



Experiment title: A NOVEL NEMATIC MESOPHASE WITH FERROELECTRIC ORDERING IN MESOMORPHIC BANANA-SHAPED 1,2,4-OXADIAZOLES: X-RAY DIFFRACTION STUDY UNDER ELECTRIC FIELD

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SC-1655

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Report:

Ferroelectric liquid crystals (FLCs) are materials of great interest for both fundamental and technological reasons. After Niori *et al.* [1], interest in mesogenic “banana-shaped” (BS) molecules has rapidly grown because of the ability of bent-core mesogens to generate ferroelectric fluid mesophases in the absence of chiral groups. Due to the sterically-induced special molecular packing of the bent molecules, smectic layers with C_{2v} , C_2 , and possibly also C_{1h} or C_1 symmetry could occur, giving rise to ferro-, ferri- or antiferroelectric properties [2,3]. However, the currently known layered smectic (Sm) phases from BS molecules (as well as from chiral molecules) lack the high fluidity and self-healing characteristics of the nematic (N) liquid crystals (LCs) which makes them so useful in electro-optical devices and that we can expect from FNLCs. Therefore, besides the fundamental interest, the development of ferroelectric N phases is a goal of great practical importance.

Recently, we have synthesized and characterized for the mesomorphic behavior [4] the homologous series of 1,2,4-oxadiazoles–asymmetric BS molecules (Fig. 1). We found that these new compounds display both the smectic (Sm) and the nematic (N) phase (which is very rare for BS molecules), the latter extending over an unusually wide temperature range. Measurements of repolarization currents under triangular wavevoltage have shown, quite surprisingly, that these compounds exhibit spontaneous polarization (P_s) and ferroelectric switching behavior in both the Sm and the N phase ($P_s \approx 50\text{-}150 \text{ nC/cm}^2$). These compounds provide the *first experimental evidence* of spontaneous polarization and ferroelectric ordering in a low-molecular weight N. In fact, even though polar ordering is not compatible with the symmetry of the N phase of conventional rod-like molecules, results of computer simulations [5] following previous theoretical studies [6] have predicted that ferroelectricity could appear even in the N phase. To our knowledge, the only experimental confirmation of this prediction has been found so far in a rod-like aromatic polyester [7]. Therefore, our compounds offer a unique possibility for studying the spontaneous polarization and ferroelectric ordering in the N phase of low-molecular weight LCs.

Previous X-ray diffraction (XRD) measurements performed at BM26 on the N phase oriented under magnetic field ($B=0.6 \text{ T}$) revealed a peculiar pattern characterized by the splitting of the low-angle signal into four symmetrically-located diffuse spots (Fig. 2). Similar SAXS patterns were found for BS oxadiazoles

(Fig.1c) fluorinated to enhance the overall molecular polarity. In principle, this atypical pattern could have been interpreted either in terms of the intrinsic structure of this N phase in the **n-m** plane, connected with the banana V-shape of the mesogens [8], or in terms of the peculiar *cybotactic* structure of the N, i.e. N consisting of a conglomerate of cybotactic clusters (few nanometer-sized) endowed with pronounced short-range SmC-like ordering [9]. The experiment reported herein has been carried out to discriminate between these two models, with the aim of understanding the mechanism underlying the ferroelectric behavior.

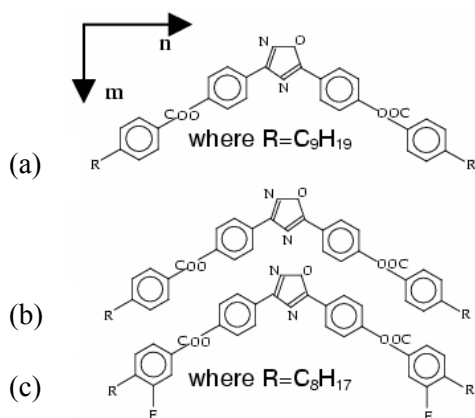


Fig 1. Molecular structure of the BS mesogens with asymmetric 1,2,4-oxadiazoles cores.

