Short-Range Smectic Order in Bent-Core Nematic Liquid Crystals

S. H. Hong, Kent State University - Kent Campus
R. Verduzco
J. C. Williams, Kent State University - Kent Campus
R. J. Twieg, Kent State University - Kent Campus
E. DiMasi, et al.

Available at: http://works.bepress.com/antal_jakli/1/
Short-range smectic order in bent-core nematic liquid crystals


Received 8th January 2010, Accepted 3rd June 2010
DOI: 10.1039/c000362j

Small angle X-ray diffraction from the uniaxial nematic phase of certain bent-core liquid crystals is shown to be consistent with the presence of molecular clusters possessing short-range tilted smectic (smectic-C) order. Persistence of these clusters throughout the nematic phase, and even into the isotropic state, likely accounts for the unusual macroscopic behavior previously reported in bent-core nematics, including an anomalously large flexoelectric effect (\(~1000\) times that of conventional calamitic nematics), very large orientational and flow viscosities (\(~10–100\) and \(\sim 100–1000\) times, respectively, typical values for calamitics), and an extraordinary flow birefringence observed in the isotropic state.

The fluid phases of bent-core liquid crystals exhibit extraordinary properties compared to their more traditional, calamitic (rod-shaped) counterparts. In addition to various reports of biaxial fluctuations\(^1\) and equilibrium phase biaxiality\(^2–4\) in the nematic state of certain specific compounds, the range of remarkable phenomena observed includes large flow birefringence,\(^5\) dramatically increased viscosities associated with both flow and orientational (optic axis or director) fluctuations,\(^6,7\) non-Newtonian fluid rheology,\(^8\) giant flexoelectricity,\(^9\) and indications of polar response in electro-optical switching measurements.\(^10,11\) The particular structural origin of these properties, as well as their compatibility with the fluid nature and relatively high symmetry normally associated with the nematic phase, is not definitely established, but the various experimental studies suggest that higher-order, short-range molecular correlations must play a significant role. For example, it is clear that the giant flexoelectric effect cannot originate purely from the shape anisotropy of individual bent-shaped molecules whose dipole moments, as in typical thermotropic nematics, exhibit no significant spatial correlations.\(^9\)

In previous work,\(^5–7\) we suggested the short-range structure of bent-core nematics could be described by an extension of the so-called “cybotactic groups” originally proposed by de Vries\(^12,13\) — i.e., layered molecular arrangements existing on short length and time scales, which are typically associated with pretransitional fluctuations of smectic order near a nematic-smectic transition. We conjectured that in bent-core systems, where the molecular shape strongly favors close packing into layers, such smectic-like clusters may exist for much longer lifetimes and over the full nematic range, and even manifest themselves in compounds that do not possess a smectic-A or C phase below the nematic. In this sense, they would differ from the purely pretransitional entities associated with the term “cybotactic”, and could exhibit, for instance, correlation lengths that are relatively insensitive to temperature. Other researchers have also suggested the possibility of micro- or nanoscopic molecular clusters, which are biaxially ordered and not necessarily based on smectic layering, and of a macroscopic uniaxial phase built up from random orientations of the biaxial director of these clusters.\(^14\) Recently, different small angle X-ray scattering (SAXS) studies\(^15–16\) on bent-core compounds used a model based on tilted smectic clusters to account for the four peak pattern of scattering observed in aligned nematic samples.

The main purpose of the present paper is to demonstrate how short-range smectic-C correlations account for the major features of two-dimensional SAXS patterns recorded on two particular bent-core nematics that exhibit the most remarkable macroscopic properties in the aforementioned list. Fig. 1 presents the chemical structure and phase sequences of these compounds, 4-chloro-1,3-phenylene bis-4-[4-(9-decenyloxy)benzoyloxy] benzoate (abbreviated CIPbis10BB) and 4,6-dichloro-1,3-phenylene bis-4-[4’-(dodecylxoy)] biphenyl] carboxylate (DCIPbis12BC).\(^17,18\) Neither liquid crystal possesses a lower...
temperature smectic phase, and both are uniaxial nematics. The evolution of the SAXS patterns on cooling from the isotropic to nematic phase reflects both the orientational ordering of the average director of the correlated smectic clusters and slightly increasing positional correlation lengths, which are typically only of order the molecular length. Remarkably, data in the isotropic phase suggest that the clusters persist (with random orientations) to temperatures significantly above the nematic-isotropic transition. We also contrast our results to data obtained on a “cybotactic” calamitic, whose structure (Fig. 1) resembles one arm of the bent-core compound CIPbis10BB, and discuss implications of our results for the origin of the unusual macroscopic behavior previously observed in bent-core nematics.

