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Orientational transition of a bent-core dopant in an anticlinic liquid crystal matrix

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Small quantities of the bent-core mesogen P-7PIMB were dissolved in an anticlinic liquid crystal consisting of a mixture of left- and right-handed TFMHPOBC, with enantiomer excess $X=0.2$. For bent-core concentrations above $C=3\,\mathrm{wt}\%$, differential scanning calorimetry shows the disappearance of the higher temperature synclinic phase, as well as the appearance of a new peak at a low temperature T_c. Polarized infrared absorption measurements indicate that the new DSC peak is due to an orientational transition of the bent-core molecules, analogous to the transition previously observed in a smectic A matrix. For $T>T_c$ the plane of the bent-core molecules lies in the tilt plane of the anticlinic matrix, with the arrow (the symmetry axis) of the bent-core molecules parallel to the smectic layers. For $T<T_c$ we deduce that the bent-core molecules lie within a single smectic layer, with the polar tilt of the arrow approximately equal to the polar tilt of the TFMHPOBC molecule and the vector connecting the two ends of the bent-core molecule perpendicular to the anticlinic tilt plane. Additionally, T_c was found to be an increasing function of bent-core concentration.

1. Introduction

Mixtures of two or more calamitic mesogens often give rise to a complex temperature–concentration phase diagram, occasionally with phases that do not appear in either of the pure components [1]. In recent years interest has grown in mixtures of calamitic and bent-core mesogens—these are sometimes known as 'banana' or 'bow-shaped' [2–6]. In particular, Pratibha *et al.* examined mixtures of a bent-core mesogen dissolved in a calamitic mesogen that exhibits an isotropic, nematic, and smectic A_2 phase, obtaining traditional bent-core 'B' phases at bent-core concentrations as small as $13\,\mathrm{mol}\%$ [2]. In the B_6 phase, for example, the symmetry axis of the bent-core molecules, which they refer to as the 'arrow,' lies parallel to the smectic bilayers, with the legs of the bent-core dopant residing in the region of the two calamitic cores that form the bilayer. At lower concentrations they observed an orientational transition of the bent-core molecules in the background smectic A_2 matrix, deducing that the arrow lies perpendicular to the plane of the smectic bilayer. Over a certain temperature range and at concentrations between ~ 4 and $13\,\mathrm{mol}\%$ the 2π azimuthal orientational degeneracy about the bilayer normal is broken, and the phase is biaxial; they refer to this as the smectic A_{2b} phase. Below $\sim 4\,\mathrm{mol}\%$ a 2π azimuthal degeneracy is present and the phase is uniaxial. At about the same time, Gorecka *et al.* examined the behaviour of a mixture of bent-core molecules dissolved in a matrix of calamitic molecules that exhibits a synclinic (ferroelectric) phase [6]. The bent-core mesogens were found to promote anticlinic (antiferroelectric) order, as the arrow lies parallel to the interface between adjacent layers and the plane of the bent-core molecules lies in the tilt plane of the anticlinic

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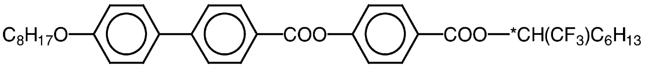

Figure 1. Structure of TFMHPOBC.

phase. For sufficiently large bent-core concentration, the synclinic phase disappears and a direct isotropic to anticlinic phase transition was observed.

