

Unusual properties of a bent-core liquid-crystalline fluid†

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In our investigations of a family of achiral bent-core *bis*-(phenyl)oxadiazole derivatives, we observed some unusual properties of the nematic phase. These include evidence of segregation into domains of opposite handedness and the formation of clusters, nematic phase biaxiality, and a strongly kinetically governed phase behaviour, which leads to the display of unique filament structures at the onset of new order. We suggest that the combination of a deviant calamitic molecular shape with a considerable transverse dipole leads to an unusual strength and combination of molecular interactions, and as a consequence these nematic materials need to be considered as fluctuating and dynamically changing, multi-hierarchical fluids.

Introduction

Complex fluids encompass a number of unique states of matter which can exist between the organised solid state and the disorganised liquid. Many of these states are stabilised by interactions that are extremely sensitive to changes in molecular topology and polarity. In recent years liquid crystal phases formed by materials possessing bent-core molecular structures have featured strongly in the conflict between the efficient packing of the molecules, which leads to the formation of curved structures, and the need for the system to form two dimensional flat layers. Materials with these molecular architectures, as a consequence, sit at the interface between the formation of calamitic liquid crystal phases and columnar mesophases. Formed by achiral molecules, these so-called ‘banana’ phases show properties such as spontaneous polar ordering¹ and spontaneous formation of chirality,² which usually are not found in calamitic phases of achiral rod-like molecules. In some cases, bent-core materials have been reported that display nematic phases at temperatures above their ‘banana’ phases.

Furthermore, borderline materials, which exhibit both ‘banana’ and layered calamitic phases, are known.³ One example is the family of materials based on the *bis*-(phenyl)oxadiazole motif that have considerably less of a bend ($\sim 140^\circ$)⁴ associated with their structures than classical bent-core systems ($\sim 120^\circ$). However, they also possess a large transverse electric dipole moment (~ 4 D) due to the central, rigid oxadiazole unit. It was a member of this *bis*-(phenyl)oxadiazole family, ODBP-Ph-C7, which after a search of over thirty years,⁵ provided the first example of the elusive thermotropic biaxial nematic phase.^{4,6} Intriguingly, our investigations of this material, and novel alkyl and alkoxy *bis*-(phenyl)oxadiazole materials with similar structures, have shown that the liquid-like nematic phase of these

achiral compounds can also segregate into chiral domains of opposite handedness.⁷

Results

Previously we established a synthetic route for the synthesis of ODBP materials with structures closely related to known biaxial nematic ODBP materials,^{4,6} but with molecular structures featuring dissimilar arms. We also reported some unexpected results on the nematic phase behaviour of these materials.⁷ Motivated by these initial results, we further examined the known biaxial nematic compound **1** (ODBP-Ph-C7)⁴ and the previously synthesised compound **3** (C7-Ph-ODBP-Ph-C5),⁷ see Fig. 1 and Table 1. We also prepared six further novel ODBP compounds **2**, and **4–8**. They feature dissimilar arms with terminal alkyl chains of different length and fluoro-substituents incorporated in the inner phenyl ring of one arm with the objective of increasing the molecular biaxiality, widening the nematic phase range, and to influence packing constraints and transverse electric dipoles of the molecules. The structures and phase transitions of the materials are listed in Table 1, and details of the synthesis for the new materials **2** and **4–8** can be found in the ESI†.

As a general trend, we found the nematic temperature range to broaden in a systematic way with decreasing chain length of the

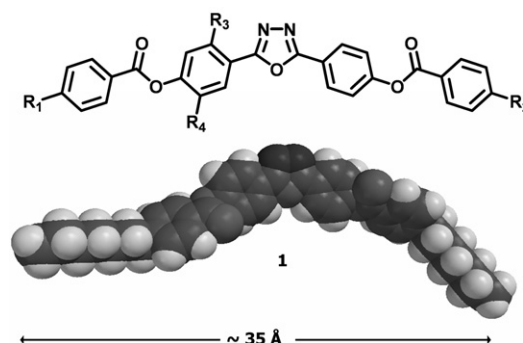


Fig. 1 General structure of the *bis*-(phenyl)oxadiazole materials investigated, and molecular length of compound **1**.

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Table 1 Phase transition temperatures of compounds 1–8. Reported are the onset temperature values for transitions observed in DSC cooling cycles at 10 °C min^{−1}

No.	R ₁	R ₂	R ₃	R ₄	Phase transitions [°C]
1	C ₇ H ₁₅	C ₇ H ₁₅	H	H	IsoLiq 222 N 173 X 151 Cr (178) ^a
2	C ₇ H ₁₅	C ₆ H ₁₃	H	H	IsoLiq 226 N 171 X 152 Cr (179) ^a
3	C ₇ H ₁₅	C ₅ H ₁₁	H	H	IsoLiq 232 N 164 X 149 Cr (174) ^a
4	C ₇ H ₁₅	C ₄ H ₉	H	H	IsoLiq 234 N 157 X 149 Cr (169) ^a
5	C ₆ H ₁₃	C ₅ H ₁₁	H	H	IsoLiq 237 N 163 X 156 Cr (178) ^a
6	C ₆ H ₁₃	C ₄ H ₉	H	H	IsoLiq 239 N 160 X 158 Cr (174) ^a
7	C ₇ H ₁₅	C ₇ H ₁₅	F	H	IsoLiq 218 N 160 X 153 Y 113 Cr (121) ^a
8	C ₇ H ₁₅	C ₇ H ₁₅	F	F	IsoLiq 219 N 124 SmC 122 X 111 Cr (142) ^a

^a In brackets: melting point on heating.

alkyl substituent in one arm, see Table 1. Overall, the compounds 1,^{4,7} 3,⁷ and the novel compounds 2, and 4–6 exhibited a similar overall phase behaviour on cooling, where a broad nematic phase is followed by a monotropic higher ordered phase, denoted X in Fig. 1, and then the solid state. In the mono-fluorinated compound 7 the N to X transition is followed by a transition to a further higher ordered phase, denoted Y, followed by the solid state. In the difluoro compound 8 the stability of higher ordered phases is reduced remarkably and a very broad temperature range nematic phase is followed first by the SmC phase, and then the X phase. In both fluorinated compounds 7 and 8 the melting points are reduced considerably.