Samples of CIPbis10BB or DCIPbis12BC were loaded into cylindrical fused quartz capillaries of 1 mm inner diameter and 0.01 mm wall thickness; the surfaces were not treated for any particular anchoring of the liquid crystals. The filled capillaries were then mounted into special aluminium cassettes (Fig. 2, top) that allowed X-ray access through a 1.5 mm hole with ±13.5° angular range for scattering. The cassettes fit into a standard hot stage (Instec model HCS402). The temperature stability was typically ±0.01 °C. High remanence, cylindrical neodymium iron boron magnets were stacked on either side of the capillaries, with a 2.5 mm spacing between the 12.7 mm diameter pole faces. The magnetic field measured at the sample position was 1.5 T. Alternatively, the magnets could be removed for studies of “powder” nematic samples (cooled from the isotropic phase in the absence of any aligning field). In all cases, the nematic-isotropic transition point \( T_{NI} \) on cooling was characterized by polarizing optical microscopy for later reference during the SAXS measurements.

The hot stage containing the sample cassette was mounted in a vacuum chamber and centered in an evacuated flight path on the SAXS beam line X6B at the National Synchrotron Light Source (NSLS). The incident beam energy was 16 keV (wavelength 0.775 Å, energy resolution \( \Delta E/E = 5 \times 10^{-3} \)); the beam cross-section was reduced by horizontal and vertical slits to 0.2 × 0.3 mm before the sample. Two dimensional SAXS images were recorded on a Princeton Instruments 2084 × 2084 pixel array CCD detector positioned approximately 1.2 m from the sample. The effective q-resolution at the detector was conservatively estimated by measuring the FWHM of the first order diffraction peak from a powder sample of silver behenate, which was filled into a capillary identical to those used for the liquid crystal samples. This measurement gives \( \Delta q = 0.0033 \text{ Å}^{-1} \). The diameter of the first order diffraction ring recorded on the CCD array, and the known lattice parameters for silver behenate, were used to determine the correspondence between pixel number and the magnitude of \( q \). Prior to the SAXS measurements, the magnetic alignment of the nematic director was carefully checked by polarizing optical microscopy and found to be uniform for all samples across the region exposed to the X-ray beam. Background scattering was measured from an empty capillary placed in the identical cassette and chamber, and maintained under the same experimental conditions, as used with the actual samples.

SAXS patterns obtained on aligned samples of CIPbis10BB and DCIPbis12BC for various temperatures in the nematic and isotropic phases are displayed in the top rows of Fig. 3 and 4. The data are represented by color-coded contours defined at discrete fractions of the maximum scattered intensity. With decreasing \( T \) from the isotropic state, we observe the following basic progression: (1) a circular ring centered on radial wavenumber 0.19 Å\(^{-1}\) for CIPbis10BB (0.20 Å\(^{-1}\) for DCIPbis12BC), corresponding to a length scale of 33 Å (31 Å) that is significantly shorter than the end-to-end (“bow string”) molecular lengths \( L = 45 \text{ Å} \) estimated from molecular simulations;\(^{19} \) (2) transformation of the ring to a pair of broad arcs — just below the nematic-isotropic transition — bisected by a horizontal axis along the magnetic field; (3) an evolution of the arcs at lower temperatures to a pattern of four diffuse spots distributed symmetrically about the field alignment direction. The four spot pattern persists to the temperature where the samples crystallize.

At the lower temperatures the outer intensity contours exhibit a “peanut” shape, while the innermost (defining the four peaks) resemble teardrops in form. These patterns resemble the contour plot generated from diffraction data and published over 30 years ago by McMillan,\(^{20} \) who studied so-called “cybotactic groups” (short-range smectic correlations) in the vicinity of the nematic to smectic-C transition in the calamitic compound, 4,4’-di-n-heptyloxazoxybenzene (HAB). It is interesting to note that the radial distance in \( q \) space to the centers of the four spots in our nematic phase data is similar to the radius of the ring in the isotropic phase; since both correspond to lengths substantially shorter than \( L \), the data are consistent — as in McMillan’s study on HAB — with short-range correlations of the smectic-C type. Indeed, if one assumes tilted layers and a layer spacing of 32 Å (average of the values deduced above) and \( L = 45 \text{ Å} \), one estimates the tilt angle to be \( \cos^{-1}(32/45) = 45° \), which is consistent with typical values in the smectic-C phase of bent-core liquid crystals\(^{3} \) as well as with flow birefringence data\(^{1} \) in the isotropic phase of our bent-core compounds.

We have simulated the diffraction patterns in Fig. 3 and 4 on the basis of the existence of short-range smectic-C type correlations (which we refer to as smectic-C “clusters”), with the additional hypothesis that in the bent-core system, the combination

\[
\frac{B}{C} = \frac{E}{E_0}
\]

