



	Experiment title: A NOVEL NEMATIC MESOPHASE WITH FERROELECTRIC ORDERING IN MESOMORPHIC BANANA-SHAPED 1,2,4-OXADIAZOLES: X-RAY DIFFRACTION STUDY UNDER COMBINED ELECTRIC AND MAGNETIC FIELDS	Experiment number: SC-1939
Beamline:	Date of experiment: from: 28 June 2006 to: 01 July 2006	Date of report: 19 Feb 2007
Shifts:	Local contact(s): Dr. Emanuela DI COLA	<i>Received at ESRF:</i>
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Report:

Ferroelectric liquid crystals (FLCs) are materials of great interest for both fundamental and technological reasons. Conventional FLCs correspond to chiral smectic (Sm)C phases, but FLC mesogens need not necessarily be chiral and, following Niori *et al.* [1], hundreds of achiral “banana-shaped” mesogens (BM) have been shown to yield Sm phases with ferro-, ferri- or antiferroelectric properties [2,3]. However, Sm phases lack the high fluidity and self-healing characteristics of nematic (N) LCs which makes them so useful in electro-optical devices and that we can expect from FNLCs. The existence of FNLC is not forbidden from a theoretical point of view [4] and recent computer simulations have demonstrated ferroelectric fluid phases from both symmetric rod-like and elongated asymmetric (tapered) molecules. Unfortunately, despite years of intensive experimental quest, and claims in some achiral polymeric systems, no successful demonstration of FNLCs has yet been made in low molecular weight thermotropic systems. A key requirement for a potential FN mesogen should be its asymmetric shape, as in particular that of BM. Although very few BM give fluid N phases, a class of these has recently been shown to produce N phases with another much sought after feature, phase biaxiality [5], showing the rich possibilities offered by these materials.

Recently, we have reported a new class of BM with asymmetric 1,2,4-oxadiazoles cores [6] that yields Sm and very wide N phases. In particular bis(4-nonyloxyphenyl)4,4'-(1,2,4-oxadiazole-2,5-diyl)dicarboxylate (Fig. 1, R=C₉H₁₉) shows the phase sequence Cr-(118 °C)-Sm-(140 °C)-N-(263 °C)-I. Repolarization current measurements have shown ferroelectric switching behavior in both the Sm and (quite surprisingly) the N phase corresponding to a spontaneous polarization (P_s) of the order of 50-150 nC/cm². Previous X-ray diffraction (XRD) measurements performed at BM26 on the N phase oriented under magnetic field **B** revealed a peculiar pattern characterized by the splitting of the low-angle signal into four symmetrically-located diffuse spots (inset of Fig.2). Similar SAXS patterns were found for BM oxadiazoles (Fig.1, R=C₈H₁₇) fluorinated to enhance the overall molecular polarity. In principle, this atypical pattern could have been interpreted either in terms of the intrinsic structure of the N in the **n-m** plane [5] 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) [7]. To discriminate between these two models, a specific XRD experiment was carried out here using planar LC cells bounded by conductive plates across which a low frequency ($f=500$ Hz) external electric \mathbf{E} was applied. The main result of this experiment is summarized in fig. 2. With no applied field, we measured a four-spot pattern (Fig. 2A) very similar to that of the inset. With applied electric field, no changes occurred until the field strength exceeded the threshold for the Fredericks transition (6 V/ μm) when the two pairs of reflections at small angle changed to the isotropic diffuse ring of Fig. 2B. These results unambiguously rule out the intrinsic V-shaped structure molecule within the model of biaxial N of ref. [5] as the origin of the peculiar four-spot pattern whereas they agree quite well with the model of cybotactic N [7]. Combining the above XRD results, repolarization current measurements and detailed computer simulations, we have demonstrated for the first time ferroelectric response in a low-molecular weight N and shown that macroscopic bulk polarization involves long-range ordering of polar cybotactic clusters [8]. This was the main purpose of the proposal and, accordingly, the outcome of the experiment has to be considered quite successful.