Recently we examined the reentrant behavior of the anticlinic smectic C* (Sm C*) phase in the presence of an electric field [7]. For relatively low enantiomer excess (*X*) mixtures of left- and right-handed TFMHPOBC (figure 1), and for sufficiently large electric field, we observed a phase sequence Sm C* – Sm C_A^* – reentrant Sm C* on cooling. Subsequent studies of the temperature – electric field phase diagram of $X=0.2$ enantiomeric mixtures of TFMHPOBC doped with small amounts of the bent-core mesogen 1,3-phenylene bis[4-(4-heptylphenyliminomethyl benzoate], also known as 'P-7PIMB' (figure 2), indicate a suppression of the Sm C* phase, consistent with the results of ref. [6]. Additionally, we observed a decrease of the Sm C_A^* – reentrant Sm C* phase transition temperature, which is not surprising given the strong suppression effect that the bent-core mesogens have on the anticlinic phase. These results will be published elsewhere [8]. More surprising, however, is an apparently new phase transition that occurs at lower temperatures for sufficiently large bent-core dopant concentrations. First observed with differential scanning calorimetry (DSC), polarized infrared absorption measurements indicate that a reorientation of the P-7PIMB bent-core molecules occurs at a concentration-dependent critical temperature $T_c(C)$, where *C* is the bent-core concentration. Above T_c the plane of the bent-core molecules lies parallel to the tilt plane of the anticlinic matrix, with the arrow parallel to the smectic layers, whereas below T_c each bent-core molecule lies approximately within a single smectic layer with the polar tilt of the arrow approximately equal to the polar tilt of the TFMHPOBC molecule and the 'bow string' perpendicular to the anticlinic tilt plane. Moreover, T_c was found to be an increasing function of *C*. The result is reminiscent of the orientational transition observed by Pratibha *et al.* [2, 3], although the surprising feature is that the bent-core molecule that promotes anticlinic order relative to synclinic order no longer orients in this way at low temperatures.

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2. Experimental

Six concentrations of bent-core molecules were prepared. For each concentration we began with an $X=(0.2\pm0.01)$ mixture of TFMHPOBC, i.e. having an excess of *R* enantiomer, where $X=([R]-[S])/([S]+[R])$ and [*S*] and [*R*] are the mole fractions of left- and right-handed TFMHPOBC. We then added bent-core P-7PIMB to the TFMHPOBC mixture, obtaining final bent-core concentrations of $C=0$, 1.0, 2.0, 3.0, 4.0, and 5.0 wt%, all having fractional uncertainties of $\pm0.1C$. The mixtures were homogenized by dissolving the materials in chloroform, then boiling off the solvent. A quantity of ~10 mg of each concentration was examined in a TA Instruments DSC, where the temperature was ramped on cooling at a rate of $1^\circ C\, min^{-1}$; results are shown in figure 3. Data at higher temperatures (not shown) indicate that the Sm C* phase is suppressed with increasing *C*, and vanishes for $C\geqslant3.0$ wt%. At these concentrations we begin to see a broad peak in figure 3 developing at approximately $T_c=55^\circ C$, where T_c increases with increasing bent-core concentration.

3. IR absorbance

Let us now turn to the infrared absorbance measurements. Cell substrates were either KBr or CaF_2, where the same material was used for both substrates for a given *C*. The substrates were spin-coated with the polyamic acid RN-1175 (Nissan Chemical Industries) and baked at 250°C for 1 h. The substrates then were rubbed unidirectionally along the *z*-axis, placed together in an antiparallel configuration separated by Mylar spacers of nominal thickness 5 μm, and cemented. Each cell was filled in the isotropic phase with a mixture having a particular concentration *C*, and

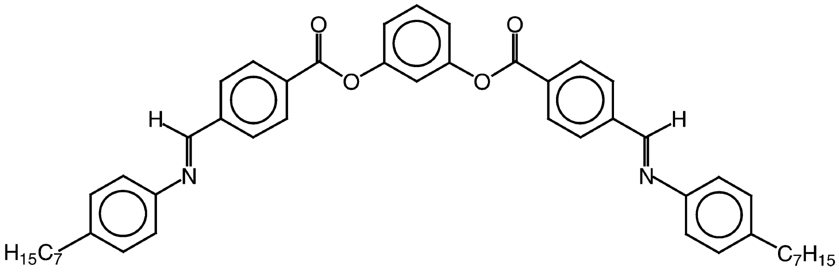

Figure 2. Structure of bent-core molecule P-7PIMB.