Fig. 2 Schematic of the sample holder used in our SAXS measurements, and geometry for the orientation of the smectic-C clusters used for the development of eqn (3) in the text. The cone shown around \( \vec{n} \) represents degenerate orientations of the layers among different clusters (with fixed tilt angle \( \theta \)), while the angles \( \theta, \phi \) allow for a distribution in \( \vec{n} \) with respect to the magnetic field \( \vec{H} \). (Note that the direction of \( \vec{H} \), which was horizontal in the actual experiment, is drawn along the vertical axis for convenience in the diagram on the right).
of molecular shape and efficient packing favors such clustering even in the absence of a stable smectic-C phase at lower temperature. We assume the significant, temperature dependent variables are a parameter (a, explained below) characterizing the orientational distribution of the director (average molecular long axis associated with the clusters and specified by unit vector ⃗n), and two smectic correlation lengths 〈xi and xi⊥ (along and perpendicular to ⃗n, respectively). Fig. 2 (bottom) shows the geometry used to define the cluster orientation (specified by the layer normal along the wavevector ⃗q0), and indicates the two angles used to describe the orientation of smectic layers in the local frame of ⃗n — the layer tilt angle θL and the azimuthal angle φL. The length of ⃗q0 is the wavenumber of the layering in the smectic-C clusters, given by 2π(L cos θL) where L is comparable to the end to end molecular length and L cos θL is the (tilted) layer spacing. We suppose that the layer orientation is degenerate on the tilt cone, so that the scattered X-ray intensity effectively integrates over φL.

Fig. 3 Upper row: Contour plots of SAXS intensity for ClPbis10BB recorded in the x–z plane parallel to the applied magnetic field (horizontal or qz axis in all images) and perpendicular to the incident X-ray beam, at temperatures T_{NI} – T (left to right): −2° (isotropic), 1°, 5°, and 12 °C (nematic). Lower row: Modeling of the intensity contours based on eqn (3) of the text, with fixed molecular length L = 45 Å and layer tilt angle θL = 50°. The units for q are Å−1. The smectic correlation lengths obtained from the simulations of the data for decreasing T below T_{NI} are (left to right) ξb, ξi = (0.8,2.5), (1.0,2.8), (1.0,3.2), all in units of L.

Fig. 4 Upper row: SAXS intensity for DCIPbis12BC, displayed similarly to Fig. 3, at temperatures T_{NI} – T (left to right): −1° (isotropic), 1°, 5°, 10°, and 29° (nematic). Lower row: Results of modeling based on eqn (3), with fixed molecular length L = 45 Å and layer tilt angle θL = 43°. The units for q are Å−1. The smectic correlation lengths obtained from the simulations of the data for decreasing T below T_{NI} are (left to right) ξb, ξi = (0.5,2.2), (0.6,2.3), (0.7,2.8), (1.0,3.5), all in units of L.
A phenomenological calculation of the scattering due to short range smectic order in the nematic phase can be based on Landau theory,\textsuperscript{22,23} or alternatively on an Ornstein-Zernike model of the fluid structure factor in which one assumes that a local maximum in correlations of the electron density gives rise to a smectic-like density wave along $\vec{q}_0$. In the former, one gets some insight into the behavior of the smectic correlation lengths and the tilt angle (and, in some formulations, the wavenumber $q_0$ as well), all of which are calculated in terms of coefficients in a free energy expansion. However, the validity of the Landau approach is generally restricted to the vicinity of a nematic-smectic phase transition; in the absence of the lower temperature smectic phase, as in our bent-core samples, the Ornstein-Zernike approach is perhaps a more appropriate starting point to describe the effect of short range positional order. In either case, the prediction for the intensity scattered at wavevector $\vec{q}$ from density correlations has essentially the same, well-established form of a Lorentzian peaked at $\vec{q} = \pm \vec{q}_0$:

$$I(\vec{q}) = I_0 \frac{\pi L_0}{1 + \frac{\pi^2}{\xi_{q,\perp}^2} (q_{\perp} - q_{0,\perp})^2 + \frac{\pi^2}{\xi_{q,\parallel}^2} (q_{\parallel} - q_{0,\parallel})^2}$$

(1)

Here $q_{\parallel} = \vec{q} \cdot \vec{n}$ and $q_{\perp} = \vec{q} \cdot (\vec{q} \times \vec{n})$, with similar definitions for $q_0$ and $q_{0,\parallel}$. The correlation lengths $\xi_{q,\parallel}$, $\xi_{q,\perp}$ in eqn (1) parametrize elliptical contours in $\vec{q}$ space, with the semi-major and minor axes along or perpendicular to $\vec{n}$. In calamitics the relevant assumption is that the intermolecular interactions differ along the extended axis of the molecule compared to those along the short axis; in the bent-core case, one assumes this is true when the extended axis is taken as the axis connecting the ends of the molecule (i.e., the “bow string”). Using the angles defined above (and depicted in Fig. 2), we may write $q_{\parallel} = q_0 \cos \theta_2 = 2\pi/L$ and $q_{\perp} = (q_0 \sin \theta_2 \cos \phi_2 + q_0 \sin \theta_2 \sin \phi_2) = (2\pi/L)(\tan \theta_2 \cos \phi_2, \sin \theta_2, \sin \phi_2)$. Inserting this into eqn (1) and integrating over the degenerate angle $\phi_2$, one calculates:\textsuperscript{24}

$$I(\vec{q}) = \frac{2\pi L_0}{\sqrt{1 + \frac{\pi^2}{\xi_{q,\parallel}^2} (q_{\parallel} - q_{0,\parallel})^2 + \frac{\pi^2}{\xi_{q,\perp}^2} (q_{\perp} - q_{0,\perp})^2}}$$