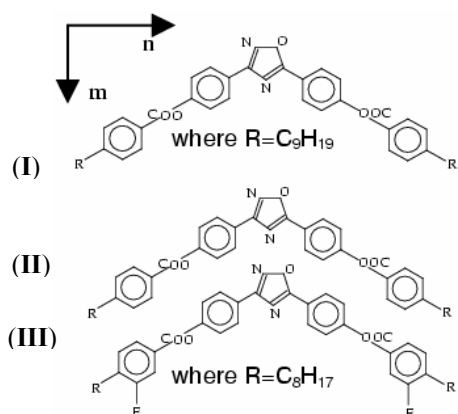


Fig 1. Molecular structure of the banana-shaped mesogens with 1,2,4-oxadiazoles cores investigated in this experiment.

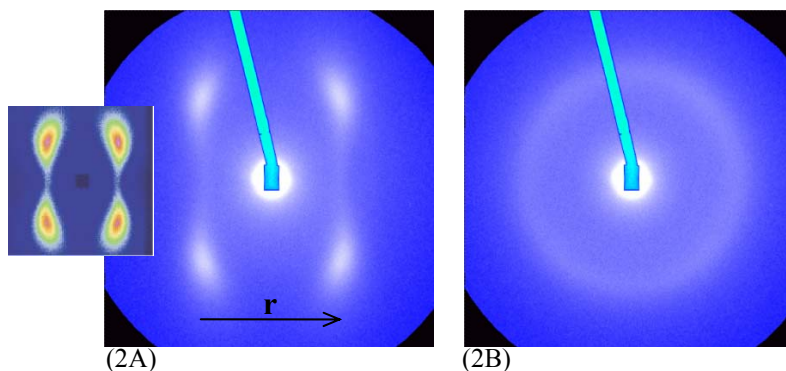


Fig 2. SAXS patterns of sample I in the N phase at $T=150^\circ\text{C}$. The inset of (2A) to a uniaxially-oriented capillary samples under horizontal magnetic field \mathbf{B} . The rest of the figure refers to SAXS measurements on a thin (20 μm) planar oriented cell samples aligned with \mathbf{n} parallel to the reference axis \mathbf{r} (imposed by the surface anchoring). (2A): $E=0$; (2B) $E= 7.5$ V/ μm

The further question that we just started to address with the present experiment concerns the uni- or biaxial-nature of this unique N mesophase and its connection with the ferroelectric response. Proving the biaxial nature of the N phase is of great importance. In fact, in spite of the great fundamental and applicative interests [9] and the extensive theoretical and simulation work, the thermotropic biaxial nematic (N_b) phase has remained experimentally elusive for more than three decades and only recently its existence seems to have been definitely confirmed [10]. To this purpose, preliminary measurements were carried out using combined magnetic \mathbf{B} and electric \mathbf{E} fields to control the orientation of both long and short molecular axes (\mathbf{n} , \mathbf{m} in fig. 1). The samples exhibit positive magnetic- and negative dielectric- anisotropy, therefore, \mathbf{B} and \mathbf{E} tend to orient parallel to the field itself the \mathbf{n} and \mathbf{m} axis, respectively. Special planar sample cells ($1\text{cm} \times 1\text{cm}$; thickness= 20 μm) were prepared using ITO-coated thin glasses as boundary plates, additionally coated with a thin film of SiO_x deposited under vacuum at 60° evaporation angle in order to achieve strong planar anchoring and homogeneous planar LC orientation (i.e. $\mathbf{n} \parallel \mathbf{r}$, where \mathbf{r} is the reference aligning direction imposed by the surface treatment). We have studied the three compounds of fig.1 as function of temperature in their N range (between $T \approx 140^\circ\text{C}$ and $T \approx 270^\circ\text{C}$). The sample was held inside a temperature-controlled hot-stage with the plates normal to the incident x-ray beam and will be oriented by the combined action of a low frequency (0 - 1 KHz) oscillating electric field (of variable intensity up to 7×10^6 V/m), applied across the plates, and a static magnetic field (up to 0.6 T), applied in the orthogonal direction parallel to the rubbing axis. SAXS patterns were acquired either with no applied fields or under proper combinations of \mathbf{B} and \mathbf{E} .