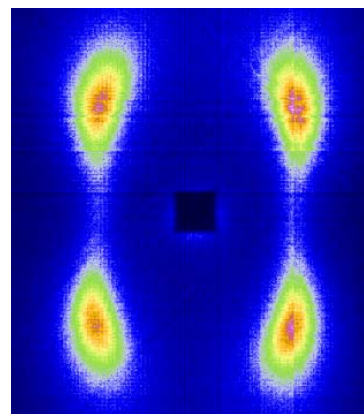


Fig 2. SAXS pattern in the N mesophase ($T=150^\circ\text{C}$) of capillary sample (a) under horizontal magnetic field ($B=0.5\text{ T}$). Sample thickness is 2mm.

Sample planar cells of $25\ \mu\text{m}$ thickness were prepared using two ITO-coated thin glass plates. Over the ITO-layers, the glass plates were further coated with a thin film of SiO_x deposited under vacuum at 60° evaporation angle in order to get strong planar anchoring of the LC molecules resulting in homogeneous planar orientation of the nematic director **n** (parallel to the long molecular axis). The cell was assembled with the glass plates facing their coated sides in a parallel-plane configuration and being separated by precision spacers. The cell ($1\text{ cm} \times 1\text{ cm}$) was filled with the LC (in the isotropic phase) by capillarity and then slowly cooled down to room temperature. This cell was used to apply an electric field across the conductive plates and study the response of the director. We have studied the mesomorphic behavior of the three compounds of fig.1 as function of temperature in their nematic range (between $T \approx 140^\circ\text{C}$ and $T \approx 270^\circ\text{C}$). SAXS spectra were collected between $q_{\min} = 0.1\ \text{\AA}^{-1}$ and $q_{\max} = 0.4\ \text{\AA}^{-1}$ with the sample held inside a temperature-controlled hot-stage (Linkam) and oriented by an external electric field of variable intensity (up to $7 \times 10^6\ \text{V/m}$), waveform (sine-, square-, -triangular, wave) and frequency (between 0 and 1 KHz). The wavelength of the incident beam was $\lambda = 1\ \text{\AA}$ and the sample-detector distance $d = 1.5\ \text{m}$. 2D diffraction patterns were recorded using a MAR CCD detector.

The adopted experimental configuration allowed orientation of both molecular axes **n** and **m** (the latter being defined as the mean orientation of the apex bisectors). Since the sample thickness is one order of magnitude larger than the value of the smectic correlation lengths ($\approx 1\ \mu\text{m}$) in highly ordered and single-domain bulk smectic phases, for all practical purposes, it is a bulk sample. Being the molecular core asymmetric, the electric dipole moment is not exactly parallel to the short molecular axis **m**. The components of the dipole moment along **n** and **m** are 0.74 D and 0.49 D, respectively. The large ($\sim 5\ \text{D}$) transverse dipole moment bisecting the oxadiazole bent-core mesogen apex dominates the negative dielectric anisotropy of the mesophase. Then, an alternate wave electric field of enough strength applied perpendicular to the plates can reorient the dipole moment, hence **m**, during XRD measurements. With no applied field, we measured a four-spot pattern (Fig. 3) very similar to the magnetic field-aligned capillary samples (Fig. 2). After correcting for the difference in sample thickness, the integrated intensity is more than order of magnitude higher than in capillary sample. This increase is consistent with the alignment of **n** parallel to the *reference* direction imposed by the aligning SiO_x layers. When an electric field is applied, no changes occur until the field strength exceeds a threshold value (for the Fredericks transition) of about $6 \times 10^6\ \text{V/m}$ (at 500 Hz) and reorients the dipole moment (hence, essentially **m**) perpendicular to the glass substrates. In these conditions, the two pairs of reflections at small angle change to an isotropic diffuse ring centered at the same q value. The two distinct diffraction patterns, with and without applied field, together with the isotropy of the SAXS pattern