To describe the scattering in the vicinity of $T_{NI}$ and given the possibility of unusual short-range molecular organization in a bent-core nematic, we should allow for a distribution in the orientation of $\vec{n}$ of finite width about an average direction of alignment ($\vec{H}$). An appropriate way to incorporate temperature-dependent, uniaxial magnetic alignment of the director (and also the temperature dependence of the nematic order parameter) is to utilize an orientational distribution function of the Maier-Saupe type, $f(\theta, \phi) d\Omega = C \exp(\alpha \cos^2 \theta) \sin \theta d\theta d\phi$.\textsuperscript{24} Here $\theta$, $\phi$ are polar, azimuthal angles describing the orientation of the cluster $\vec{n}$ with respect to the field direction $\vec{H}$, the inverse square root of the temperature dependent, dimensionless parameter $\alpha$ effectively determines the width of the distribution for small angles $\theta, d\Omega$ is an element of solid angle, and $C = \int f(\theta, \phi) d\Omega$ is the appropriate normalization constant. Expressing $q_{\parallel}$ and $q_{\perp}$ in terms of the laboratory $\vec{q}$, which we define in terms of components $q_z = \vec{q} \cdot \vec{H}$ ($z$ axis along $\vec{H}$) and $q_x$ (component of $\vec{q}$ in the detector plane perpendicular to $\vec{H}$), we have $q_0 = q_x \cos \theta + q_z \cos \phi$ and $q_{\perp} = (q_z \cos \phi - q_x \sin \theta)^2 + q_x^2 \sin^2 \phi)^{1/2}$. Then substituting these expressions into eqn (2), and multiplying by and then averaging over the distribution $f(\theta, \phi)$, we finally obtain,

$$I(q_z, q_x) = \int_0^{2\pi} \int_0^{\pi/2} I_0 \exp(a \cos^2 \theta) \sin \theta d\theta d\phi \left\{ \begin{array}{c} 1 + \frac{\pi^2}{\xi_{q,\parallel}^2} (q_z \cos \phi - q_x \sin \theta)^2 + q_x^2 \sin^2 \phi \right\}^{1/2} \pi q_{0,\parallel} \tan \theta_2 \right\}^{2}$$

(3)

where the symbol $\Pi$ means the product of the square root with “+” sign in the argument and that with the “−” in the argument, and where we have absorbed the normalization constants into $I_0$. Note that eqn (3) does not depend on the choice of reference axis for $\phi$ in the plane perpendicular to $\vec{H}$, as it should not.

The measured diffraction is a convolution of the scattered intensity determined by correlations in electron density of the sample — modeled, for example, by the expression in eqn (3) — with the instrumental resolution of the scattering set-up. Since the minimum FWHM of the diffraction peaks measured in our samples is still 9--10 times the operational $q$ resolution of the experiment, and since this minimum was approached only at a few temperatures in one sample (the calamitic nematic compound shown at the bottom in Fig. 1 and used for comparison with the bent-core nematics), it is reasonable to ignore the effect of instrumental resolution on $R(q)$. The second row of contour plots in Figs. 3 and 4 are simulations of the diffraction data for CIPbis10BB and DCIPbis12BC at several different temperatures, based on numerical calculation of eqn (3) using Mathematica. The modeling was performed as follows. Three distinct cuts through the lowest temperature data ($q_x$ cuts for $q_z = 0$ and $q_x$ fixed at a peak intensity position, and a $q_z$ cut for $q_z$ fixed at a peak) were simultaneously fit to eqn (3), with $L = 45$ Å\textsuperscript{16} and with the layer tilt angles adjusted to $\theta_1 = 50^\circ$ and $43^\circ$ for CIPbis10BB and DCIPbis12BC, respectively. These values of $\theta_1$ are close to, though not precisely the same as, the 45° value inferred in our discussion above from the ring of diffraction recorded in the isotropic phase. In our simulations, the tilt angle is not varied; this is consistent with McMillan’s finding that in the case of a first-order nematic to smectic-C transition, the tilt angle for the cybotactic groups is approximately constant in the nematic phase.\textsuperscript{22} The parameters freely varied in fitting the cuts were the correlation lengths $\xi_{\parallel}$, $\xi_{\perp}$ and the quantity $\alpha$ that determines the width of the orientational distribution. Color contours were then generated at relative intensities that gave a good match to the corresponding contour plots of the experimental data. We then proceeded to model the higher temperature nematic phase data in Fig. 3 and 4 by manually adjusting the low temperature results for $\xi_{\parallel}$, $\xi_{\perp}$, and $\alpha$ until the best visual match to the contour data was obtained. This led to successively lower values of these parameters as $T \rightarrow T_{NI}$ (Manual adjustment proved more efficient than automated fitting, which converged very slowly.) Table 1 summarizes values for $\xi_{\parallel}$, $\xi_{\perp}$, and $\alpha$ obtained from the simulations in the nematic phase. The
correlation lengths decrease with increasing temperature, as one would expect, and are clearly consistent with short range smectic order (i.e., $\xi$ of the order of $L$). The parameter $\alpha$ also decreases toward $T_{NI}$ as one would expect from the reduction in the magnitude of the nematic order parameter, and therefore a decrease in the diamagnetic susceptibility anisotropy, associated with a weakly first order transition.