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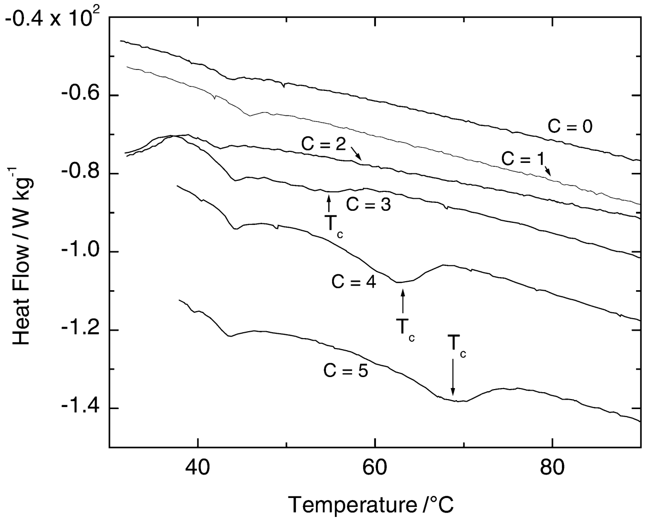

Figure 3. Differential scanning calorimetry traces on cooling at 1°C min^{-1}. Curves for different bent-core dopant concentrations C are shifted vertically for easier reading. T_c first appears for $C = 3$ wt%, and increases with increasing concentration.

cooled slowly into the Sm C_A^* phase. The bookshelf alignment of the samples was examined using a polarizing microscope, and only samples showing a good monodomain texture were used in the infrared studies. IR light was incident along the y-axis, perpendicular to the plane of the cell, i.e. perpendicular to the xz-plane. For each concentration, measurements were made for three different incident polarizations: $\Phi = 0°$, 45°, and 90°, where Φ corresponds to the angle relative to the smectic layer planes, i.e. relative to the x-axis. Thus $\Phi = 90°$ corresponds to a polarization that is parallel to the rubbing direction (along the z-axis), and therefore parallel to the layer normal, whereas $\Phi = 0°$ corresponds to a polarization along the x-axis. At a given temperature $50 \leqslant T \leqslant 80$°C and polarization angle Φ, sixteen scans were accumulated at a resolution of 8 cm^{-1} using a BioRad Excalibur FTS-3000 MX Fourier transform infrared spectrometer. The temperature was controlled by an Oxford Instruments Microstat N control unit. The angle Φ was then changed, and another scan was made. The process was repeated a third time, after which the temperature was reduced by 1 or 2°C, and scans were again made for all three polarizations Φ. Thus, data were collected over the entire temperature range at a single concentration C for the three polarizations. This process was repeated for all six concentrations.

Data interpretation was hampered by the fact that the concentrations of P-7PIMB were small, making it difficult to separate the bent-core molecule's absorbance peaks from that of the TFMHPOBC matrix. In fact, over the range of wavenumbers k investigated, viz. $500 \leqslant k \leqslant 3000$ cm^{-1}, nearly all measurable temperature-dependent absorbance changes—these are all quite small—occur in regions where there are multiple overlapping absorbance peaks. This makes it especially hard to quantify orientational changes of P-7PIMB that occur at T_c. It transpires, however, that the vibrational band [ν_a(C–O–C) + ν(C–O)] that peaks at $k = 1127$ cm^{-1} [9] is sufficiently isolated from other absorbance peaks that orientational changes could be analysed. The [ν_a(C–O–C) + ν(C–O)] band occurs in both TFMHPOBC and in the P-7PIMB bent-core molecule. Throughout the analysis we assume that no abrupt changes occur in the neighborhood of T_c in either the molecular conformation or orientation (see below) of TFMHPOBC. Since the [ν_a(C–O–C) + ν(C–O)] absorption is approximately parallel to the 'bow string' of the bent-core molecule, i.e. perpendicular to the symmetry axis and parallel to the bent-core plane, we can associate the abrupt change in absorbance that occurs for $\Phi = 90°$ (and to a lesser extent for $\Phi = 45°$) in the vicinity of T_c with an orientational transition of the bent-core dopant.