with applied electric field unambiguously rule out the intrinsic structure of the N in the $\mathbf{n-m}$ plane [6] to be the origin of the observed four-spot pattern. In such case, in fact, with applied field the two pairs of reflections at small angle should change to one pair of diffuse reflections along the *reference* direction, whereas for a conventional uniaxial N, no modification at all of the pattern should be observed. On the contrary, the experimental evidences agree with the model of cybotactic N [9]. In fact, without field the four-spot anisotropic pattern is due to the tilted SmC-like layer organization within the cybotactic clusters axially oriented, on average, parallel to the *reference* direction. Application of the electric field above the threshold causes bulk reorientation of the cybotactic clusters with their dipolar axes parallel to the field but with a random orientation in the normal plane (uniaxial orientation), which explains the observed isotropic SAXS pattern. Really, a very thin layer of LC ($\sim 1 \mu\text{m}$) close to the boundary surfaces maintains its original axial orientation (along the *reference* direction) in the transversal plane, which reflects into the very small azimuthal intensity-modulation of the (quasi-)isotropic diffuse ring evidenced by a more careful analysis of the intensity profile. The cybotactic N model accounts for spontaneous polarization within the single cluster if ferroelectric layering organization occurs with synclinic layer interfaces. On the other hand, the repolarization current measurements point to spontaneous polar ordering of the clusters, which explains the observed ferroelectric switching response of the sample. Accordingly, polar ordering occurs on different length scales, i.e. ordering within the nanocluster, *short-range* order, and ordering involving the polar clusters as an ensemble of single polar entities, *long-rang* order.

In summary, the reported experiment has provided new essential information on the structure of this novel nematic mesophase which allowed us to explain its unique ferroelectric properties [10]. An important question still open concerns the uni- or biaxial- nature of this N mesophase. In fact, even though detailed computer simulations [10] show a remarkable increase of phase biaxiality under electric-field application, the present experimental setup did not allow us to get a conclusive answer to this question. A properly designed experiment involving molecular orientation under combined magnetic and electric field is planned to specifically address this point.

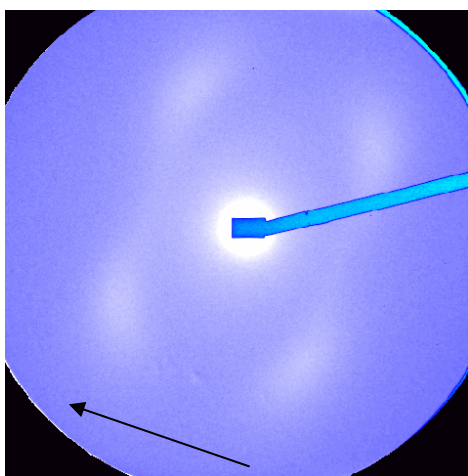


Fig. 3 SAXS pattern of the N phase of sample of sample (a) with no applied electric field ($T=150 \text{ }^\circ\text{C}$). Arrow indicates the planar-orientation direction on \mathbf{n} in the LC cell

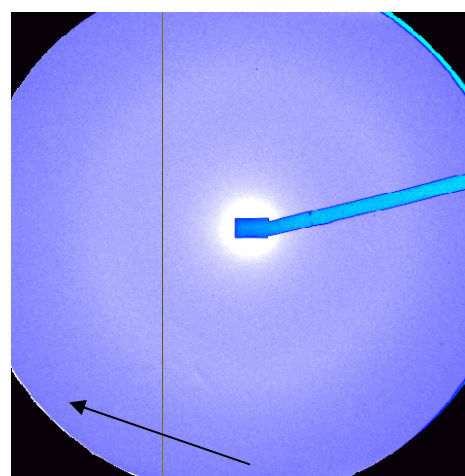


Fig. 4 SAXS pattern of the N phase of sample of sample (a) with an applied electric field above the threshold for the Fredericks transition ($T=150 \text{ }^\circ\text{C}$).

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