In order to estimate a rough error bar on our values for the correlation lengths, we tested the sensitivity of our modeling to changes in $\xi_{\|}$ and $\xi_{\perp}$, keeping the other parameters fixed. Fig. 5 shows a sample of results for the lowest temperatures. We see that altering the lengths by a factor of two, as well as forcing them to be equal, give noticeably inferior reproductions of the data. Similar results were obtained at higher temperatures. We conclude that, within the framework of the model used, the correlation lengths in Table I are likely accurate to better than a factor of two, and that their expected anisotropy is definitely established. We also demonstrate in Fig. 5 that a significant reduction in the tilt angle (by $10^\circ$), again with the other parameters fixed, also very substantially degrades the quality of the simulations, and thereby further establishes the relatively high value of the tilt.

The model based on nanoscopic tilted smectic clusters supplies a good qualitative representation of the diffraction data and its evolution with temperature, with reasonable values and temperature dependence of the key parameters. In particular, at lower temperature, the “teardrop” shape of the four intensity maxima is clearly represented by the model, and the “peanut” shape of the outer contours is suggested, though not fully reproduced. However, it is prudent to note some respects in which eqn (3) may be incomplete. Outside of Landau theory, there is no reason to exclude a distribution of tilt angles, or of cluster sizes (i.e., correlated volumes). Moreover, eqn (3) does not explicitly treat the form factor for single molecule scattering. For small angle diffraction from bulk thermotropic nematics, this factor has been modeled as a smoothly decaying function of $q$ (e.g., a Gaussian or Lorentzian centered on $q = 0$),20 with a characteristic decay parameter given by a length scale that corresponds to a significant change in the electron density along the molecule. For smectics A or C, the intralayer scattering has

### Table I

<table>
<thead>
<tr>
<th>Compound</th>
<th>$T_{NI} - T$ (°C)</th>
<th>$\xi_{|}/L$</th>
<th>$\xi_{\perp}/L$</th>
<th>$\alpha$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ClPbis10BB</td>
<td>1</td>
<td>0.8</td>
<td>2.5</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>1.0</td>
<td>2.8</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>12</td>
<td>1.0</td>
<td>3.2</td>
<td>4.5</td>
</tr>
<tr>
<td>DCIPbis12BC</td>
<td>1</td>
<td>0.5</td>
<td>2.2</td>
<td>6</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.6</td>
<td>2.3</td>
<td>9</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>0.7</td>
<td>2.8</td>
<td>12</td>
</tr>
<tr>
<td>6OO8</td>
<td>29</td>
<td>1.0</td>
<td>3.5</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>0.6</td>
<td>3.0</td>
<td>10</td>
</tr>
<tr>
<td></td>
<td>10</td>
<td>2.0</td>
<td>10</td>
<td>15</td>
</tr>
<tr>
<td></td>
<td>20</td>
<td>3.0</td>
<td>18</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>30</td>
<td>4.0</td>
<td>28</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>40</td>
<td>6.8</td>
<td>50</td>
<td>60</td>
</tr>
</tbody>
</table>

---

**Fig. 5** Calculated contour plots using different values of the correlation lengths from those obtained for the “best case” modeling of the lowest temperature data in Fig. 3 and 4. The “best case” is presented in the top row (for ClPbis10BB on the right and DCIPbis12BC on the left), and uses the parameter values listed in Table I. The second and third rows from the top correspond, respectively, to results after doubling and halving the correlation lengths, while the fourth row from the top corresponds for equal lengths ($\xi_{\perp} = \xi_{\|} = 2L$). The tilt angle, molecular length, and parameter $\alpha$ were held fixed at the values for the “best case”. The fifth row from the top shows calculated results after reducing the tilt angle by $10^\circ$, with the other parameters held at the “best” values. Units for $q$: Å$^{-1}$.
been described in terms of a “layer” form factor,26 approximated by a Gaussian whose width defines a length scale over which the layers fluctuate positionally. In either approach, the relevant length is a fraction of \( L \), and for scattering at \( q = q_0 \), the form factor should not vary strongly and should not substantially alter the main features of the structure factor arising from the inter-layer correlations. We have also conducted wide-angle X-ray diffraction on CIPbis10BB,27 which should detect form factor effects on the scale of both of the molecular dimensions. The data show no higher order peaks that would be expected in the scattering from sharply defined objects - for example, rigid cylinders. However, the form factor may contribute to the overall diffuse diffraction, especially in quantitative fitting of the 2D lineshape for larger values of \( |q| \).