On examination of the nematic phases of the novel achiral oxadiazole derivatives 2 and 4–8 by polarising optical microscopy (POM), we observed the formation of chiral domains of opposite handedness, similar to the behaviour of the nematic phase of compounds 1 and 3 we already reported.⁷ Fig. 2 (a–c) shows the textures of the nematic phase for compound 5, compound 4, and compound 8. When pristine samples, sandwiched between a glass slide and a cover slip, were studied under crossed polarisers, an apparently normal nematic phase was formed first on cooling from the isotropic liquid. However, on uncrossing the polarisers it became apparent that the mesophase also exhibited two different kinds of domains, with distinct walls separating one kind of domain from the other. The domains were characterised by showing exactly opposite colour dispersion on rotation of the analyser. For example, in the nematic phase of compound 5 one type of domain appeared green upon a 20° clockwise rotation of the analyser and turned pink upon a reverse 20° anticlockwise rotation of the analyser, whereas the other domains behaved in exactly the opposite way, as shown in Fig. 2(a). The observation of exactly complementary colour dispersion in the two different domains on rotation of the analyser indicates the domains are of opposite handedness. The observation of areas of opposite handedness in a nematic phase evidently has to be due to a helically twisted superstructure with opposite twist in the two domains with opposite optical properties.

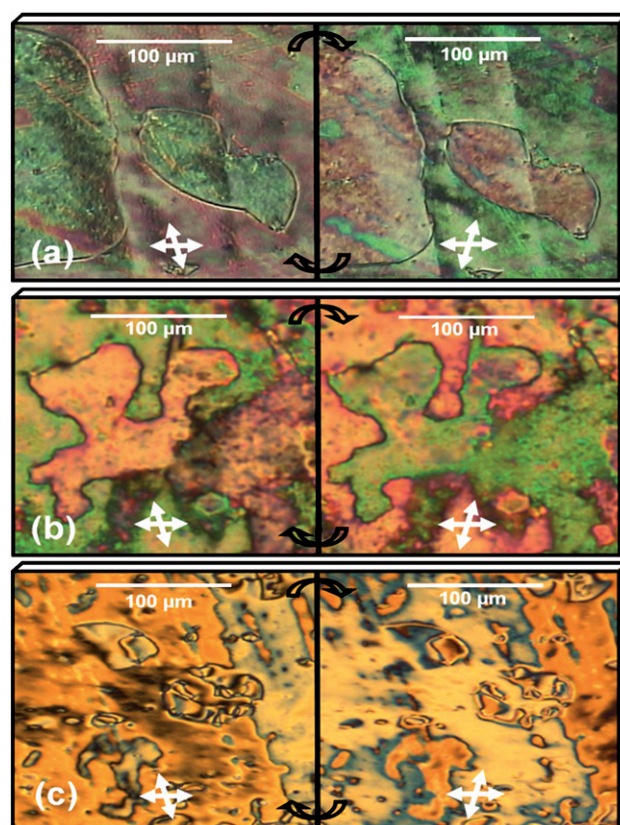


Fig. 2 (a)–(c): POM images of the nematic phase of (a) 5 at 204 °C, (b) 4 at 232 °C, and (c) 8 at 149 °C, left: 20° anticlockwise, right: 20° clockwise rotation of the analyser ($\times 100$).

The domains of opposite handedness formed spontaneously and existed in approximately equal proportions over the whole of the preparation. They also occurred at random, and could be altered by shearing or change in temperature. Hence, their formation was dependent on the thermal and mechanical history of the sample, indicating a kinetically based rather than thermodynamic process.

It has to be noted that the pitch of the twisted superstructure in the domains of opposite handedness is clearly larger than the sample thickness and the texture and colours observed under crossed polars are the textures and birefringence colours of a nematic phase. However, the two domains we observed in our bent-core materials on uncrossing the polars are clearly different in appearance from surface induced twist domains which can occur in any nematic material. Firstly, the domains we observed in pristine samples are not fixed which suggest the place they occur is not controlled by the surface. Secondly, the two domains occur with equal probability which suggest a degeneracy of opposite helical twist directions. Thirdly, we observe opposite colour dispersion on equal angles of rotation of the analyser which suggests that the pitch of the helically twisted superstructure in the two areas is not only of opposite sense but also of the same magnitude.

A situation where a nematic material would show this behaviour not as a spontaneous intrinsic property, but due to the surface forcing the orientation of the material to propagate in a twisted fashion from the top to the bottom surface would require a careful

control of the alignment. It would indeed require the manufacture of a twisted nematic cell with defined thickness and an offset of the top and bottom planar alignment surfaces of exactly 90° . This would be necessary to ensure the energetic degeneracy of the two possible opposite twist directions and hence the observation of two twist domains of exactly opposite twist in equal proportions, which then would also show exactly opposite colour dispersion on equal angles of rotation of the analyser. However for the POM pictures shown in Fig. 2 we used simple preparations of our bent-core nematic materials between an untreated glass slide and a circular untreated glass cover slip.

