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A Twist-bend Nematic to an Intercalated, Anticlinic, Biaxial Phase Transition in Liquid Crystal Bimesogens

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Abstract

In this article we describe for bimesogens the first observed transition from a “heliconical” twist-bend nematic liquid crystal to a novel biaxial, anticlinic, intercalated lamellar phase. The phase behaviour and structures of both polymorphs is similar to that of polymers, confirming that bimesogens can act as model systems for main chain liquid crystal polymers, and in principle are separate soft-matter branches of self-organising systems.

Introduction

There has been a resurgence of interest in dimeric liquid crystalline materials and bimesogens in recent years, driven by interest in wide temperature range blue phases, [1,2] flexoelectric behaviour, [3-5] and the ability of some dimeric materials to exhibit a lower temperature nematic mesophase denoted N_X or N_{TB}, [6-18] where ‘X’ or ‘TB’ refer to unknown and twist-bend respectively. The local structure of the N_X/N_{TB} phase is still hotly debated, with the heliconical model proposed independently by Meyer [19] and Dozov [20] being supported by ^{2}H NMR studies, measurement of the electroclinic effect and freeze-fracture transmission electron microscopy (FFTEM). [21-23] All three of these methods suggest a local helical structure of extremely tight pitch, in the region of 8 nm for the well-studied material 4',4'''-(heptane-1,7-diyl)bis(([1,1'-biphenyl]-4-carbonitrile)) CB7CB. [23] Polarised Raman spectroscopy has also been used to measure both $<P_2>$ and $<P_4>$ order parameters in the nematic and N_{TB} phases. [24]

This view of the local structure has also been disputed, with solid state ^{2}H NMR, [25] FFTEM, [26] and measurement of elastic constants [27] found to be odds with the heliconical model. Most recently the observation of direct isotropic to N_{TB}/N_X phases has provided a further challenge to future theoretical treatments. [28, 29] In addition, it has been demonstrated that unlike the nematic phase, the N_{TB} exhibits focal-conic and parabolic defects, and forms free-standing films which are typical properties of smectic phases. [12]

There is significant interest not only in the local and bulk structures of the N_{TB} phase but also the molecular features that give rise to this unique state of matter. Although predominantly exhibited by methylene-linked bimesogens, the N_{TB} phase has also been reported in bent-core materials, [11] covalently and hydrogen bonded trimers. [16,17] Methylene linking groups are not a prerequisite, with both imine, [6] ether and mixed ether-ester materials are also known to exhibit this phase. [13,14,30] Although the N_{TB} phase is known to exhibit local spontaneous chirality [21] it has also been observed in neat chiral materials [31,32] and also upon the introduction of a chiral dopant into an achiral system. [12,28]

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Furthermore structure-property correlations suggest that the formation of the N_{TB} phase is driven primarily by molecular shape, [15,18,30] which influences the packing of the molecules together coupled with the minimisation of the free volume. [33] Mesogenic dimers have often been viewed as model compounds for main-chain liquid crystal polymers, [34] and it has long been noted that the transitional properties of dimers, as with main-chain liquid crystalline polymers, exhibits a critical dependence on the length and parity of the central spacer. [35,36] In this article we investigate a new sequence of phase transitions for a bimesogen that has a conformationally bent structure by thermal optical microscopy (POM), differential scanning calorimetry (DSC), X-ray diffraction, and in applied electrical fields. Our results suggest that the material may exhibit a new phase variant that is based on the condensation of the N_{TB} phase.

Results

The material that is the subject of this report is nonane-1,9-diyl *bis*(4,1-phenylene)-*bis*(4'-propyl-[1,1'-biphenyl]-4-carboxylate), [abbreviated as **9-(3BEP)2**] as shown in Figure 1. Its transition temperatures (°C), and enthalpies and entropies of transition are given together in Table 1.

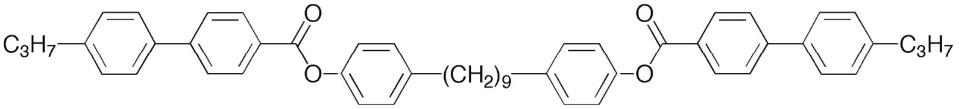

Figure 1: Structure of nonane-1,9-diyl *bis*(4,1-phenylene)-*bis*(4'-propyl-[1,1'-biphenyl]-4-carboxylate), **9-(3BEP)2**.