Let us briefly address the issue of helicity. Ordinarily the anticlinic phase is twisted into a double helix, with the azimuthal orientation in each layer approximately 180° out of phase with its neighbouring layer [10]. The helical pitch for optically pure ($X = 1$) TFMHPOBC varies from approximately 0.6 to 1.0 μm over the temperature range of interest [11]. Thus, for an enantiomeric excess $X = 0.2$, we would expect a pitch ranging between 3 μm at lower temperatures and 5 μm at higher temperatures. This pitch is sufficiently long that we might expect the helices to be unwound, i.e. in a surface-stabilized state. Supporting this conclusion are the apparent absence of pitch lines on cooling the $C = 0$ mixture through the entire temperature range, and the near temperature independence of the absorption spectrum at $C = 0$ (figure 4). Had a finite pitch set in at lower temperatures, the azimuthal rotation of the molecule about the layer normal axis would have resulted in a very different spectrum.

In figure 5 we show the quantity $R \equiv A(T) - A(T_o)$ for several temperatures in the region around $k = 1127$ cm^{-1} for all three polarization angles Φ at $C = 5$ wt%. Here A is the absorbance, which corresponds to $-\log_{10}(t)$, where t is the transmittance; thus, $R = \log_{10}[t(T_o)/t(T)]$. $T_o = 76$°C is a temperature chosen arbitrarily that is well above T_c, and T corresponds to other temperatures at which the absorbance was measured for each polarization. We collected data at approximately 25 different temperatures T, but for clarity we present data for only seven different temperatures. From figure 5 we see that there is little

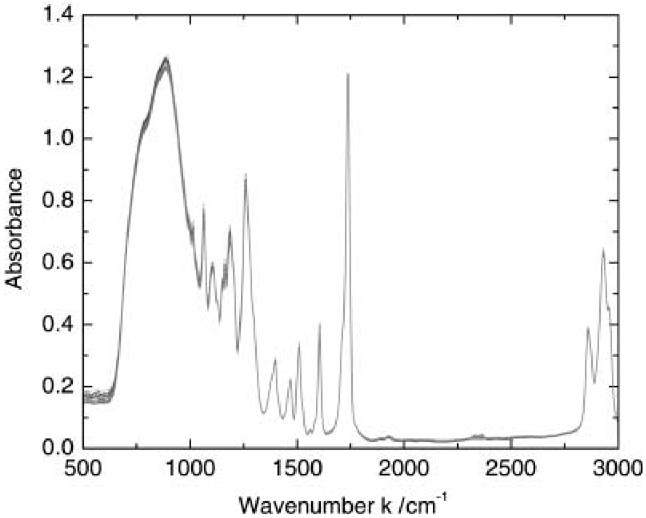

Figure 4. Absorbance (offset by an arbitrary factor) vs. wave vector k at 18 different temperatures for $C=0$ and $\Phi=0$. The absence of a significant temperature dependence indicates that the liquid crystal helix remains unwound at all temperatures.