The preliminary result of fig.3 is very promising in view of a next more extended and systematic study of the *potential* biaxility of the N phase of these mesogens. In fact, it clearly shows that starting from the configuration of fig.2B, when the initially planar LC sample cell (with horizontal \mathbf{r}) has been subjected to the external electric field above threshold (fig.3A), further application of a strong magnetic field \mathbf{B} (fig. 3B) is able

to reorient the long axes parallel to **B** without changing previous orientation of the short axes parallel to **E**. In addition, the noticeable sharpening of the four-spot feature (with respect to that of fig.2A) gives evidence of a strong increase of the spatial extent of the SmC-like positional ordering that may be a sign of a field-induced N→SmC phase transition, a new as unexpected as striking effect that certainly deserves further investigation. Based on these results, by means of a proper combination of **E** and **B**, together with the additional aligning field imposed by the surface treatment, it is possible to obtain monodomain cell samples where the two molecular axes **n,m** are differently oriented with respect to the incident x-ray beam. In these conditions one can probe the structural organization of the mesophase along different directions, that in key in experiments aimed to establish the biaxial nature of a mesophase.

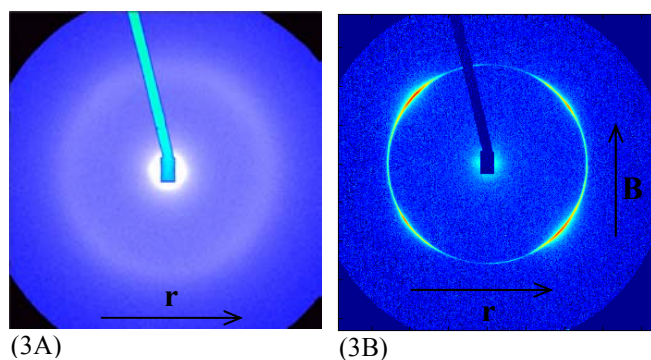


Fig. 3 SAXS patterns of sample **I** in the N range at $T=150^{\circ}\text{C}$: (A) with $B=0$ and $E=7$ V/mm (above threshold for the Frederick's transition); (B) $E=7$ V/mm and $B=1$ T (above threshold for the Frederick's transition). Arrow is the planar-orientation direction of **n**.

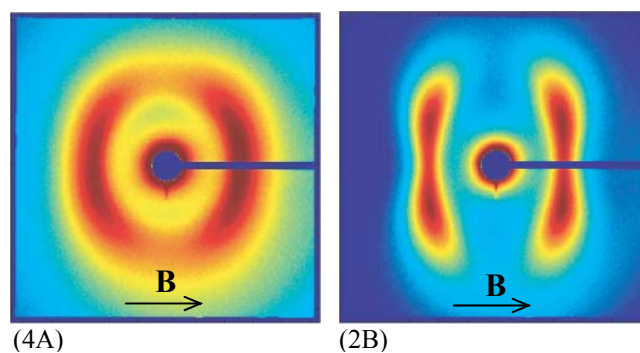


Fig. 4 The two SAXS patterns of the magnetically aligned cell sample of **III** observed in the N phase at different temperatures.: (3A) the typical pattern of a conventional uniaxial nematic; (3B) the four-spot pattern of the *potentially biaxial* cybotactic nematic phase.

An important role in this study will be played by sample **III** that, on the basis of this preliminary study, has revealed a unique thermotropic behaviour never observed so far for bent-core mesogens. In fact, as shown in Fig.4 it exhibits in sequence at different temperatures within the N mesophasic range both the typical pattern of a conventional uniaxial N (fig. 3A) and the four-spot pattern of the *potentially biaxial* cybotactic nematic (Fig. 3B). Additional experiments are necessary to establish the true biaxial nature of the cybotactic nematic mesophase of these compounds, exploiting the possibility demonstrated in this experiment of orienting separately and simultaneously the two molecular axes by electric and magnetic fields. However, any further study of such kind will require an extension of the investigated q range to the WAXS region in order to be able to probe the typical average intermolecular distances involved in these soft condensed materials.

References

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