	Cryst		Anticlinic		N_{TB}		Nematic		Liquid
Temp (°C)	•	129.3	•	137.1	•	168.2	•	244.9	•
ΔH (kJ mol^{-1})		[30.19]		[1.63]		[0.01]		[1.36]	
ΔS/R		{9.02}		{0.48}		{0.003}		{0.316}	

Table 1: Transition temperatures (°C) and associated enthalpies (kJ mol^{-1}) and dimensionless entropies of transition.

Polarized Light Microscopy: The first studies **9-(3BEP)2** were performed on using thermal polarized light optical microscopy (POM). Cooling the material of thickness ~50 μm, sandwiched between untreated cover slip and slide, from the isotropic liquid resulted in the formation of a typical *schlieren* defect texture associated with the nematic phase. Cooling into the N_{TB} phase resulted in the formation of two distinct textures dependent on the homeotropic or homogeneous alignment surfaces of the glass. One texture, corresponding to homogenous orientation, exhibited quasi-

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focal-conic domains that showed long range out-of-plane correlations, seen as steps/blocks in the texture, Figure 2(a)). Upon sustained cooling the blocky texture yields a rope-like texture as described previously, [12] and shown in Figure 2(b), whereas shearing of the sample leads to homeotropic alignment of the N_{TB} phase and renders the sample optically extinct.

Neither of these paramorphotic defect textures are typically associated with nematic phases, and indicate that the N_{TB} phase has long-range order as we have reported previously. [12, 28] Further cooling resulted in the formation of another phase, which exhibited textures characteristic of a smectic phase. For instance, a focal-conic defect texture was formed in areas of homogeneous orientation; see Figure 2(c). The focal-conic domains characteristically showed elliptical and hyperbolic lines of optical discontinuity indicating that the phase had long-range order perpendicular to the concentric arrangement of layering or helical structuring in the domains. Moreover the focal-conic domains possessed defect lines parallel to the elliptical optical discontinuities. However, their lines were not equally separated from one another, and therefore are not related to any form of supramolecular helical ordering (pitch lines) or patchwork domains associated with internal structures (tilt domains). The lines are in fact more reminiscent of those associated with the orthorhombic lattice of the biaxial crystal E phase, and suggests that the bulk phase is biaxial. In the homeotropically oriented areas a *schlieren* texture, possessing two and four point defects, was observed as shown in Figure **2**(d). The fingerprint pattern showed non-regular line spacings (Figure **2**d) and as with the focal-conic defects, the irregularity does not support helix formation.

As the third phase in the phase sequence exhibits focal-conic and schlieren defect textures without helix formation, one would assume that the phase has a layered structure. The presence of two point defects in the schlieren indicates that the phase has an anticlinic structure, which supports the observation that the phase is biaxial. Additionally, the appearance of lines in the focal-conic domains points to the phase having long-range order perpendicular to the layer planes. These observations combine to identify unequivocally the nematic and N_{TB} phases, and to classify the third phase as a biaxial, anticlinic, lamellar phase.

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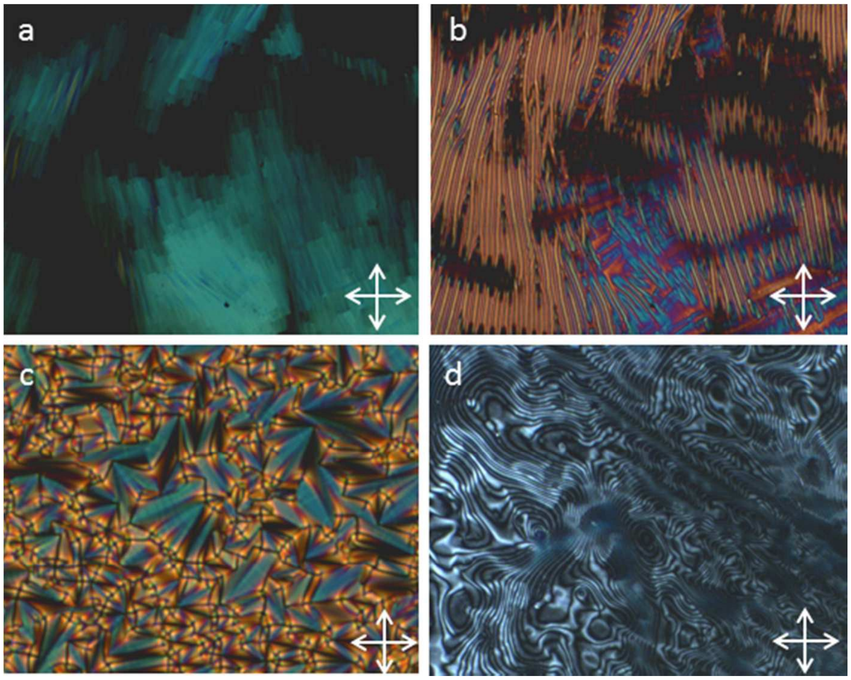