Indeed, in preparations between two parallel oriented planar alignment surfaces we observed the formation of a uniformly planar aligned nematic monodomain in our materials, i.e. the formation of twisted domains of opposite handedness is suppressed by the planar alignment surfaces.

Differential scanning calorimetry (DSC) performed at low scan rate ($0.5^\circ\text{C min}^{-1}$) around the isotropic liquid to nematic transition indicated that the transition to the nematic phase of the ODBP materials is preceded by a thermal event in the isotropic phase. For example, Fig. 3 shows consecutive DSC heating and cooling traces for compound **2** performed with decreasing scan rate around the nematic phase to isotropic liquid phase transition, starting with a rate of $10^\circ\text{C min}^{-1}$ down to a rate of $0.5^\circ\text{C min}^{-1}$. The corresponding Table 2 lists the onset temperature values of the observed transitions for each run. The consecutive runs shown in Fig. 3 clearly document a change in appearance of the nematic to isotropic liquid transition with decreasing rate. At high rates, such as $10^\circ\text{C min}^{-1}$ in heat 1 and cool 1, only one thermal event is resolved, which corresponds in appearance to a typical transition peak expected for a first order nematic to isotropic liquid transition. However, with decreasing rate a second transition is increasingly resolved. As can be seen

Table 2 The nematic phase to isotropic phase transition of compound **2** in consecutive DSC heating and cooling cycles, as shown in Fig. 3. The table reports the onset temperature values for DSC transition peaks observed in a temperature interval between 220 – 232°C . (The total enthalpy change ΔH in each cycle is approximately 0.5 kJ mol^{-1} .)

Run	Rate [$^\circ\text{C min}^{-1}$]	Peak 1 T(onset) [$^\circ\text{C}$]	Peak 2 T(onset) [$^\circ\text{C}$]
Heat 1	10	226.05	—
Cool 1	–10	226.05	—
Heat 2	5	225.99	—
Cool 2	–5	226.02	(shoulder)
Heat 3	2	226.05	(shoulder)
Cool 3	–2	225.95	(shoulder)
Heat 4	1	225.95	226.24
Cool 4	–1	226.00	226.23
Heat 5	0.5	225.90	226.20
Cool 5	–0.5	226.04	226.24

from the onset values listed in Table 2, this second transition occurs in the liquid state, i.e. at a temperature slightly above that to the nematic phase, suggesting that the liquid is structured at temperatures just above the formation of the liquid-crystalline state.

On further investigation of the mesophase behaviour of the materials **1** and **3**, which before we only studied by POM for their behaviour in the nematic phase⁷ and on investigation of the new materials **2**, and **4–6**, we observed, under certain conditions, an unusual behaviour at the lower temperature changeover from the nematic phase. This behaviour was exhibited *both* in conventional preparations between untreated glass cover-slips and slides, and in planar aligned cells of various thicknesses (5 – $15\text{ }\mu\text{m}$). The transition from the nematic phase on cooling was found to be dependent on the thermal and mechanical history of the sample. The expected phase sequence I–N–X–Cr was

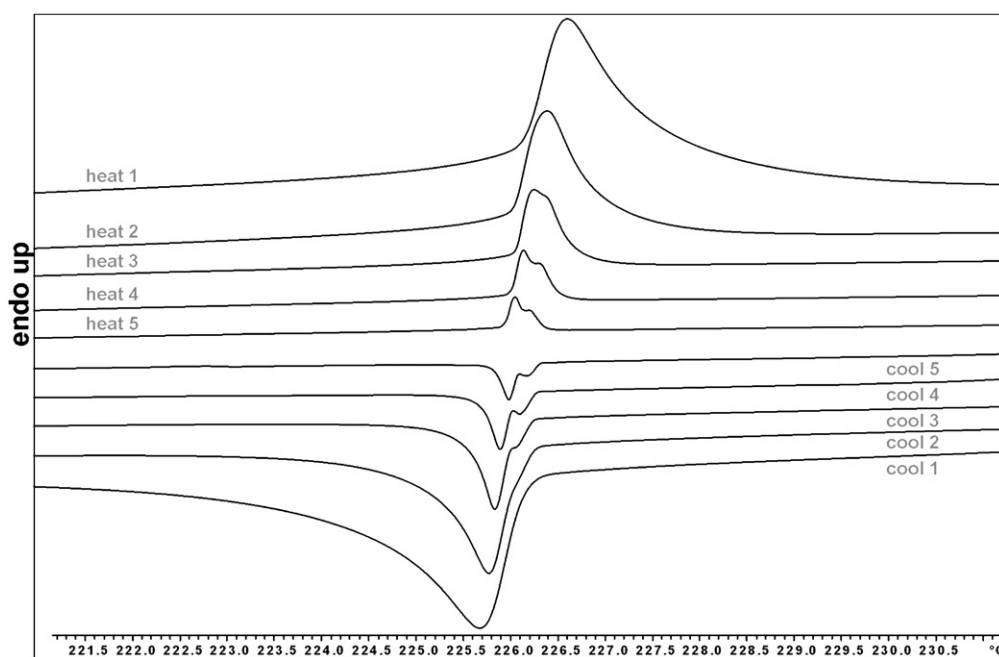


Fig. 3 Consecutive, increasingly slow DSC heat and cooling cycles of compound **2** around the N to I phase transition. With decreasing rate a second thermal event is resolved above the N to I transition peak. Cycling rates and transition temperatures are listed in Table 2.

observed without fail only on cooling directly from the isotropic liquid or from above a defining temperature in the nematic phase. However, after heating back to the nematic, but to temperatures below the mentioned limit, in many cases altered behaviour was observed upon cooling, with filaments occurring at the transition from the nematic phase.

