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Resonant X-ray scattering studies of the B2 phase formed by bent-core molecules

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We have performed resonant X-ray scattering on two bent-core liquid crystal compounds exhibiting the B2 phase using three sample geometries: free-standing film and two others with free surface arrangements. The results conclusively demonstrate the two-layer orientational periodicity in this phase suggested by optical studies. We have performed the first resonant scattering experiments on liquid crystals at the chlorine K-edge, opening up a new class of compounds for resonant X-ray scattering studies. Furthermore, we have achieved an excellent alignment of the B2 phase with a free surface.

1. Introduction

Several new liquid crystal mesophases formed by bent-core (banana-shaped) molecules without a chiral group have been identified [1]. Of considerable interest is the observation of ferroelectric and antiferroelectric responses from these achiral molecules. Due to their shape, bent-core molecules may be packed with C_{2v} symmetry, which has been proposed to allow ferroelectric behaviour [2]. In particular, one of these phases, B2, has been shown to have an antiferroelectric response. Link *et al.* [3] presented depolarized reflected light microscopy results that supported an achiral antiferroelectric structure for the B2 phase in free-standing films. Subsequently, Olson *et al.* [4] demonstrated by studying one-layer films that single layers in the B2 phase are chiral. The simplest explanation for the antiferroelectric behaviour observed in films is a two-layer unit cell for the B2 phase, in which the molecules have a finite tilt relative to the layer normal that is the same in all layers (synclinic structure) as displayed in figure 1. The two-layer periodicity is accounted for by the bend of the molecule and concurrently the polarization being oriented in opposite directions in adjacent layers. To date, most studies of the B2 phase have been primarily optical [3, 4] and have been difficult because banana compounds do

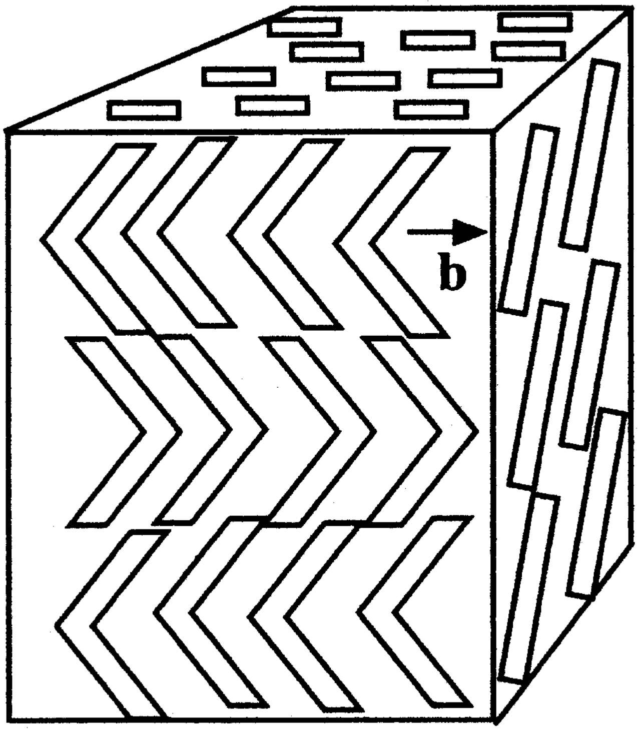

Figure 1. The proposed structure for the B2 phase observed in free-standing films. The bend of the molecules described by the vector **b** points in the opposite directions in adjacent layers. The molecules tilt perpendicular to **b** and in the same direction in adjacent layers.

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not easily align in the bulk or support thick uniform free-standing films.

As in chiral smectic phases, the B2 phase is mainly characterized by orientational periodicities. Such orientational structures can be readily and directly determined by resonant X-ray scattering (RXS) [5]. It is important to apply such an experimental tool to check the proposals made using more indirect structural probes as in optical techniques. In addition, RXS does not have a strong requirement for films to be uniform; thus thicker, less uniform samples can be studied. This allows us to confirm the B2 structure in thicker samples which are presumably less influenced by surface effects [6]. We also obtained high quality results from bulk samples that were aligned on glass treated with a surfactant.