Figure 2: Photomicrographs (x100) of compound **9-(3BEP)2** as a function of temperature (°C); (a) the stepped or blocky texture of the N_{TB} phase (162 °C); (b) the rope-like texture of the N_{TB} phase (142 °C); (c) the focal-conic defect texture of the anticlinic phase (136 °C); and (d) the *schlieren* texture of the anticlinic phase (°C).

Differential Scanning Calorimetry: Confirmation of the phase behaviour as a function of temperature was achieved using differential scanning calorimetry (DSC). The thermograms for the first heating and cooling cycles for **9-(3BEP)2** are shown in Figure 3a. The melting point, the anticlinic to N_{TB}, and N to liquid transitions were found to be first order, however, the nematic to N_{TB} phase transition was shown to be rather broad, appearing as second order or as a glass transition, see the inset in Figure 3b. In order to elucidate the nature of the N_{TB}, to N transition, the first order derivative of the heatflow as a function of temperature was determined, as shown in Figure 3c. The Gaussian fit to the data plot suggests that the transition is probably associated with a glass transition (Tg) and not a step in the heat capacity as expected for a true second order phase transition. The sharpness of the other peaks in the thermogram indicates that the broadness of the N_{TB} to N transition peak is real and not an artefact of the experiment, supporting the earlier findings of Tripathi *et al.* [9]. This type of result has been seen previously for a number of materials, notably CB11CB for which the N_{TB} to N transition was shown to 'sharpen' to give an almost first order peak as the DSC scan rate was lowered. [12] This phenomenon was associated with the materials exhibiting polymeric properties and a high degree of kinetic behaviour at the phase transition.

Determination of the enthalpies and entropies from the DSC thermograms shows that the N_{TB} to anticlinic transition is strongly first order, with the transition being two orders of magnitude larger than the relative enthalpy for the N_{TB} to N transition (1.63 kJ mol^{-1} to 0.011 kJ mol^{-1} respectively). The associated entropy of transition ($\Delta S/R$) was also significantly larger for the N_{TB} to anticlinic phase transition than for the N_{TB}-N transition (0.48 versus 0.003). These results indicate

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that the anticlinic phase has an associated lattice, whereas the N_{TB}-N phase transition tends to be continuous with the two phases having similar disordered structures lacking lamellar ordering.