On formation the filaments grew linearly rather than curved, and at a rapid speed. However, when they came into contact with other filaments, defect walls or air bubbles, they curved, turned and curled up easily and quickly, revealing their liquid-like nature. This behaviour was documented for compound **3** in a real time video-clip which is available in the ESI†. The filaments for *bis*-(phenyl)oxadiazole materials **1–6** formed in a rather similar way to twist grain boundary (TGBA) filaments for a chiral material.⁸ However, they bore no resemblance in appearance or growth behaviour to the helical filaments characteristic for the B7 phase of an achiral bent-core material.³

Sets of photomicrographs show typical sequences of events observed on cooling from the nematic for compound **3** in Fig. 4(a) (left to right), and in Fig. 4(c) (left to right). As the temperature was lowered, the growth and numbers of filaments increased. With more filaments being formed, opportunities to bend increased, and eventually the whole preparation became filled with filaments. In textures of **3** with disc-like regions, developed by tempering, the process of filamentary growth was not accompanied by an increase in number or size of the discs. In a filament that developed a triangular area, disappearing and reappearing parallel lines perpendicular to the main filament axis were observed, as shown in Fig. 4(b). The spacing between the lines of around 6–7 μm could indicate a large scale superstructure or lattice.

In addition to the filaments, pinkish-red coloured planar textures, which were not stable over long periods of time, were occasionally observed in 5 μm planar alignment cells under

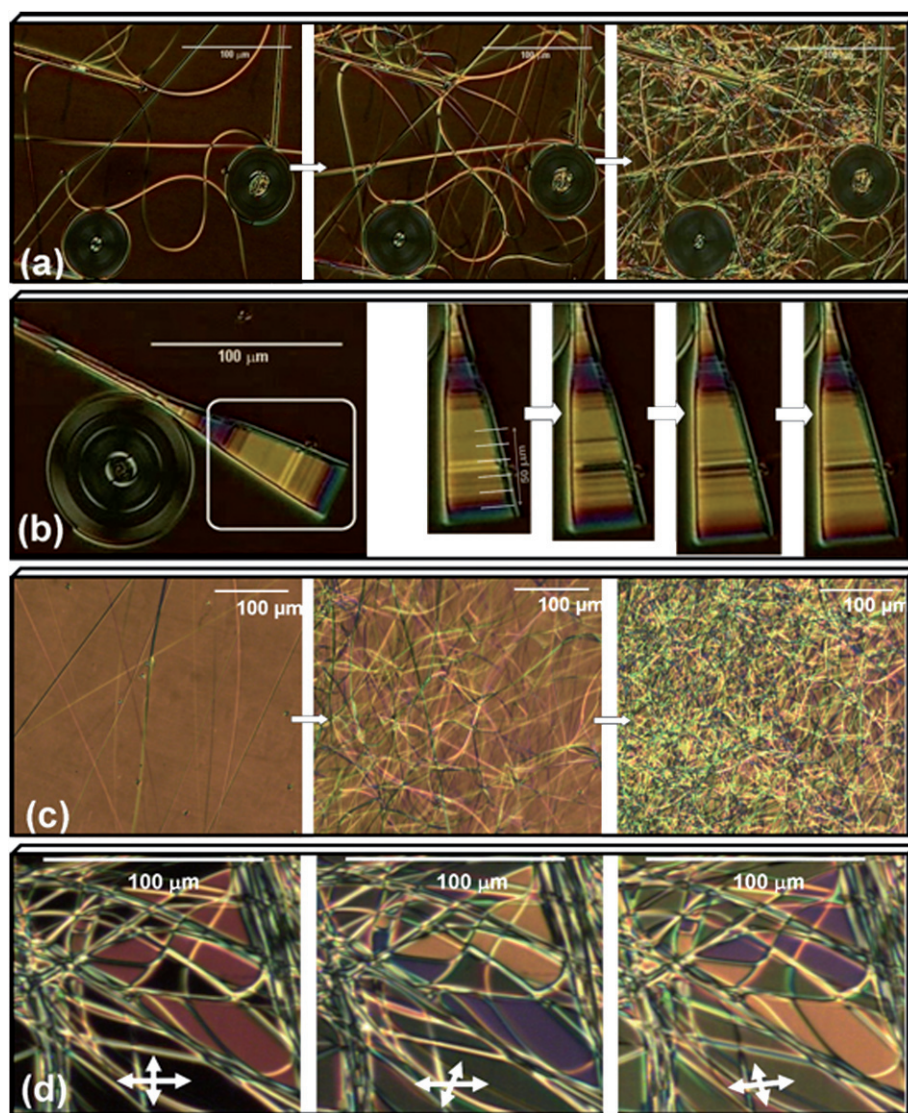


Fig. 4 (a) Left to right: Filament growth and disc-like regions in **3**, tempered and cooled from 175 °C, crossed polars; (b) left to right: textural changes in a triangular area of **3**. (c) left to right: filament growth on cooling **3** from 178 °C, pictures at 169.9 °C, crossed polars; (d) filament texture of **1** at 177.5 °C, left: crossed polars, middle: 20° clockwise rotation of analyser, right: 20° anticlockwise rotation of analyser. All in 5 μm planar alignment cells ($\times 100$).

crossed polars, as shown for compound **1** in Fig. 4(d). They were observed in a variety of areas between and below the filaments, but not across the whole of the sample preparation. The appearance of this texture indicates that it propagates from the surface. Under crossed polars, the colour of these regions was of the same pinkish-red everywhere across the preparation, and did not change upon rotation of the sample-stage. However, a 20° clockwise rotation of the analyser revealed purple colour dispersion in some domains, whereas the colour changed to yellowish-orange in others. Upon a reverse 20° anticlockwise rotation of the analyser the respective domains behaved in exactly the opposite way. This suggests that the areas are chiral helical domains. Areas of the same handedness as well as of opposite handedness exist as either identical or complementary colour changes are observed on equivalent angles of rotation.