For comparison and to further clarify the nature of smectic clustering in our bent-core nematics, we obtained SAXS data on a calamitic liquid crystal, 4-n-octyloxyphenyl 4’-n-hexyloxybenzoate (abbreviated 6OO8), whose structure and phase sequence are shown at the bottom of Fig. 1. This phenyl benzoate was chosen because its chemical structure approximates one “arm” of the bent-core molecule CIPbis10BB, but unlike the latter, it exhibits a smectic-C phase just below the nematic. One might therefore expect evidence of short-range smectic-C layering in the nematic range of 6OO8, and indeed the SAXS images in Fig. 6, taken on a magnetically aligned sample, clearly exhibit the appropriate four peak small angle diffraction pattern. The modeled patterns, calculated using eqn (3) are presented on the bottom row in Fig. 6. The layer tilt angle and molecular length used in the calculations are \( \theta_1 = 30^\circ \) and \( L = 26 \text{ Å} \). Note that the variation of \( \xi_1 \) and \( \xi_\parallel \) with temperature, summarized in Table I, is much more significant than in either bent-core compound (where the correlation lengths are relatively insensitive to temperature and there is no lower temperature smectic phase). The comparison with DCIPbis12BC is particularly illustrative, since the latter possesses a nematic range nearly comparable to that of 6OO8. The stronger temperature dependence and large values of \( \xi_1, \xi_\parallel \) at lower temperature in 6OO8 can clearly be attributed to nematic-smectic-C pretransitional behavior in this compound, similar to that observed by McMillan in the calamitic material HAB. We should also remark here that the larger values of the parameter \( a \) (40 and 60) listed for 6OO8 in Table I are not really meaningful, since for the corresponding temperatures, model contours similar to those in Fig. 6 could be obtained assuming the strictly uniform orientational distribution as in eqn (2).

Even in apparently well-aligned nematic samples, certain features of the SAXS from the bent-core liquid crystals differ from the lineshape observed for conventional “cybotactic” nematics. In Fig. 7, results for the normalized scattered intensity (after subtraction of background levels) are plotted for cuts through one of the four peaks in the SAXS data with \( q_\parallel \)-cut at fixed \( q_\perp \) and \( q_\perp \)-cut at fixed \( q_\parallel \). For convenience of comparison, the \( q \) axis is reduced by the values \( q_0\parallel \) or \( q_0\perp \), corresponding to the peak intensity. The plots for the bent-core compounds represent the lowest temperatures studied, while for 6OO8, the temperature is \( T = T_N - 20^\circ \text{C} \). Also shown are data for the calamitic compound HAB studied by McMillan,20 at a temperature chosen to match the peak width of the 6OO8 data along \( q_\parallel \). For the \( q_\perp \) cuts, eqn (2) predicts the lineshape (associated with any of the four peaks) should be symmetric about \( q_\perp \)-cut of the parameter \( q_0\perp \). As seen in the examples in Fig. 7, this is basically accurate for the case of the “cybotactic” calamitic nematics. However, examination of the \( q_\perp \) data for the bent-core nematics reveals that the peaks are asymmetric and somewhat broader on the \( q_\perp > q_0\perp \) side; this is especially evident for CIPbis10BB.

(Of course, the overall peaks are broad compared to the calamitics, due to shorter correlation length \( \xi_\parallel \).) The \( q_\perp \)-cut also demonstrates different behavior between the lineshapes for the bent-cores and calamitics. Here, for large \( q_\perp \), one expects from eqn (2) that \( I \sim 1/q_\perp^2 \). This dependence is observed with 6OO8 and HAB, but for the bent-cores, the intensity falls off more sharply at large \( q_\perp \) than the prediction. The discrepancies noted in the

**Fig. 6** Upper row: SANS intensity for the calamitic liquid crystal 6OO8 (chemically related to our bent-core compounds) recorded for similar conditions as in Fig. 3 and 4, at temperatures \( T_N - T \) (left to right): \(-5^\circ \) (isotropic), \(5^\circ, 10^\circ, 20^\circ, 30^\circ \), and \(40^\circ \) (nematic). The lowest temperature is about \( 1^\circ \text{C} \) above the nematic to smectic-C transition. Lower row: Results of modeling based on eqn (3), with fixed molecular length \( L = 26 \text{ Å} \) and layer tilt angle \( \theta_1 = 30^\circ \). The units for \( q \) are \( \text{Å}^{-1} \). The smectic correlation lengths obtained from the simulations of the data for decreasing \( T \) below \( T_N \) are (left to right) \( \xi_\perp, \xi_\parallel = (0.6,3.0), (2.0,10), (3.0,18), (4.0,28), (6.8,50) \), all in units of \( L \).
here suggest that further development of the model in eqn (2) and (3) will be needed to provide a complete description of the line
shape measured for the bent-core nematics.