2. Experimental results and analysis

While ordinary X-ray diffraction is sensitive to average electron density and thus to positional order, RXS provides a means to probe the order that is orientational. In RXS, applied in the Bragg geometry, the diffracted intensity depends on the orientation of the generally asymmetric local bonding environment of the resonant atom relative to the polarization of the incident X-ray beam. We determined and then tuned the energy of the incident X-rays to the peak of the white line in the absorption spectrum of a heavy atom, the resonant atom, in the core of the constituent molecule. Under these circumstances, the X-ray structure factor (XSF) becomes a tensor. In the molecular reference frame, such a tensor can be represented as [7]:

$$S_M = \begin{pmatrix} -f/3-\Delta & 0 & 0 \\ 0 & -f/3+\Delta & 0 \\ 0 & 0 & 2f/3 \end{pmatrix}$$

where $2f/3$ is the principal structure factor along the long axes of the molecules and Δ represents the anisotropy perpendicular to the molecular long axes associated with the bonding environment of the resonant atom. The XSF in the layer reference frame, S_L, is found by rotating S_M through appropriate angles. The XSF for the composite structure, S, is calculated by summing S_L multiplied by the appropriate phase factor over all the layers in the film. Using this method, Levelut and Pansu [7] demonstrated that for a two-layer repeat unit structure, with the X-ray scattering wave vector in the Q_z reciprocal space direction where z denotes the smectic layer normal, resonant peaks occur at $Q_z/Q_0 = L + M(1/2+\varepsilon)$ where L is an integer, and $M = \pm 1, \pm 2$. This result was presented with the factor ε, which represents a shift or splitting of the peaks associated with a pitch observed in chiral liquid crystal phases. For the B2 phase in free-standing films, every layer has opposite chirality to its nearest-neighbours, thus $\varepsilon = 0$. Accordingly, only the first order ($M = \pm 1$) satellite appears distinctly and the second order ($M = \pm 2$) one should overlap with a non-resonant Bragg peak.

The high degree of polarization and the energy tunability needed in RXS as described above requires a synchrotron X-ray source. The experiment described in this paper was conducted at beamline X19A at the National Synchrotron Light Source (NSLS) at Brookhaven National Laboratory. We present resonant X-ray scattering (RXS) results from two compounds, (14PMB)Cl [8] and $(16OTBB)_2$ [9], exhibiting the B2 phase. Figure 2 shows the molecular diagrams of these two compounds. The phase sequence for (14PMB)Cl is isotropic(I)(127°C)B2(68°C)crystal(Cr); and I(119°C)B2-(108°C)Cr for $(16OTBB)_2$. The compounds were chosen for the presence of resonant atoms in the core of the molecule: chlorine in (14PMB)Cl and sulphur in $(16OTBB)_2$, with convenient resonant energies of 2821 and 2475 eV, respectively. Moreover, the (14PMB)Cl has a very large temperature range for the B2 phase that is stable at relatively low temperatures.

Three types of sample preparation were used, as shown in figure 3. In each case the sample was housed in a two-stage oven with temperature stability of 5 mK. The oven was mounted on a vertical translation stage connected to a chi arc on a two-circle Huber goniometer. The front-end design included a chamber for fluorescence measurements. The resonant edge energy was determined by measuring the total fluorescence signal of

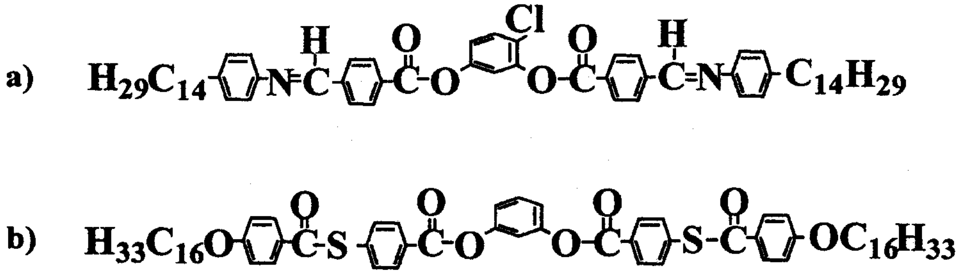

Figure 2. The chemical structures of the (14PMB)Cl and $(16OTBB)_2$ compounds are shown in (*a*) and (*b*), respectively. (The molecules are drawn straight to conserve space.)