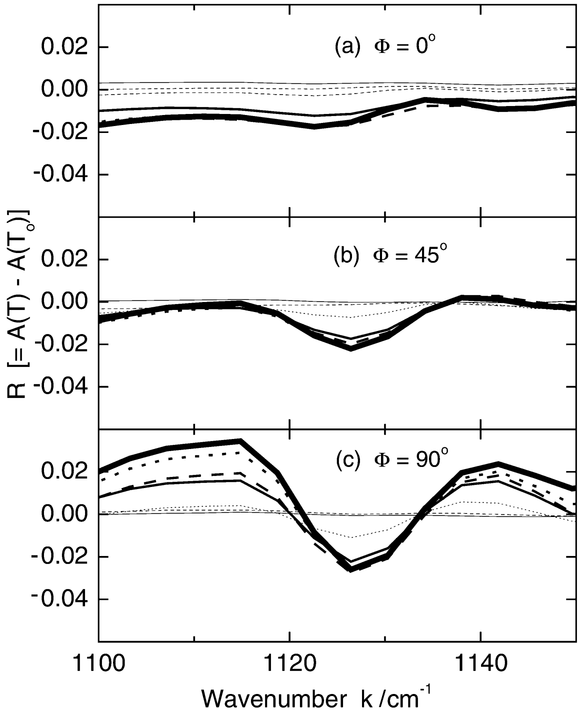

Figure 5. $R[\equiv A(T)-A(T_o)=\log_{10}(t(T_o)/t(T))]$ vs. wavenumber k at three different polarizer orientations Φ. R corresponds to the fractional change of transmittance between temperatures T and $T_o=76$°C. A dip in R indicates an increase in transmittance and a decrease in absorbance at temperature T. Here $T=75$°C (light solid line), 74°C (light dashed line), 72°C (light dotted line), 70°C (medium solid line), 68°C (medium dashed line), 66°C (medium dotted line), and 64°C (heavy solid line).

change in absorbance at $\Phi=0°$ on cooling over the entire temperature range, whereas for $\Phi=90°$ there is a relatively large decrease in absorbance (corresponding to an increase in transmittance and thus to a dip in the quantity R) for $[\nu_a(\text{C–O–C})+\nu(\text{C–O})]$ at $1127\,\text{cm}^{-1}$ on cooling below T_c. Results for $\Phi=45°$, figure 5 (*b*) fall between these two extremes. Figure 6 shows R for the other concentrations at $\Phi=0°$ and $\Phi=90°$; for clarity only two temperatures, one well above T_c and one well below T_c, for each pair Φ,C are shown. Trends similar to that of the $C=5$ wt% mixture apply to $C=3$ and 4 wt%, i.e. a large decrease in absorbance at $\Phi=90°$, figures 6 (*h*) and 6 (*j*), a smaller decrease at 45° (not shown here), and no clear absorbance change at 0°, figures 6 (*g*) and 6 (*i*). The depths of the dips in R (corresponding to a decrease in absorbance) decrease with decreasing C, due in part to the smaller bent-core molecule concentrations. For still lower concentrations, $C \leqslant 2$ wt%, we observe no significant change in absorbance at $\Phi=90°$ and $\Phi=45°$ (not shown) on cooling over the entire temperature range, figures 6 (*b*), 6 (*d*) and 6 (*f*); there the $[\nu_a(\text{C–O–C})+\nu(\text{C–O})]$ absorbance maximum remains approximately unchanged with T.