Turning to results in the isotropic phase, we observe (Fig. 3, 4, and 6) that all three compounds we studied exhibit a diffuse circular ring (halo) of small angle scattering. The conventional interpretation of the SAXS halo in the isotropic phase is based on a combination of a molecular form factor, modeled as a smoothly decreasing function of $\mathbf{q}$, and a structure factor derived from the excluded volume of the molecules. Here, in the absence of smectic-like correlations, the otherwise weaker effects of the form factor scattering become important. If this interpretation applies to our bent-core samples, we would expect, in addition to the development of an isotropic ring of scattering, a sharp drop in the intensity integrated around the ring and a shift in the peak position on heating through $T_{NI}$, due to the disappearance of any short-range smectic correlations that exist in the nematic. As a test of this scenario, we calculated the integrated intensity, $I(\mathbf{q}) = \int \rho(\mathbf{q}) \cos \chi(\mathbf{q}) \sin \chi(\mathbf{q}) d\chi$, and normalized it to the background intensity level measured at the outer edge of the detector, for the SAXS data for ClPbis10BB and 6O08 at various temperatures on either side of $T_{NI}$. (Here $\chi$ is the angle in the 2D detector plane between $\mathbf{q}$ and a reference axis passing through the origin, $\mathbf{q} = 0$.) The results are displayed in Fig. 8. Surprisingly, whereas the calamitic 6OO8 shows the expected substantial decrease in the peak value of $I(\mathbf{q})$ and a clear shift in peak position, the profile of the scattered intensity in $|\mathbf{q}|$ for the bent-core compound is essentially unchanged across $T_{NI}$. This near constancy through the transition, which is seen starting with either randomly aligned “powder” (i.e., no applied magnetic field) or magnetically aligned nematic samples, indicates that the short-range smectic clustering in the bent-core

**Fig. 7** Normalized SAXS intensity of the bent-core and calamitic nematics studied by us and by McMillan, plotted as a function of reduced scattering vector for cuts taken through one of the four-fold peaks with $\mathbf{q} \perp \mathbf{H}$ (top panel) and $\mathbf{q} \parallel \mathbf{H}$ (bottom panel). The corresponding temperatures are $T_{NI} - T = 12^\circ C$ for ClPbis10BB (green), $29^\circ C$ for DCIPbis12BC (blue), $20^\circ C$ for 6O08 (red), and $18.3^\circ C$ for HAB (open squares). The data for HAB are reproduced from ref. [20].

**Fig. 8** SAXS intensity in the isotropic and nematic phases for randomly aligned (“powder”) and well-aligned nematic samples of ClPbis10BB, and for an aligned nematic sample of the chemically related calamitic compound 6O08, plotted as a function of the magnitude of $\mathbf{q}$ after integrating in the plane of the detector over azimuthal angle. The temperatures $T_{NI} - T$ are $-9^\circ C$ (blue), $-4^\circ C$ (green), $1^\circ C$ (red), $6^\circ C$ (black) for ClPbis10BB (unaligned); $-4^\circ C$ (light blue), $-0.5^\circ C$ (blue), $1^\circ C$ (green), $5^\circ C$ (red), $10^\circ C$ (black) for ClPbis10BB (aligned); and $-5^\circ C$ (light blue), $-0.5^\circ C$ (blue), $1^\circ C$ (green), $5^\circ C$ (red), $10^\circ C$ (black) for 6O08. (The CCD camera integration time was 8 times lower for the data on the powder sample).
system actually persists well into the isotropic state (though with a loss of orientational order of the clusters). The modeled diffraction patterns for the isotropic phase in Fig. 3, 4, and 6 are based on eqn (3) with $\alpha = 0$ and, in the case of the bent-core materials, with the smectic correlation lengths fixed to the values determined from the modeling of data just below $T_{NI}$.

Smectic-C-like clustering in the nematic state (and above) may also account for some of the interesting macroscopic properties of our bent-core compounds — namely, the giant flexoelectric effect$^8$ observed in the nematic phase and the large specific flow birefringence$^8$ in the isotropic phase (respectively, $\sim 1000$ and $\sim 10$ times typical values for calamitics), as well as the greatly enhanced shear flow$^6$ and director-mode (orientational)$^7,28$ viscosities (up to $\sim 1000$ and $\sim 10$–100 times, respectively, the values in calamitics). Let us first comment on the flexoelectric effect. Within the conventional theory$^{29}$ for flexoelectric response of nematics, one can expect$^9$ a maximum 10–100 fold increase in flexoelectric coefficient due to the shape and composition of our bent-core molecules compared to traditional rod-shaped molecules (such as the cyanobiphenyls). This is well below the observed increase. However, consider the additional presence of smectic bent-core clusters with the polar layer organization observed in smectic-CP phases of bent-core compounds. If the smectic cluster dimensions are of order $\xi$ ($\sim L$) and $\xi_L$ ($\sim 3L$), as inferred from the SAXS data, they effectively replace a volume of uncorrelated molecular dipoles with an equivalent one of strongly correlated dipoles, which should result in an additional, substantial enhancement of the flexoelectric polarization. One could imagine this enhancement even in the case of antiferroelectric layering, since the small correlation lengths and odd-even effect could still produce a significant net cluster polarization. The combined effects of single molecule properties and short-range correlations may therefore account for the giant flexoelectric response observed in the bent-core nematics investigated here. Furthermore, recent studies$^{30,31}$ indicate ferroelectric and/or antiferroelectric response to applied electric field, as well as an unusual collective mode detected in dielectric spectra of bent-core nematics,$^{31}$ all of which suggest some sort of polar molecular organization.