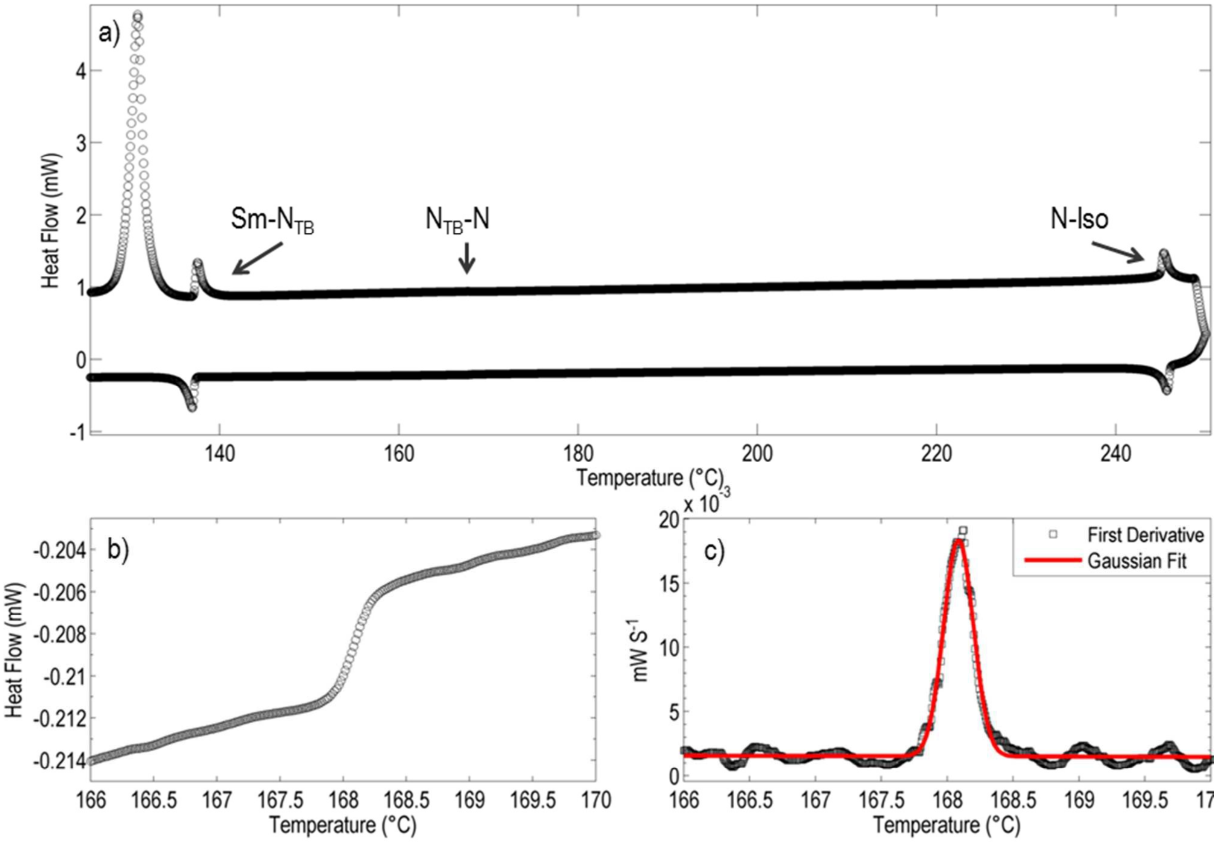

Figure 3: DSC thermogram for **9-(3BEP)2**. (a) Top, first heating cycle with positive heatflow, bottom, first cooling with negative heatflow. Inset (b) shows an expansion for the nematic to N_{TB} transition. Inset (c) shows a alot of the first order derivative for the DSC thermogram for the N to N_{TB} phase transition for **9-(3BEP)2**, where the solid line show a two term Gaussian fit to the data. A heat/cool rate of 10 °C min^{-1} was used with measurements made every 100 ms.

X-ray Diffraction: The structures of the mesophases of **9-(3BEP)2** were investigated using small angle X-ray diffraction on magnetically aligned samples, and a plot of the integrated scattering intensities as a function of temperature and d-spacings are shown Figure 4(a). The nematic phase was well-aligned in the magnetic field, and it gave a typical diffuse small-angle scattering pattern as found for other examples of bimesogens with odd parity methylene linking chains, see Figure 4b). [18] Conversely, the N_{TB} phase appeared only partially aligned, as shown in Figure 4(c), and the anticlinic phase was apparently unaligned by the magnetic field, see Figure 4(d).