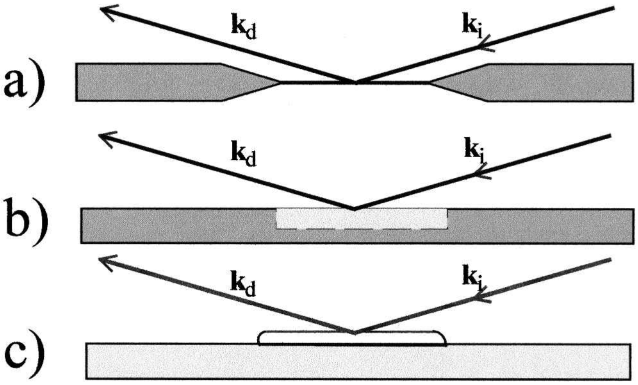

Figure 3. The three geometries used in the experiments: (*a*) the film supported by steel knife edges, (*b*) the trench geometry and (*c*) the sample on treated glass. The X-ray scattering wavevector in the Q_z direction is $\mathbf{Q}_s = \mathbf{k}_d - \mathbf{k}_i$.

powder samples of the (14PMB)Cl and the $(16OTBB)_2$ compounds while the incident energy was tuned through the K-absorption edge of the heaviest element.

After the fluorescence chamber, the front-end included a beamstop, vertical and horizontal slits, and a filter unit. After the monochromatic beam diffracted off the film, it passed through another pair of slits to a silicon X-ray detector. The entire beam path was flushed with helium to reduce attenuation of the X-rays. The set-up was mounted on a table with motorized vertical and horizontal translation perpendicular to the flight path. This allowed us to align the set-up with respect to the incident X-ray beam. A typical experiment involved lining up theta, two-theta, chi, sample height, and table position, and scanning through Q_z/Q_0 on a sample held at constant temperature in the B2 phase.

Typically, phases formed by bent-core molecules do not readily support uniform thick free-standing films of a sufficiently large area, although some groups have been able to prepare thick films in the B2 phase [4]. We were able to prepare free-standing films several hundred smectic layers thick of the (14PMB)Cl compound. This geometry is shown in figure 3 (*a*). Free-standing films provide excellent sample alignment and yield sharp layer reflections at $Q_z/Q_0 = n$. With the experimental set-up used, measurements of the $Q_z/Q_0 = 1$ and $Q_z/Q_0 = 2$ peaks had full-width-at-half-maximum (FWHM) values of 0.0035 ± 0.0005 Q_z/Q_0. Scans at several temperatures indicated a layer spacing that increased from 46.8 to 47.6 Å on cooling from 100 to 71°C.

Scans through Q_z/Q_0 revealed resonant satellite peaks at the 1/2 order position as predicted by calculations by Levelut and Pansu [7] for a two-layer structure. A typical scan through the resonant peak is shown in figure 4. The position of each resonant peak at all temperatures was confirmed to be at $Q_z/Q_0 = 1.500$ to within our resolution, and the peak FWHMs were $0.004 \pm 0.001 Q_z/Q_0$. On increasing the incident X-ray energy to 100 eV above the resonant energy, the $Q_z/Q_0 =$ 1.500 peak disappeared as illustrated in figure 4. Thus the $Q_z/Q_0 = 1.500$ peak was confirmed to be a resonant peak.

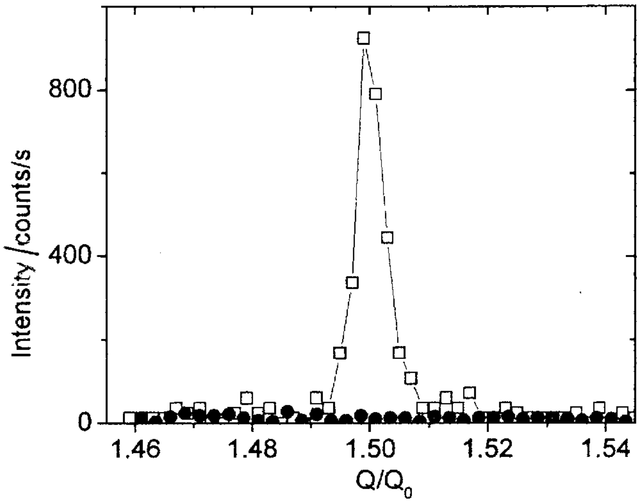

Figure 4. A scan through the resonant satellite peak in the free-standing film geometry at the resonant energy (squares) and 100 eV above the resonant energy (circles) for the (14PMB)Cl compound at 100°C.