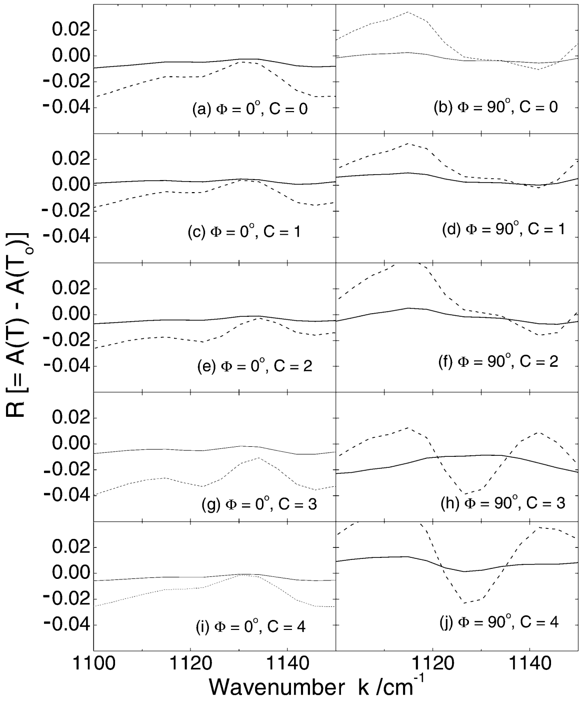

Figure 6. $R[=A(T)-A(T_o)]$ vs. wavenumber k at polarizer orientations $\Phi=0°$ (first column) and $\Phi=90°$ (second column). Each row represents a different concentration C. Here $T_o=75$°C, and $T=70$°C (solid lines) and 55°C (dashed lines). In panels (*h*) and (*j*) the dip in R at $k=1127\,\text{cm}^{-1}$ indicates an orientational change of the bent-core molecule.

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4. Proposed molecular arrangement

Based on these results, we propose an arrangement for bent-core P-7PIMB dopant molecules in the TFMHPOBC matrix as shown in figure 7. As observed by Gorecka *et al.* [6] and by our current measurements, the suppression of the synclinic phase by the bent-core molecules at higher temperatures occurs because of packing considerations in the anticlinic matrix, which we show schematically in (*a*) (front view) and (*b*) (side view). In this configuration the C–O–C vibrations for the P-7PIMB molecule, which occur along the *z*-axis, would give rise to significant absorption at $k=1127\,\mathrm{cm}^{-1}$ for a polarizer orientation $\Phi=90°$ (polarization along the *z*-axis), a lesser absorption at $\Phi=45°$, and little absorption at $\Phi=0°$ (polarization along the *x*-axis). For $C\leqslant 2$ wt% there is no obvious absorbance change at lower temperatures for $\Phi=90°$, indicating that the orientation shown in figures 7 (*a*) and 7 (*b*) holds at low concentration *for all temperatures*. However, for concentrations $C\geqslant 3$ wt%, the absorbance shows a sharp decrease on decreasing the temperature through T_c, giving rise to the dips in the quantity R for $\Phi=90°$ in figures 5 and 6. For $\Phi=0°$ the absorbance at both high and low temperatures is similar for *all* concentrations C, with no apparent dips in R for [ν_a(C–O–C) + ν(C–O)] at $1127\,\mathrm{cm}^{-1}$. This would indicate that C–O–C remains perpendicular to the $\Phi=0°$ polarization, i.e. perpendicular to the *x*-axis, for all temperatures and concentrations. In light of the data in figures 5 and 6 and the fact that the helices remain unwound at all temperatures, we propose in figures 7 (*c*) (front view) and 7 (*d*) (side view) a picture of the orientation at temperatures below T_c for $C\geqslant 3$ wt%. In this picture the bent-core molecules reside approximately within individual smectic layers, and the plane of the P-7PIMB is tilted by about the same polar angle θ associated with the TFMHPOBC molecules. In this case C–O–C lies approximately perpendicular to the optical polarization, i.e. C–O–C lies along the *y*-axis, for all polarizations Φ lying in the *xz*-plane. Thus little or no absorption of the light for the [ν_a(C–O–C) + ν(C–O)] band at $1127\,\mathrm{cm}^{-1}$ by the bent-core molecules is expected to occur. This is consistent with the results of figures 5 and 6.

