ESRF	**Experiment title:** X-RAY DIFFRACTION STUDY OF THE BIAXIAL NEMATIC PHASE IN BENT-CORE THERMOTROPIC MESOGENS	**Experiment number**: SC-2042
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Names and affiliations of applicants (* indicates experimentalists):

Prof. O. Francescangeli, Dipartimento di Fisica e Ingegneria dei Materiali e del Territorio, Università Politecnica delle Marche, Via Brecce Bianche, I-60131, Ancona, Italy

Dr. V. Stanic, Dipartimento di Fisica e Ingegneria dei Materiali e del Territorio, Università Politecnica delle Marche, Via Brecce Bianche, I-60131, Ancona, Italy

Dr. I. Dolbnya, Diamond Light Source Ltd., Rutherford Appleton Laboratory, Chilton, Didcot, Oxfordshire, OX11 0QX, UK

Dr. C. Ferrero, ESRF, 6 rue Jules Horowitz, B.P. 20, F-38043 Grenoble Cedex, France

Report:

Predicted theoretically by Freiser more than 30 years ago [1], the biaxial nematic phase N_b has been a contsant challenge in liquid crystal (LC) research. However, in spite of the significant theoretical and simulation work, it was only recently that strong experimental evidence has been produced for the existence of such mesophase in a low molar mass bent-core thermotropic mesogen [2-3]. The announcement has created considerable excitement, for it opened new areas of both fundamental and applied research. The discovery has important implications. For example, recent electro-optic switching experiments [4] on bent-core N_b demonstrated that the response of the short moelcule axis **m** to an applied field is indeed much faster than that of the long molecular axis **n** (the nematic director), a results that is expetced to be the herald of application in fast electro-optical switching devices. From a fundamental point of view, the exietsnce of a biaxial nematic raises the question of the mechanism underlying its formation. In addition, it opens a new frontier field addressed to the relationships between N biaxiality and macroscopic ferroelectric ordering in the N mesophase. Indeed, ferroelectricity is another intriguing and much sought after feature in nematics and 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 [5].

In this experiment we have carried out an X-ray diffraction (XRD) study of a bent-core LC mesogen with chemical structure similar to thaose of refs.[2-3], that displays the *potentially* biaxial nematic phase. The main aim was to achieve full characterization of this unusual state of matter and possibly to provide evidence of the true biaxial nature of the mesophase. The structure of the investigated bent-core LC mesogen, **ODBP-Ph-OC_4** (Fig. 1), is based on the 2,5- substituted oxadiazole heterocycle ring, specifically the oxadiazole biphenol (ODBP) core. This homologous term of the series ODBP-Ph-OC_n has the shortest terminal alkyl chains and exhibits only a nematic phase that, according to preliminary optical studies, appeared to be biaxial (Fig. 2). The unusually wide thermal range (175°C-280°C) offered a unique opportunity of investigation even though the high transition temperatures were experimentally challenging.

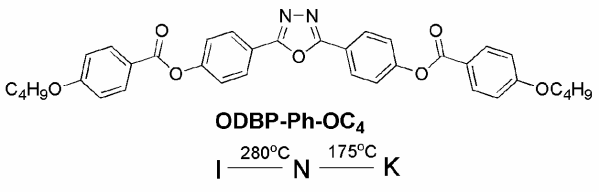

Fig. 1 The chemical structure of the bent-core mesogen **ODBP-Ph-OC4** along with its phase sequences and transition temperatures.

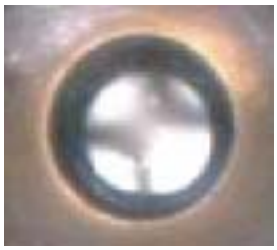

Fig.2. Conoscopic image of the homeotropic N phase of **ODBP-Ph-OC_4**.

XRD analysis was carried out (*i*) on capillary sample uniaxially aligned under a static magnetic field **B** (up to 0.6 T) and (*ii*) on planar LC cell sample (20 μm) aligned under the combined action of a static magnetic field **B** (nornal to the x-ray beam) and of a low-frequency (0-500 Hz) electric field **E** (up to 10^5 V/m) applied across the cell (parallel to the beam). The sample planar cell was be 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 parallel-plane configuration and separated by high precision spacers. Finally, the cell (1cm x 1cm) was filled by capillary with the LC in the fluid phase and then slowly cooled down to room temperature. We have studied the mesomorphic behavior of the samples over the entire mesophasic range as function of temperature.