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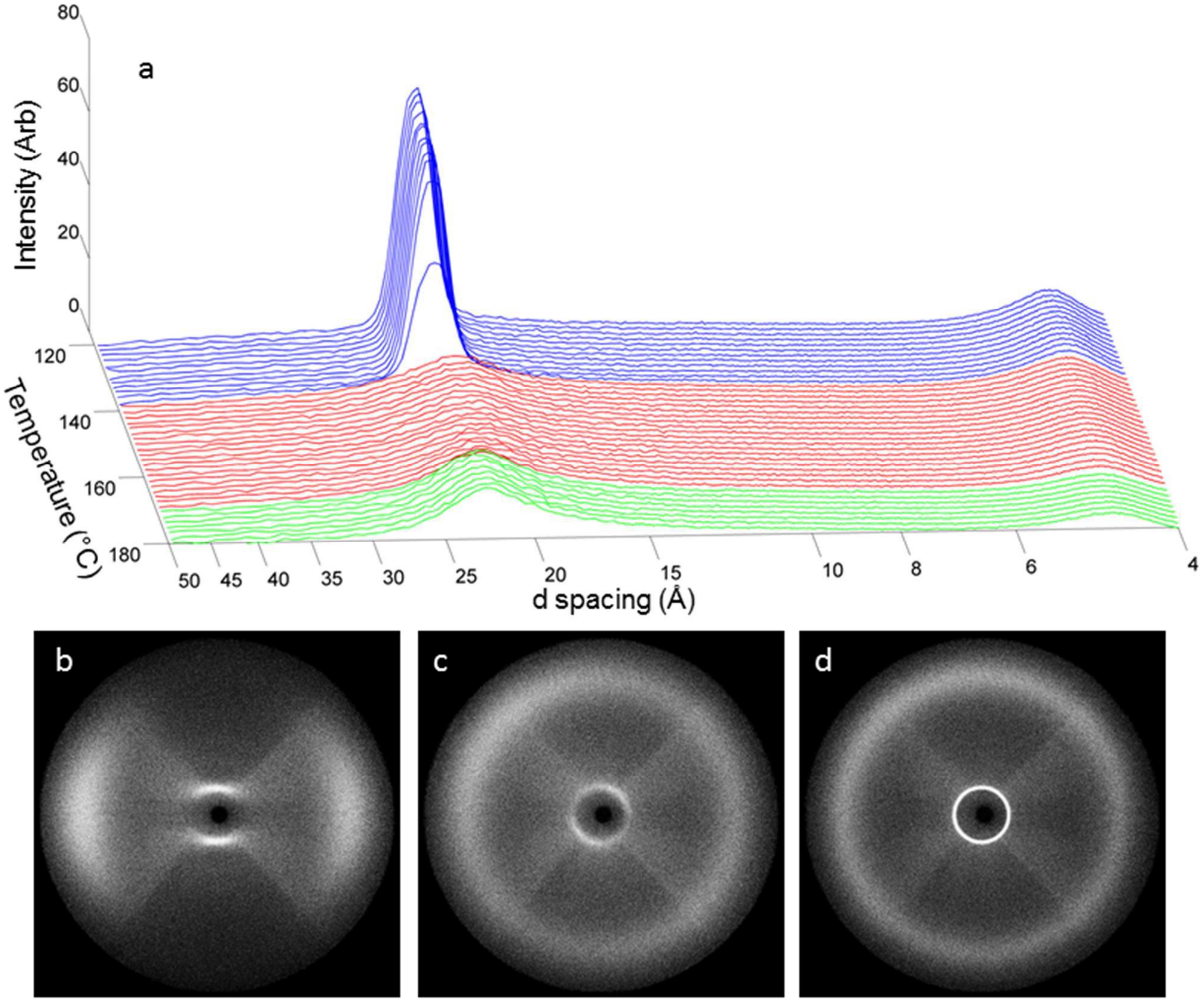

Figure 4: (a) A plot of the integrated scattering intensities and d-spacings (Å) for a magnetically aligned sample of **9-(3BEP)2** as a function of temperature (°C); the small angle scattering patterns for **9-(3BEP)2**, (b) in the nematic phase (163 °C), (c) in the N_{TB} phase (143 °C), and (d) in the anticlinic phase (105 °C).

The integrated diffraction intensity as a function of temperature in the wide-angle region corresponds to the average lateral separation between adjacent molecules. It is therefore unsurprising that the scattering in this region shows extremely broad peaks in the nematic phase, before becoming somewhat more defined following the transition into the N_{TB} phase. This increase in definition is accompanied by a reduction in the d-spacing in the wide angle scattering region, which results from the average lateral molecular separation being larger in the nematic phase than in the N_{TB}, which is in turn larger than that in the anticlinic phase. Qualitatively this is indicative of the order parameter increasing with reducing temperature as expected. However quantitative measurements are not possible for two reasons; firstly, the sample alignment is not consistent across all three phases, and secondly the well-known relationship between the orientational distribution function and scattered intensity in the wide angle region assumes that the molecules have cylindrical symmetry,[37,38] whereas bimesogens such as **9-(3BEP)2** are molecularly biaxial.

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Focusing now on the small angle region, a reduction in the d-spacing of the diffuse peak can be seen on going from the nematic to the N_{TB} phase. This reduction from d = 22.66 Å to d = 21.64 Å is due to the molecules tilting away from the nematic director on entering the N_{TB} phase by ≈15°. For the anticlinic phase, a sharp small angle peak was observed, with a near temperature independent layer spacing of 22.59 Å, this corresponds to 0.57 times the molecular length, which was determined to be 38.96 Å at the B3LYP/6-31G(d,p) level of DFT.