The varying behaviour of compounds **1–6** at the transition from the nematic phase to higher order was also documented in DSC measurements. For example, compound **3** was subjected to six consecutive cycles at 0.5 °C min⁻¹, in each of which the sample was not heated above the clearing point, see Fig. 5. Instead the cycling was reversed in the nematic phase at 190 °C (Fig 5b, traces I and VI) or at the defining temperature (established by POM and DSC) of 178 °C (Fig 5b, traces II–V).

In curve I, heated to 190 °C, the same phase behaviour was observed as in a standard cycle at 10 °C min⁻¹, conducted through the whole phase sequence (Fig 5a). The much lower cooling rate of 0.5 °C min⁻¹ used in curve I results in the observation of the transitions N–X and X–solid at higher temperature. Interestingly, heating less into the N phase also has the general effect that the X–solid transition peak on cooling moves up in temperature and comes close to the monotropic

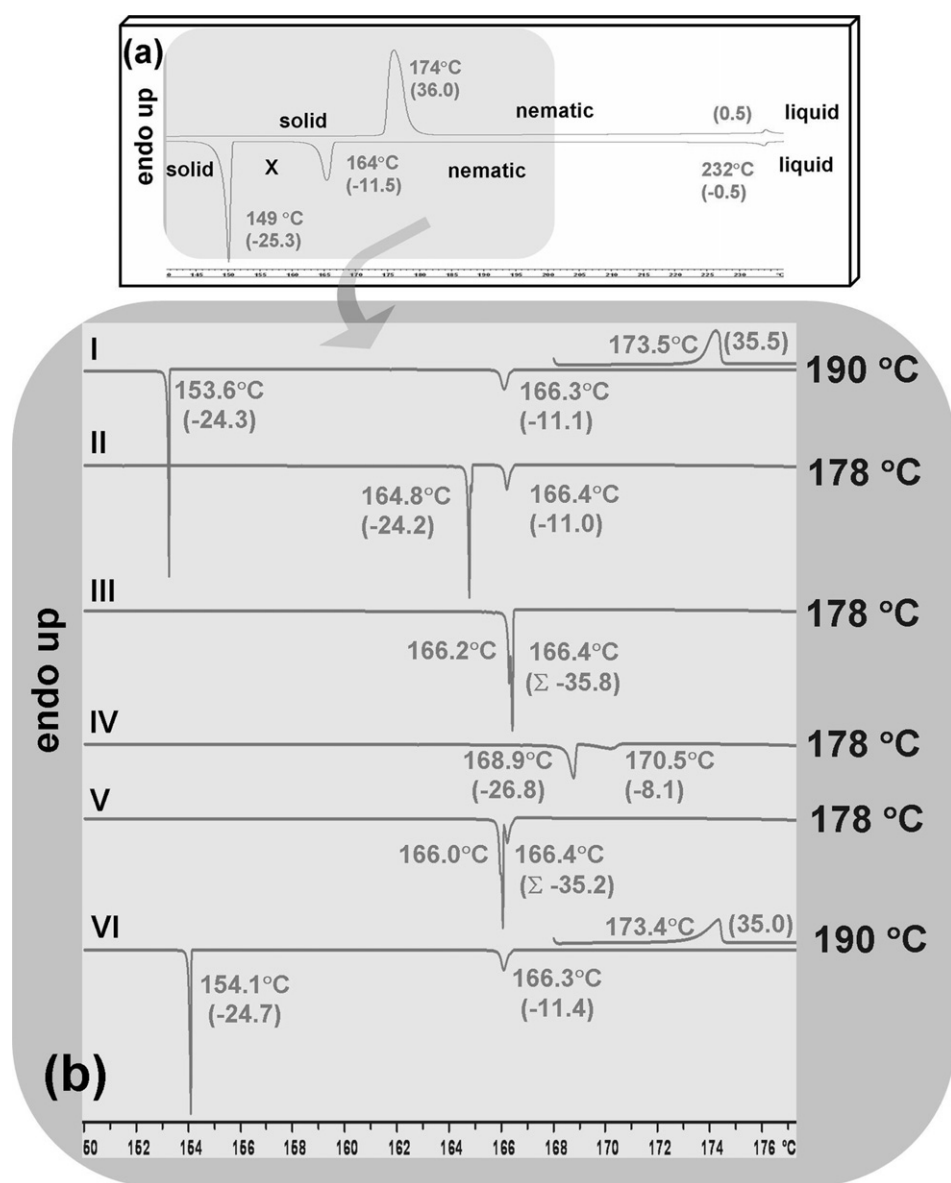


Fig. 5 DSC of compound **3**, (a) full cycle at 10 °C min⁻¹, (b) consecutive cycles at 0.5 °C min⁻¹ down from indicated temperature to 140 °C, transition labelled with T(onset) and in brackets ΔH in kJ mol⁻¹.

N–X transition. This can be observed in curves II, III, and V, for which heating was reversed at 178 °C. The shift is more pronounced than the shift due to a change in cooling rate.