Studies of the (14PMB)Cl compound were also performed using two free-surface sample configurations. The 'trench' geometry is displayed in figure 3 (*b*). Here a hole approximately 0.5 mm deep was milled into a piece of aluminum. Sample was loaded into the trench and heated into the isotropic phase at which point it filled the trench uniformly. Usually a free surface in a liquid crystal phase will order before the interior layers [6]. In this case we hoped to achieve a homeotropically-aligned sample by cooling slowly into the B2 phase. The peaks were typically very broad in this geometry and the intensity was low. Rocking scans through theta demonstrated that the sample surface was curved, and we concluded that a single free surface was not sufficient to align the sample well. Nonetheless, we observed a very weak resonant satellite peak at one temperature in the trench geometry.

The third sample configuration, as shown in figure 3 (*c*), was a sample on a glass surface treated with hexadeciltrimethylammonium bromide (HTAB). A monolayer of HTAB on the glass has been employed, in general, to promote homeotropic alignment of a liquid crystal sample [10]. We obtained high quality results using this sample configuration on both (14PMB)Cl and $(16OTBB)_2$. We resolved resonant satellite peaks at the 1/2 order position in both compounds using this technique as shown in figure 5. The peaks shown have been normalized to

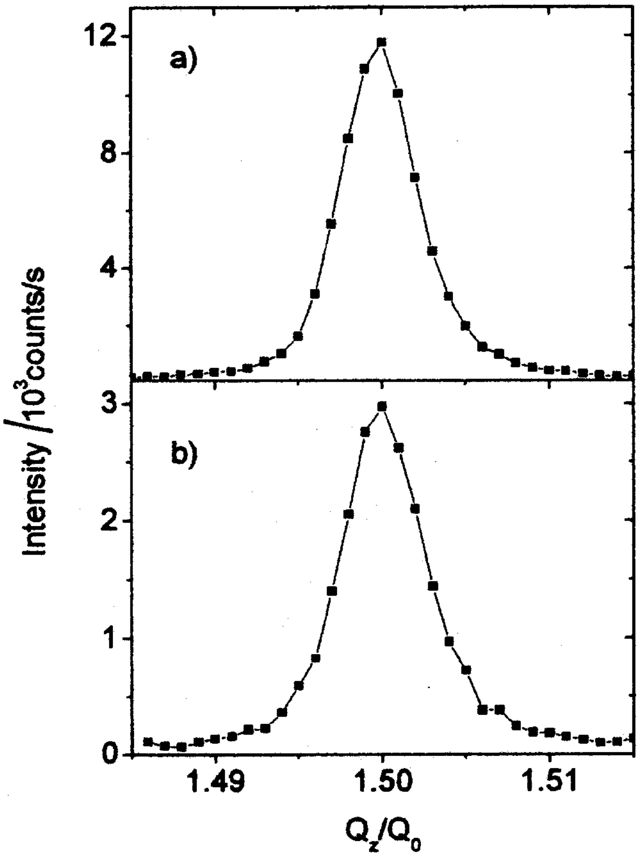

Figure 5. (*a*) Scan through $Q_z/Q_0=1.500$ for $(16OTBB)_2$ at 116°C. (*b*) Scan through $Q_z/Q_0=1.500$ for (14PMB)Cl at 100°C. Both scans were made with no attenuators.

the same incident intensities as used in the scan shown in figure 4. By comparing the peaks in figures 4 and 5, we see that additional scattered intensity can be gained using this free surface configuration without a significant increase in peak width. Detailed measurements of the $Q_z/Q_0=1.000$, $Q_z/Q_0=1.500$, and $Q_z/Q_0=2.000$ peaks in the $(16OTBB)_2$ compound showed that the two-layer structure remained as a function of temperature throughout the B2 phase window while the layer spacing remained roughly constant at 41.4 Å.

3. Summary

We have studied two bent-core compounds exhibiting the B2 phase using resonant X-ray scattering. The results on the (14PMB)Cl compound are the first resonant scattering results obtained on liquid crystal compounds containing chlorine. This will increase the number of possible compounds that may be studied in resonant scattering experiments. It is interesting to note that the position of the chlorine atom off a central benzene ring in the molecule is similar to the position of bromine [11] in other liquid crystal compounds that yielded much weaker scattering amplitudes in resonant X-ray experiments. We have directly confirmed the existence of a two-layer orientational periodicity in the achiral B2 phase. Finally, we found that the bent-core compounds exhibiting the B2 phase can be aligned on glass using a surfactant. This will open up the possibility of studying other novel phases formed by bent-core molecules using resonant X-ray scattering.

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