The in-plane correlation length (ξ), defined as $\xi = 2\pi/\Delta q$, was found to decrease from an average of 7.1 Å in the nematic phase to an average of 6.2 Å in the N_{TB} phase as shown in Figure 5. The in-plane correlation length increases again to an average of 15.9 Å in the anticlinic phase, and although this is significantly larger than either the nematic or N_{TB} phases it is an order of magnitude too small to be indicative of long-range in-plane order. Thus, the anticlinic phase has long-range ordering outof the plane but only short-range ordering in the plane of its lamellar structure.

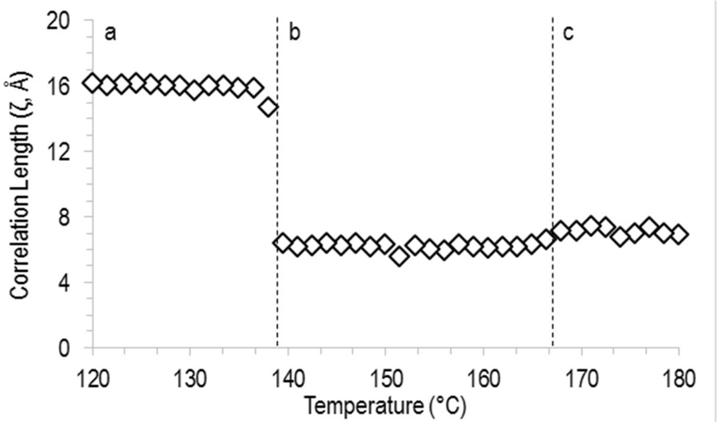

Figure 5: Plot of the in-plane correlation length ($\xi = 2\pi/\Delta q$) of **9-(3BEP)2** vs. temperature (°C) as determined by small angle X-ray scattering. Regions (a), (b), and (c) correspond to the anticlinic, N_{TB} and nematic phases respectively.

Additionally **9-(3BEP)2** was investigated at smaller 2q values in order to exclude the possibility that structural features of the anticlinic phase, or indeed N_{TB} phase might give diffraction patterns at larger d-spacings, see Figure 6. However in the region of 20-140 Å, no additional peaks associated with supramolecular stucturing were observed.

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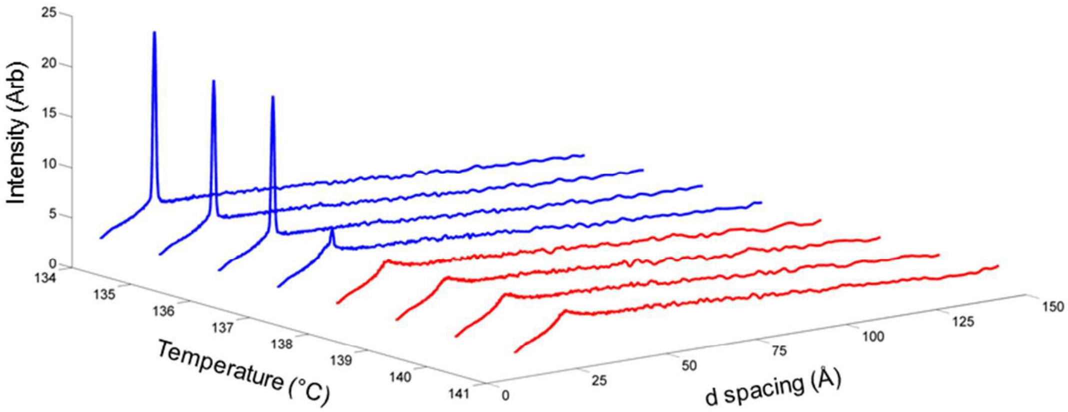

Figure 6: Plot of integrated small angle diffraction intensity as a function of temperature for **9-(3BEP)2** yielding d-spacings in the range 20-140 Å.