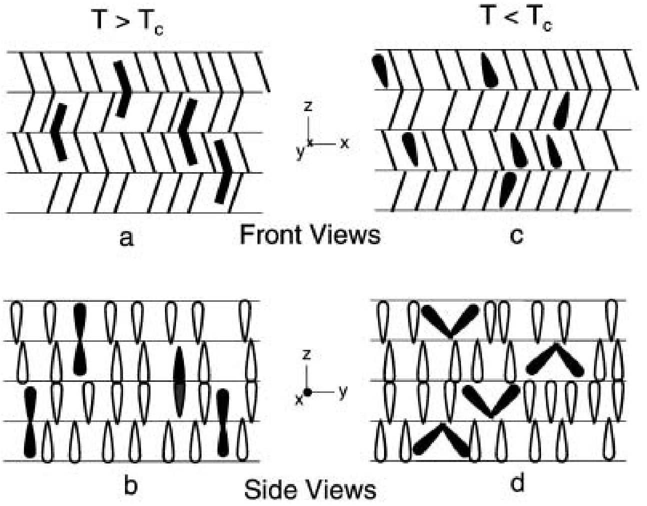

Figure 7. Schematic representation of molecules. Panels (*a*) and (*b*) represent the orientation above T_c for all concentrations C. In panel (*a*) the light lines represent TFMHPOBC and the heavy lines the bent-core P-7PIMB molecules. In panel (*b*) the open figures represent TFMHPOBC and the solid figures the bent-core P-7PIMB molecules. Panel (*b*) shows the side view, as if panel (*a*) were viewed from the right. The wider parts of the molecules inidicate that those parts are tilted toward the viewer. Panels (*c*) and (*d*) show the deduced orientations below T_c for $C\geqslant 3$ wt%. In panel (*c*) the light lines represent TFMHPOBC and the heavy lines the bent-core P-7PIMB molecules. In panel (*d*) the open figures represent TFMHPOBC and the solid figures the bent-core P-7PIMB molecules.

Let us consider another possible orientation below T_c. Ikeda *et al.* have measured the layer spacing d of optically pure TFMHPOBC in the anticlinic phase approximately 3.5°C below the Sm C_A^* – Sm A phase transition temperature, finding $d=3.35$ nm [12]; the optical polar tilt angle θ at this temperature is $\theta=25°$ [13]. Assuming that the layer spacing of the Sm A phase of TFMHPOBC corresponds to the molecular length l, we find $l=d/\cos\theta=3.7$ nm. Patel, *et al.* have reported the polar tilt angle θ for $X=0.2$ (with $C=0$) over this temperature range, and have found that θ varies smoothly between $\theta=29°$ at $T=80°$C and $\theta=30°$ at $T=50°$C [7], which would correspond to layer spacings of $d=3.24$ nm at high temperature and $d=3.2$ nm at low temperature. Although structural information about P-7PIMB is unavailable, data exist for other homologues P-*n*PIMB—1,3-phenylene bis[4-(4-alkylphenyliminomethyl benzoate]—whose two alkyl tails terminate in C_nH_{2n+1}. Nonlinear optical experiments on monolayers of P-12PIMB yield a splay angle $\Theta=127°$ [14] for the two legs of the bent-core molecule. X-ray measurements of the smectic A_b layer thickness of pure P-*n*PIMB are nearly linear in n [15], and can be interpolated to give a layer spacing of approximately 3.5 nm for P-7PIMB. This can be associated with the end-to-end molecular length $L=3.5$ nm, corresponding to the length of the bow string. Thus, even below T_c P-7PIMB in principle could reside almost entirely within a layer with the arrow oriented along the *y*-axis and the bow-string tilted by an angle θ in the *xz*-plane. However, on cooling through T_c such an orientation would give rise to an increase in absorbance at $\Phi=0$ for $C\geqslant 3$ wt%, which was not observed. Below T_c the data appear to be consistent with figures 7 (*c*) and 7 (*d*) in the higher concentration regime. Although the increase in polar tilt angle θ of TFMHPOBC is relatively small over the measured temperature range [7], the bent-core angle $\Theta = 127^\circ$ would, in principle, favour a smaller value of θ. The worsening fit of the bent-core and tilted TFMHPOBC molecules with decreasing temperature may, in part, be responsible for the orientation transition below T_c. Clearly other factors also come into play, including the tilt susceptibility and the dispersive interactions associated with the orientations of the two species. A full treatment of all of these factors is beyond the scope of the present work, although future measurements as a function of homologue P-*n*PIMB would help shed light on these issues.

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