Furthermore, although in curves II–V heating in each case is reversed at 178 °C, reproducibility of the transitions is clearly lost. The original behaviour can however be re-established by cycling to above the defining temperature, as is documented in curve VI (to 190 °C). Yet, heating less into the nematic phase has, within the errors of the experiment, has no effect on the temperature at which the N–X transition is observed on cooling. If it is observed (as indicated by the same ΔH value for the first transition on cooling in curves I, II, and VI), it occurs at 166.4 °C, or 166.3 °C respectively, as can be seen in Fig 5b in curves I–III, V, and VI. In curve III the N–X and X–solid transition appear to occur almost simultaneously together. However, in curve IV both transition peaks on cooling are observed well above the expected N–X transition. They also differ in shape and ΔH values from the transitions in any of the other cooling cycles.

This is in accordance with our POM studies. If filaments occur at the transition from the nematic phase, they are observed at temperatures above the expected N–X transition and usually no N–X transition is observed. For example, the photomicrographs in Fig. 4 (c) show the filamentary growth of compound **3** at 169.9 °C, which is 3.5 °C above the N–X transition and in good agreement with the first transition on cooling observed for this compound in curve IV of our DSC cycling experiment. Hence, it is unlikely that the filaments are a symptom of a simultaneous appearance of the X and the solid phase. Instead, the filamentary texture seems to be the manifestation of a kinetically governed alteration of the phase sequence, and the N–X transition is replaced by the transition to a filamentary texture. This is documented in curve IV of Fig. 5b where the transition to the solid state at 168.9 °C clearly is preceded by a broad transition with maximum at 170.5 °C. In this context it is worthwhile noting again that in our POM studies the filaments appeared very liquid-like and their growth could be stopped and reversed.

The phase behaviour was further probed by analysing the small angle X-ray diffraction of compound **1** in 15 μm cells under planar alignment conditions. Photomicrographs were taken with direct reference to the X-ray diffraction studies, as shown in Fig. 6(a)–(f). In diffraction studies of the filament texture, typical scattering patterns for smectic liquid-crystalline materials with some degree of long range orientational ordering were observed, as shown in the diffraction pictures 6(b) and (d). A layered structure with a spacing of approximately 32 Å was determined. The calculated molecular length for compound **1**, obtained from molecular modelling was approximately 35 Å (see Fig. 1), hence the structure is composed of molecular layers, as opposed to bilayers and in terms of the layer spacing the phase is probably orthogonal with the major axes of the molecules on average normal to the layer planes. It should be noted, that the calculated molecular length is to some extent arbitrary as it depends on the degree the molecules are bent in the minimisation process.

Our X-ray diffraction study of compound **1** also showed that the X phase for this material has a layered structure with a layer spacing of approximately 27 Å, see Fig. 6(e) and (f), and hence clearly is different to the structure associated with the filament texture. The small angle scattering image obtained in the X-ray

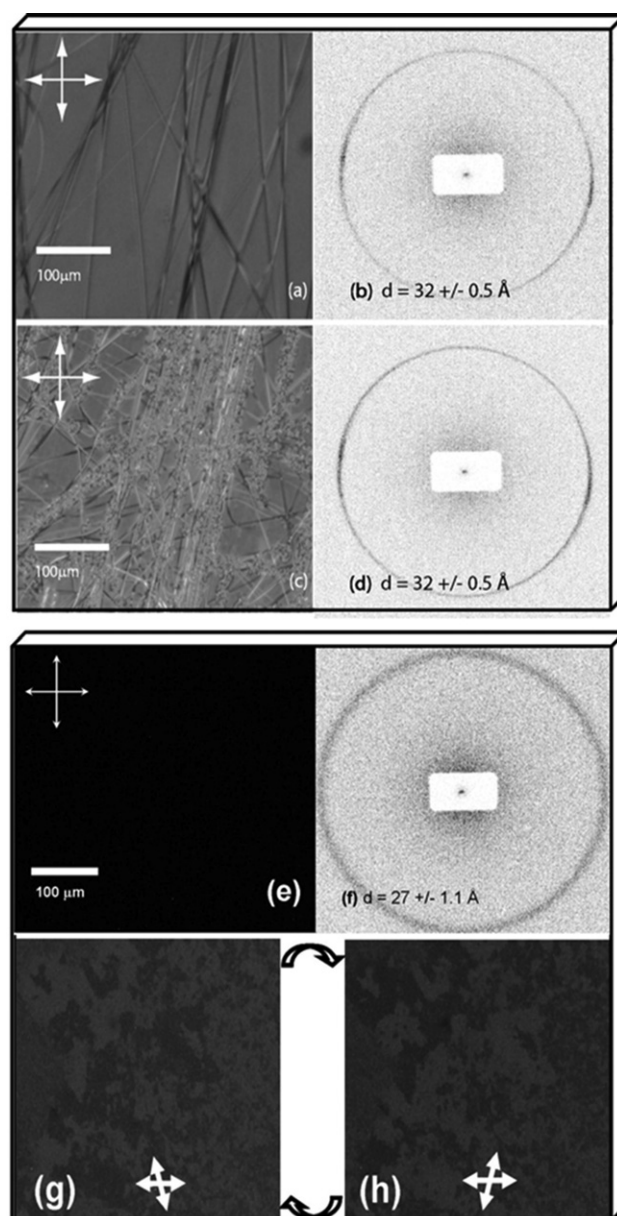


Fig. 6 Textures and X-ray diffraction for **1**; (a) beginning filament growth with (b) X-ray diffraction and layer spacing, preferred scattering perpendicular to the average direction of the main filament axes; (c) developed filament growth with (d) X-ray diffraction and layer spacing; (e) dark texture of the X phase of **1** with (f) X-ray diffraction and layer spacing, crossed polars ($\times 100$); (g) X phase at 170 °C, 20° anticlockwise, (h) 20° clockwise rotation of analyser ($\times 100$).

