Fig. 2) *without* an underlying tilted smectic phase. On the basis of the quantitative study and interpretation of the temperature dependence of small XRD from the nenatic phase the different ODBP mesogens we have shown conclusively [8] that the nematic phase of these V-shaped mesogens is comprised of inherently biaxial clusters of mesogens, clusters that contain a stratified, tilted supramolecular arrangement. This inherently biaxial supramolecular structure—clusters of stratified and tilted mesogens—embedded in an otherwise translationally disordered nematic host medium may account for the NMR biaxiality observed in nematic phases of ODBP mesogems.We are presently investigating, by means of complementary techniques, wheter this local ordering turns into a macroscopic biaxiality (and possibly ferroelectricity) in our BS mesogens and, if so, is this phenomenon spontaneous or field-induced/stabilized.

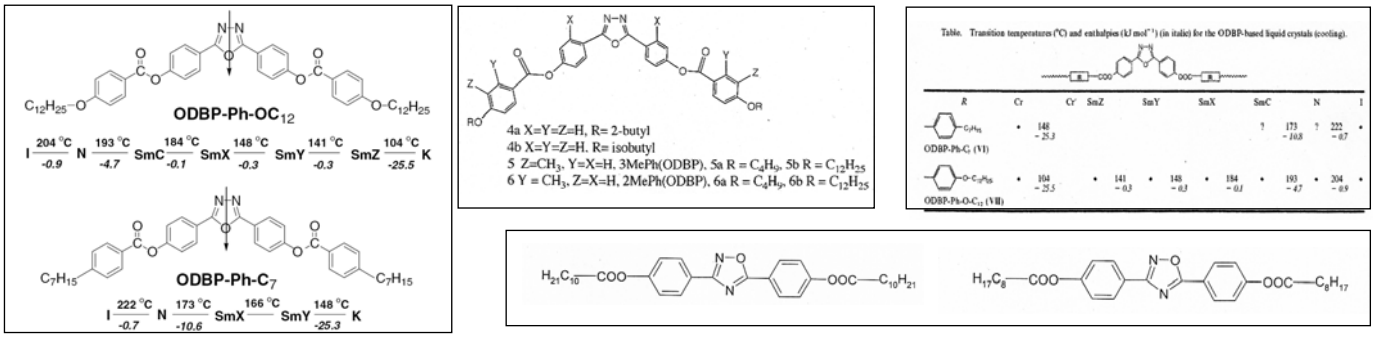

Fig. 1. The chemical structure of the four homologous series of *banana-shaped* molecules, along with their phase sequences and transition temperatures.

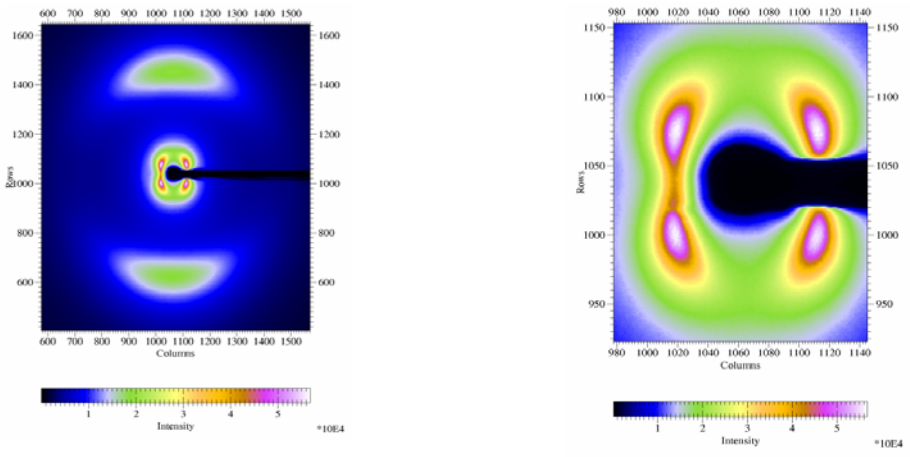

Fig. 2. (A) Representative XRD pattern of the oriented cybotactic N phase of ODBP-Ph-C7. (B) A particular of the SAXS region of the pattern in Fig. (A).

References

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