Electrooptic Response: In order to study the behaviour of **9-(3BEP)2** under applied electric fields the material was first doped with 3 wt% of the BE8OF2N (Figure 7) to allow potential ferroelectric or antiferroelectric switching to be observed in the anticlinic phase as opposed to dielectric switching which would be expected to occur without addition of a chiral dopant. The mixture of **9-(3BEP)2** + BE8OF2N was filled into a glass cell with ITO electrodes and wires were affixed to the cell using indium metal as a solder placing an upper limit on measurements of 155 °C, *i.e.* 10 °C below the melting point of indium, and for this reason it was not possible to study the behaviour in the nematic phase. A modest reduction in the anticlinic to N_{TB} transition temperature was observed (132 versus 137.1 °C for the undoped material). No true switching process could be observed in either the N_{TB} or anticlinic phases with a triangular waveform and $20V_{PP}$ amplitude at a range of frequencies from 0.1 Hz to 100 Hz, although it was possible to observe some electrohydrodynamic instabilities, which arise as a result of space charge and ionic impurities, possibly from degradation of the material under applied voltages and relatively high temperature. The lack of switching in both the N_{TB} and anticlinic phases is perhaps associated with two possible behaviors. Firstly, there is no coupling between the chirality of the dopant, **9-(3BEP)2**, and the applied field. For the N_{TB} phase there is no electroclinic response and for the anticlinic phase there is no ferroelectric response. For the anticlinic phase this indicates the molecules are not in tilted arrangements. The second possibility is that molecules are intercalated in both mesophases. Overcoming intercalation in order to observe a switching process *via* application of an applied field would seemingly require a larger torque than could be applied. The constituent mesogenic units of 9-(3BEP)2, calculated to be 2.35 Debye at the B3LYP/6-31G(d) level of DFT, are less polar than those of other NTB materials such as CB9CB and M2, determined to be 5.82 and 3.03 respectively at the same level of theory. CB9CB and M2 have been observed to undergo weak switching processes even under higher voltages than those utilized here. [10].

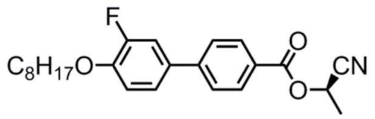

Figure 7: The molecular structure of the chiral dopant BE8OF2N ((R)-1-cyanoethyl 3'-fluoro-4'-(octyloxy)-[1,1'-biphenyl]-4-carboxylate)

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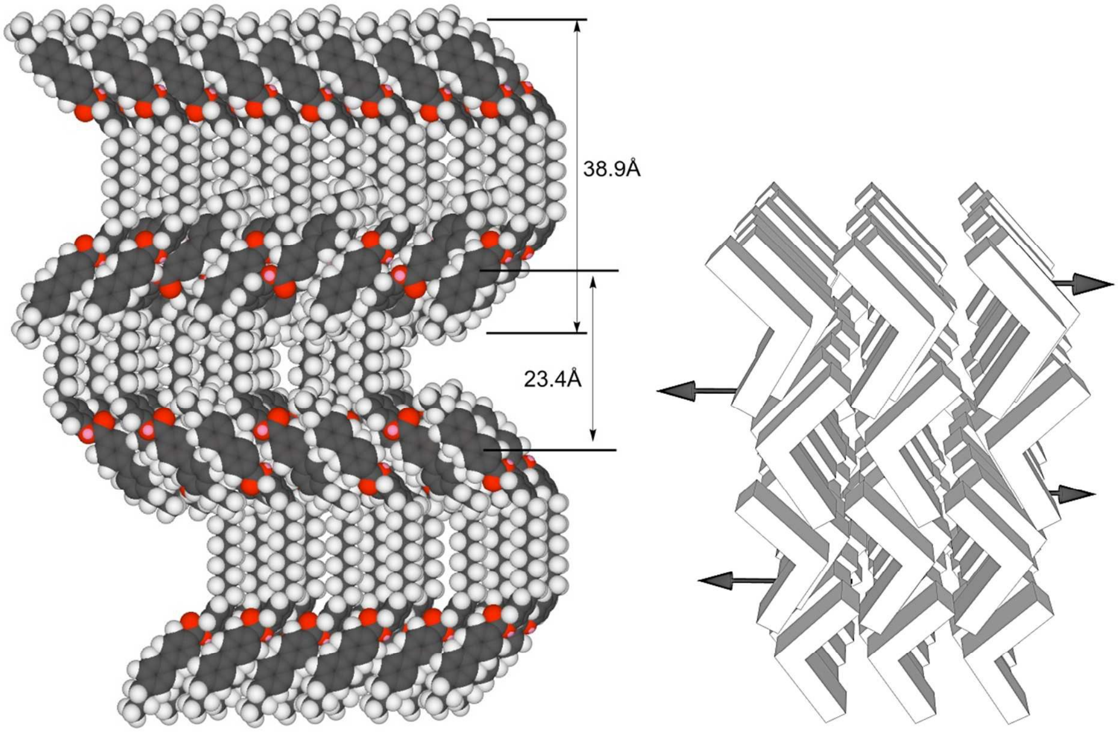
Discussion