The XRD measurements on the capillary sample revealed a peculiar pattern characterized by the splitting of the low-angle signal into four symmetrically-located diffuse spots (Fig.3). In principle, this atypical N pattern could have been interpreted either in terms of the V-shape of the mesogen and the intrinsic structure of the N in the **n**-**m** plane (within the model of N biaxility of ref.[3]) or in terms of the *cybotactic* structure of the N (i.e. a N consisting of a conglomerate of cybotactic clusters endowed with pronounced short-range SmC-like ordering) [5]. The measurements carried out on the planar cell sample (Fig. 4) allowed us to discriminate between these two models. In fact, with no applied electric field (and also B=0) we measured a four-spot pattern (Fig. 4A) very similar to that of Fig. 3 with the only difference that now the planar orientating action along the reference direction **r** was provided by the surface anchoring. With applied electric field **E**, no changes occurred until the field strength exceeded the threshold for the Fredericks transition for reorientation when the two pairs of reflections at small angle changed to the isotropic diffuse ring of Fig. 4B. These results unambiguously rule out the molecular V-shape and intrinsic structure of the N [3] as the origin of the peculiar four-spot pattern whereas they agree quite well with the model of the cybotactic N [5]. Accordingly, the pattern change from Fig.4A to Fig.4B is no more a sufficient condition for biaxility that, on the contrary, require additional experimental evidences to be firmly and finally established.

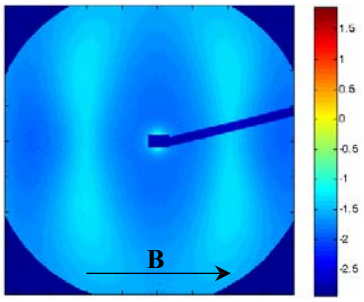

Fig.3. SAXS pattern of the capillary sample of **ODBP-Ph-OC_4** uniaxially aligned under static magnetic field in the N phase at T=230°C.

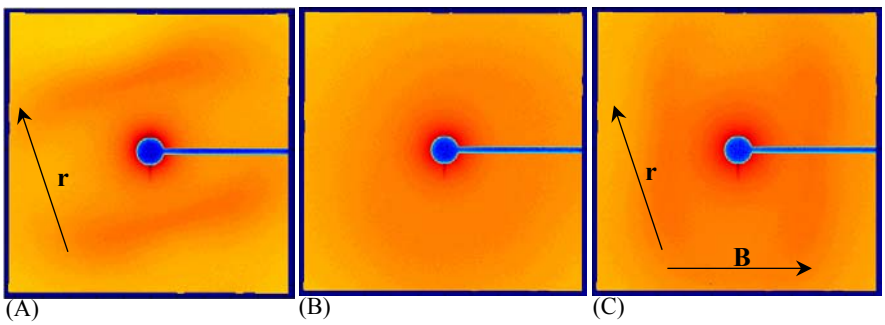

Fig. 4 SAXS pattern of the planar cell sample (20 μm) of **ODBP-Ph-OC_4** in the N phase at T=230°C: (A) no external field: E=0, B=0; (B) E=2.5 V/μm at 500 Hz (above threshold), B=0. (C) E=0, B=0.7 T (avone threshold for reorientation).

Fig.4C shows the effects of the application of a static magnetic field **B** (above the threshold for the Fredericks transition) to the cell of fig.4A, in the absence of electric field. Comparing fig.4A with fig.4A a roration of the four-spot pattern is clearly apparent, which is the consequence of a uniform reorientation of the long moelcular axes (hence the nematic director **n**) towards the direction of **B**. This is consistent with the positive diamagnetic anisotropy of the mesogen which reorients the long axes parallel to **B**. The parallel alignemnt to **B** in Fig.3C is not perfectly achieved because of the competing actions of surface anchoring and magnetic field. Based on the above results, we can conclude that it is possible to get monodomain cell samples where the orientations of the two axes **n**,**m** are individually and simultaneously controlled by external magnetic and electric field, respectively. This result is key for any future XRD study aimed at establishing the biaxial nature of the nematic, opening the possibility of aligning at command the monodomain sample in different ways with respect to the x-ray beam, hence the possibility of probing the structural organization of the mesophase along distinct directions. In view of a a future study fully oriented to the question of the biaxility of these N mesophases, this opportunity will have to be further combined with an extension of the investigated q range to the WAXS region in order to cover the typical average intermolecular distanced involved in these soft condensed materials (a few Å).

References

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