studies is rather diffuse and completely isotropic and in POM studies the phase appeared completely dark under crossed polars. However, a successive small uncrossing of the polars in opposite directions revealed domains of complementary brightness change in certain areas, see Fig. 6(g) and (h), especially when the texture was allowed to grow slowly from the preceding nematic. This indicates the optical activity of these domains, where the complementary domains are of opposite handedness. There are several reports in the literature describing optically dark isotropic phases with macroscopically chiral domains in other bent-core compounds, which exhibit similar X-ray diffraction patterns.^{3,9}

Discussion

We have presented results that demonstrate the unusual properties of the nematic phase of the bent-core ODBP materials studied. Our investigations show that the nematic phase can segregate into chiral domains of opposite handedness even though the constituent molecules are achiral. We proposed that the helical twist domain formation observed may be driven by a self-assembly that creates helical molecular clusters.⁷ For the ODBP molecules chiral molecular conformations exist in the bond rotational profile but, at the relevant temperatures, are expected to rapidly interchange in a dynamic equilibrium. However, due to the strong transverse dipole in the ODBP molecules, unusually strong intermolecular associations may exist that enable chiral recognition among the molecules. In this process the ODBP molecules would self-template to give the most stable matched helical self-assembled structure, i.e. chiral conformers of one hand pack together to give a matched-handed helical macrostructure, which in turn stabilises the chiral molecular conformation. Helical structures of one sense may then assemble into spiraling ribbons, and because of the sizes of the ribbons, fluctuating up and down domains are formed by segregation. The speculation satisfies the criterion that the process is kinetically driven and that the energy barrier to conformational flipping is raised through the self-assembly. However, helix formation can be suppressed by external forces such as surface interactions. The length scales of the self-assembled structures are such that diffusion is slow enough to allow the stabilisation of domains with an excess of one chirality sense. Similar spontaneous segregation of enantiomeric conformers into domains have already been reported as a possible cause for the display of macroscopically chiral domains in layered but fluid bent-core 'dark conglomerate phases'. It is assumed however, that only the confinement within layers allows for those close and directed intermolecular interactions needed for chiral recognition to occur.³

Recently, we were able to confirm the existence of a thermotropic biaxial nematic phase in C5-Ph-ODBP-Ph-OC12 by Raman and small angle X-ray scattering.¹⁰ The material exhibits a uniaxial to biaxial nematic phase transition and the biaxial order parameters, which are zero in the uniaxial phase, increase continuously with decreasing temperature within the biaxial nematic phase. The very same compound is also a member of the *bis*-(phenyl)oxadiazole family of materials which we already reported to show chiral domains of opposite handedness in the nematic phase.⁷ As noted, the earlier report on ODBP-Ph-C7 (compound **1**) shows the material exhibits a thermotropic biaxial phase.^{4,6} It was suggested by the authors that intermolecular associations originating from the large transverse dipole reinforce the transverse orientational correlations driven by shape packing of the molecules,⁴ and may be indispensable for the exhibition of the biaxial nematic phase by this compound.

This view is supported by the results of an atomistic simulation, where the nematic phase of compound **1** was also shown to be biaxial.¹¹ A formation of ferroelectric domains in the nematic phase was found, with a parallel association of the transverse oxadiazole dipoles, i.e. the domains are essentially composed of supramolecular clusters. The simulation also showed a destabilisation of the ferroelectric domains and the phase biaxiality on

removal of the electrostatic interactions. The thermal event we observe in the isotropic phase of the ODBP materials (Fig 3) indicates that the liquid is structured at temperatures just above the formation of the nematic state. This suggests that the formation of the nematic phase is accompanied and preceded by a process of molecular self-assembly that creates supramolecular clusters before self-organisation into the mesophase occurs.

For ODBP-Ph-C7 (compound **1**),¹² and a bent-core nematic twin-mesogen,¹³ an electric field induced uniaxial–biaxial nematic transition has been found, with the persistence of a metastable biaxial state for the latter after removal of the field. It has been argued that, as the electric field strengths used are clearly too low to address individual molecules, the emergence of macroscopic biaxial nematic ordering in ODBP-Ph-C7 (compound **1**) and other bent-core nematic materials can only be explained by the spontaneous or field induced collective alignment of inherent, randomly ordered, biaxial clusters.¹⁴

Hence, it appears that unusually strong transverse intermolecular associations leading to supramolecular clusters are indeed necessary to restrict rotation around the molecular long axis to a degree that allows for correlations between the short axes of the molecules on a length scale where the biaxial molecular shape is transferred to macroscopic bulk phase biaxiality.

It has been proposed that bent-shaped molecules naturally induce bend deformations in a nematic phase.¹⁵ However, a uniaxial nematic phase does not allow for the spontaneous formation of uniform states of bend (or splay), i.e. a uniaxial nematic phase cannot be spontaneously polar.¹⁶ Dozov suggested that an escape from macroscopic spontaneous polarisation in the nematic phase of bent-shaped molecules then only can be achieved *via* a symmetry breaking of the uniaxial phase in two possible ways.¹⁵ Consequently, he predicted the occurrence of two lower symmetry ground state nematic phases with local spontaneous polar properties in bent-core materials; one a biaxial nematic phase with oscillating splay-bend deformations, the other a nematic phase with two fold degenerate chiral helical superstructure, i.e. conical twist-bend deformations, as shown in Fig. 7.