On the basis of the calculated molecular length from DFT minimised geometry and determination of the layer spacing from X-ray scattering experiments the molecules will not likely to be tilted in their layers. Assuming that the molecules are packed together so that the intermolecular $\pi-\pi$ interactions will be the strongest interactions between the molecules, then an intercalated alternating tilted structure such as the one shown in Figure 8(a), where the aromatic regions associate together results. The measured layer spacing from this arrangement is ~23 Å, which is very close to measured value. In this arrangement the lateral dipoles will alternate from one layer to the next, and the phase will be potentially antiferroelectric. However, the molecules will not have complete rotational freedom about their long axes, thereby rendering the phase less susceptible to a response to an applied electric field, as was observed.



(a) (b)

Figure 8: (a) The modelled structure of the anticlinic phase of **9-(3BEP)2**, and (b) a schematic representation of the intercalated of the anticlinic phase.

As the anticlinic phase is intercalated it suggests that the N_{TB} phase might also have an intercalated structure. In this arrangement the minimisation of the free volume for the packing arrangement of the molecules is via a spiralling organization giving a twisted rope-like structure, where the periodic order arises from the helical pitch length. However, the molecules have no periodic ordering along the twist axis. In this scenario there is no modulation of electron density along the director and thus the periodicity associated with the N_{TB} helix is not revealed by X-ray scattering studies (see

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Figure 7). The formation of such ordering will be dependent on the kinetics of the system, and thus the DSC results would be expected to show glass-like behaviour rather than sharp first order phase transitions, which was observed.

Potentially at the phase transition from N_{TB} to anticlinic phase, the condensation of the N_{TB} phase results in a suppression of the heliconical structure and alignment of the molecules into layers to gain from the reduction in the free energy due to lattice formation. Thus the spiralling nature of the intercalated N_{TB} phase transforms into the intercalated anticlinic phase, both of which have quasi-polymer structures as a consequence of their intercalation and long out-of-plane correlation lengths. Bimesogens therefore are good models for polymeric liquid crystals. Watanabe and Hayashi have demonstrated as much for the liquid crystal behaviour of main chain polymers, such as BB-5 shown in Figure 8, where the methylene spacer unit was of odd parity and anticlinic phases are formed [39]. Similarly, there are numerous examples in the literature for the formation of helical fibres in liquid crystal systems. For example, collagen, poly-L-glutamine [40, 41] poly-benzyl L-glutamate (PBLG) [42,43], etc. all exhibit chiral fibres of one type or another. Of particular interest are the liquid crystal properties of PBLG, which show microscopic textures that are almost identical to those of the N_{TB} phase. [18]

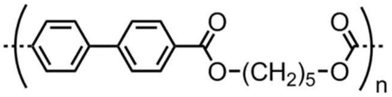

Figure 8: Molecular structure of the polymer BB-5. [39]

Conclusion

The N_{TB} and anticlinic phases reported here are modulated forms of tightly packed, intercalated soft-matter systems that are akin to polymers. The difference between such systems and those formed by low molar mass materials is one of molecular dimensions (nano- versus meso- scale) and restricted motion that drives the minimisation of free volume. For low molar mass materials, at the nanoscale diffuse reorientational motion results in the formation of nematic and smectic phases, whereas for bimesogens, at the mesoscale the result is the formation of quasi-polymeric soft-matter systems. In the case of the anticlinic phase, the out-of-plane order is long-range, whereas the in-plane ordering is short-range, and the phase therefore could be considered as a one-dimensional crystal. Conceptually, this leads to the possibility for the formation of a variety of phases of soft-matter where order can be different in 3D space, for example the formation of two dimensional crystals etc.

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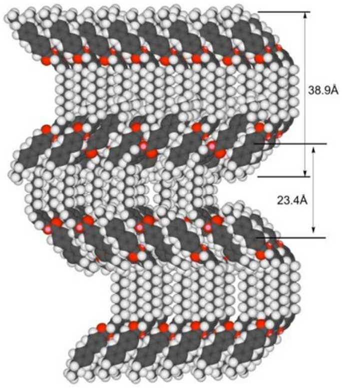

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