Perhaps the most unconventional feature of the flow birefringence measurements in the isotropic phase — that the optical axis induced under shear develops at $\sim 45^\circ$ angle to the shear flow direction$^8$ even at high shear rates — is also explained by the persistence of randomly-oriented smectic-C clusters above $T_{NI}$. In this situation, a flow alignment of the with the enhanced shear flow$^6$ and director-mode (orientational)$^7,28$ viscosities (up to $\sim 1000$ and $\sim 10$–100 times, respectively, the values in calamitics). Let us first comment on the flexoelectric effect. Within the conventional theory$^{29}$ for flexoelectric response of nematics, one can expect$^9$ a maximum 10–100 fold increase in flexoelectric coefficient due to the shape and composition of our bent-core molecules compared to traditional rod-shaped molecules (such as the cyanobiphenyls). This is well below the observed increase. However, consider the additional presence of smectic bent-core clusters with the polar layer organization observed in smectic-CP phases of bent-core compounds. If the smectic cluster dimensions are of order $\xi$ ($\sim L$) and $\xi_L$ ($\sim 3L$), as inferred from the SAXS data, they effectively replace a volume of uncorrelated molecular dipoles with an equivalent one of strongly correlated dipoles, which should result in an additional, substantial enhancement of the flexoelectric polarization. One could imagine this enhancement even in the case of antiferroelectric layering, since the small correlation lengths and odd-even effect could still produce a significant net cluster polarization. The combined effects of single molecule properties and short-range correlations may therefore account for the giant flexoelectric response observed in the bent-core nematics investigated here. Furthermore, recent studies$^{30,31}$ indicate ferroelectric and/or antiferroelectric response to applied electric field, as well as an unusual collective mode detected in dielectric spectra of bent-core nematics,$^{31}$ all of which suggest some sort of polar molecular organization.

Next, let us consider how the rheological features of the bent-core fluids may compare to the smectic cluster model. Although the reduced symmetry of the bent-core mesogens might result in greater molecular entanglements, and hence a larger barrier to rotational or translational diffusion, the individual molecules are still small, and it is hard to imagine that this effect alone gives rise to the orders of magnitude increase actually observed in the flow and orientational viscosities. It is also tempting to suggest that the smectic-like correlations may be primarily responsible for the enhancement of these parameters. Yet both theory and experiment$^{32,33}$ indicate significant viscosity increases only very close to a smectic phase, and the layer correlations we observe in our bent-core samples are always short range. A more interesting speculation is again the possibility of polar layering producing a net volume or surface polarization of the smectic clusters.$^{10,41}$ Then enhanced dipole–dipole interactions among the clusters could lead to substantially increased viscosities in analogy to the behavior observed in electrorheological (ER) nanofluids (wherein the dipole moments on nanoparticles in concentrated solution are induced by an applied electric field, as opposed to being spontaneously present).$^{14}$ Pursuing the analogy somewhat further, one could associate the finite yield stress observed for shear flow in CIPbis10BB$^1$ with the Bingham-like flow characteristic of ER fluids. We believe it would be interesting to follow up on this comparison by performing electric field-dependent rheological studies on the bent-core fluids.

To conclude, we have demonstrated that the small angle X-ray diffraction patterns recorded in the nematic phases of two related bent-core compounds are consistent with a fluid organized from nanoscopic molecular clusters possessing short-range smectic-C-type layering. With a small number of temperature dependent parameters, this model reproduces the main qualitative features of the SAXS data. However, our results indicate that further refinement of the model to treat particular details of clustering-bent-core nematics, which may be distinct from traditional “cybotactic” calamitics, is required for a full quantitative description of the two-dimensional intensity distribution. We have also argued how the smectic cluster model accounts for unusual macroscopic properties previously observed in the nematic and isotropic phases of our bent-core materials. Additional investigation of this connection, and the insights it may yield for molecular design, could point the way toward important new applications of this class of liquid crystals.$^\dagger$

Acknowledgements

We thank Dr Lin Yang for useful conversations at NSLS pertaining to the analysis of some of our experimental results. The Kent State authors are grateful to the NSF for funding through grant no. DMR-0606160. The SAXS beamline X6B at NSLS is supported by the DOE under contract DE-AC02-98CH10886.

References


$^\dagger$ Note added in proof: Not all bent-core nematics produce SAXS patterns indicative of short-range smectic layer correlations. For instance, the low angle reflections from a series of V-shaped thiadiazoles correspond to length scales considerably shorter than the molecular length,$^{35}$ and suggest a different type of local molecular organization.$^{36}$


19 D. Demus and K. Fodor-Csorba, private communication.


35 Sayten Kumar, private communication.