We note that the observation of chiral domains of opposite handedness has been reported for the nematic phase of other achiral bent-core molecules.^{3,9,17} However, to our knowledge the coinciding in one system of biaxiality and chiral domains of

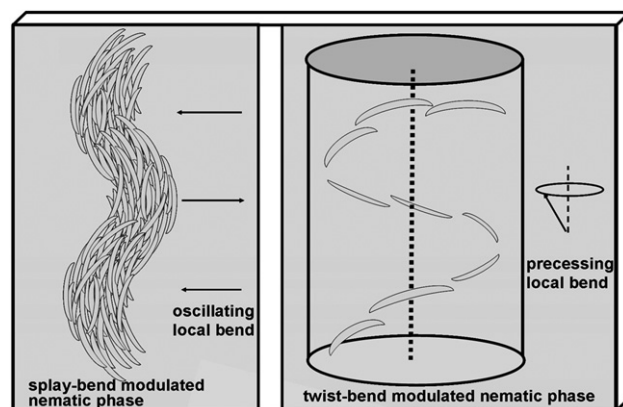


Fig. 7 Spontaneously modulated nematic phases of bent-core molecules, redrawn after Dozov.¹⁵

opposite handedness has not been reported before. The differences between the two bent-core nematic states may not be large in our systems. Hence, the spontaneous formation of domains of opposite handedness due to twist-bent deformations may be easily suppressed by external forces such as surface interactions. Indeed, we observed that the formation of chiral twist domains of opposite handedness in our materials is suppressed in planar alignment cells. Instead, a uniformly aligned homogeneous nematic phase is observed, which was shown to be biaxial in case of compound **1**^{4,6} and C5-Ph-ODBP-Ph-OC12.¹⁰ In planar cells, chiral helical domains were only observed as temporarily stable structures in conjunction with the observation of filaments, i.e. with the onset of breaking of the planar alignment (see Fig. 4d).

In compounds **1–6** we observed the N–X transition to be replaced by the transition to a filamentary texture under certain conditions. The strong dependency on the thermal history of the sample suggests that the formation of filaments is kinetically driven rather than thermodynamically, and is a manifestation of a kinetically governed alteration of the phase sequence in case a defining temperature in the nematic is not exceeded. Hence it appears that time- and temperature-dependent clustering occurs in the nematic phase and a large non-equilibrium cluster size may be important for the ability to form filaments at the onset of new order.

Spontaneously distorted liquid crystal phases can display frustrated states at the onset of new order.¹⁸ Originally, de Gennes predicted that a bend or twist deformation of a nematic liquid crystal can lead to intermediate frustrated states based on periodic defects.¹⁹ For example, the chiral nematic phase inherently forms a spontaneous state of twist. Frustration is caused at the transition by the desire to form layered structures and the competing need to maintain helicity due to molecular chirality, and is relieved in the formation of the twist grain boundary (TGB) phase.^{20,21}

The equivalent phase stabilised by a lattice of edge dislocations in achiral materials would be caused by a competition between layer formation and the maintenance of bend at the transition from a nematic phase which has inherent polar properties. It was suggested that this ‘bend grain boundary’ phase could be induced by electric fields in the nematic phase of molecules with polar structure due to their proposed increased flexoelectric effects and that some bent-core molecules may even have a tendency to form a ‘BGB phase’ in the absence of electric fields due to spontaneous bending.²² Harden *et al.* measured a flexoelectric coefficient of $|e_3| \approx 62 \text{ nC m}^{-1}$ for the bent-core nematic material CIPbis10BB, which is more than three orders of magnitude larger than that of 5CB.²³ This result cannot be explained by a phase model based on individual molecules, and the authors propose an arrangement of molecules in polar clusters of a few tens of molecules as a satisfying explanation for the magnitude of $|e_3|$. Their results are corroborated by a dynamic light scattering study of the nematic phase and the isotropic to nematic transition of CIPbis10BB which also indicates local clustering or an association of the molecules within the nematic, and pretransitional organisation based on supramolecular clustering in the isotropic liquid.²⁴

The results presented suggest that the nematic phases of the ODBP materials studied could be considered as bent-core nematic phases with inherent polar properties. It seems thus

reasonable that at the onset of new order a frustration from the competing needs for layer ordering and the preservation of bend could arise, especially in a kinetically controlled environment, where the inherent polar properties would be increased considerably due to a non-equilibrium size of polar supramolecular clusters. Hence one could speculate a dislocation lattice based on edge dislocations to be the base of the internal filament structure, with molecular layers radiating from the centre, and with the molecular long axes orthogonal to the central line defect. The textural observation of regions with parallel lines spaced 6–7 μm could indicate a large scale superstructure or lattice due to the dislocations forming grain boundaries.

Conclusions

In our investigations of a family of achiral bent-core *bis*-(phenyl)oxadiazole derivatives we observed some unusual properties of the nematic phase. These include evidence for the formation of clusters and segregation into domains of opposite handedness, nematic phase biaxiality, and a strongly kinetically governed phase behaviour, which leads to the display of unique filament structures at the onset of new order. Overall the results presented indicate strongly competing influences with respect to the phase behaviour of the *bis*-(phenyl)oxadiazole materials studied, and are a testimony to the existence of a delicate balance of molecular properties. We suggest that the combination of a deviant calamitic shape and a considerable transverse dipole leads to unusually strong intermolecular interactions in these systems. Thus templating and the formation of fluctuating domains or clusters occur because of restricted motions and hence the phase behaviour is strongly kinetically governed. It is implied that the length and time scales we normally use to describe liquid crystals are not necessarily valid as the unusual strength and combination of molecular interactions lead to a breaking of apparent homogeneity on an observable level. It thus seems that we need to consider these bent-core liquid crystalline systems as fluctuating and dynamically changing, multi-hierarchical fluids.

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