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Progression from nano to macro science in soft matter systems: dimers to trimers and oligomers in twist-bend liquid crystals†

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In this article we report on the characterization and properties of several unsymmetrical phenyl-benzoate bimesogens that exhibit the soft-matter, twist-bend nematic (N_{TB}) phase. We use this study as a basis to examine the phase behaviour of associated novel trimeric and tetrameric materials, in order to investigate the potential for oligomeric materials to form the N_{TB} phase. Based on our results we hypothesise that higher oligomers and even polymers are highly likely to exhibit the N_{TB} phase, provided they retain a gross bent structure between consecutive mesogenic units. Thus we show at the level of nanoscale organization, dimers can template with respect to one another to form mesophases that are also found in macromolecular systems.

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Introduction

The discovery of a new phase of matter lacking lamellar ordering of the molecules while at the same time exhibiting properties associated with such ordering, has motivated a great deal of study into liquid crystal bimesogens and their behaviour.[1–19] The presently favoured model for this mesophase is that of the 'heliconical twist-bend nematic' phase, predicted independently by Meyer and Dozov,[1,2] in which there exists a helix with extremely tight pitch with the nematic director inclined from the heli-axis by an acute angle.[2,9–11] This model is experimentally supported by both freeze-fracture TEM studies and carbon *K*-edge SAXS on CB7CB, which allow direct measurement of the nanoscale helix.[10,19] The orientational order parameters of the N_{TB} phase, determined by polarised Raman spectroscopy as well as ^{2}H and ^{129}Xe NMR,[15,16] appear to be consistent with the heliconical model of Dosov and Meyer. It should, however, be noted that studies on surface freezing[20] and ^{2}H NMR have resulted in alternative models.[21–23]

A growing number of materials exist that are known to exhibit the N_{TB} phase,[24–29] the bulk of which are symmetrical bimesogens possessing a methylene spacer of odd parity. One notable exception is etheric bimesogens,[30,31] which can be designed to be unsymmetrical in structure by exploiting bifunctional spacer groups, such as bromoalcohols, during chemical synthesis.[31] Many of the materials known to exhibit the N_{TB} phase contain polar functional groups, most often nitriles as in the CBnCB series of materials. Polar functional groups can, through dipole–dipole interactions, lead to anti-parallel pairing of molecules,[32–34] with the extent to which this occurs being functional group dependent. This article covers two closely related topics. Firstly we describe how, by moving from symmetrical bimesogens to unsymmetrical, the possibility of stabilising/destabilising the N_{TB} phase in methylene linked bimesogens is possible by manipulating the strength of intermolecular interactions, as shown by the target materials in Scheme 1.

Secondly, given that the chemical space surrounding mesogenic dimers that exhibit the twist-bend phase has been somewhat explored, we considered targeting the two oligomeric materials shown in Scheme 2 in the context of the formation and stability of the N_{TB} phase.

Experimental

Full experimental details for the synthesis and characterization of products **1** to **9** are provided in the ESI.† Compounds **3–7** were synthesised, as shown in Scheme 1, *via* the EDAC/DMAP mediated Steglich esterification between compound **1** (4-(9-(4-hydroxyphenyl)nonyl)phenyl 4-cyanobenzoate), prepared as described previously,[29] and an appropriate benzoic acid.

Fortuitously the chemical intermediate required to prepare unsymmetrical methylene linked phenylbenzoate dimers was also be used as a platform chemical in the synthesis of oligomeric materials, as shown in Scheme 2.[29] Compound **8** was prepared *via* the EDAC/DMAP mediated Steglich esterification between compound **1** and 1,4-terephthalic acid (Scheme 2). Compound **9** was prepared *via* the EDAC/DMAP mediated Steglich esterification of compound **1** and 4,4′-(nonane-1,9-diyl) dibenzoic acid.[26,29]

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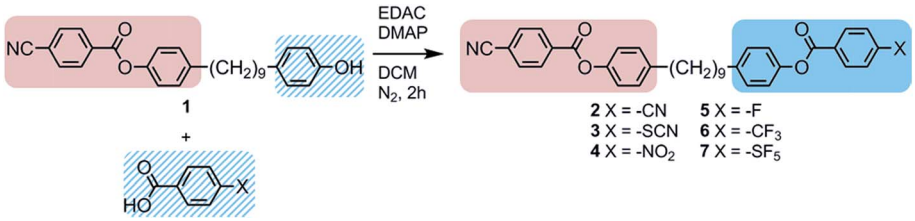
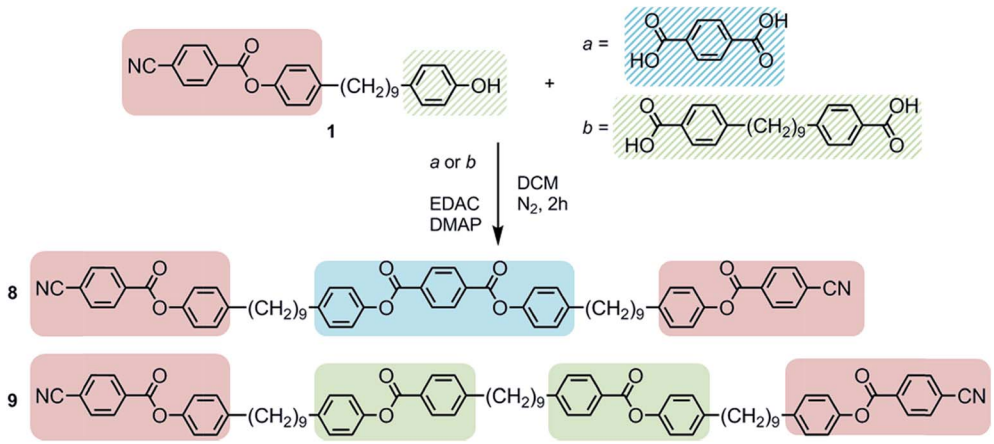
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c6ra03594a



Scheme 1 Target dimeric materials.



Scheme 2 Target oligomeric materials.

Small angle X-ray scattering was performed on a Bruker D8 Discover equipped with a temperature controlled, bored graphite rod furnace, custom built at the University of York. Computational chemistry was performed at the B3LYP/6-31G(d) level of DFT in Gaussian G09,[35] with Gaussian output files rendered using Qutemol.[36] Full experimental details, including chemical characterisation and descriptions of instrumentation used, are available in the ESI.†

Results and discussion

The liquid crystalline properties of the **1** and **2** were studied by a combination of polarised optical microscopy (POM) and differential scanning calorimetry (DSC), the results for which are presented in Table 1.

Although compound **1** can be described unequivocally as a dimer (or bimesogen), **2** is harder to define in such absolute terms due to its ability to form intermolecular hydrogen bonds between the phenol and nitrile groups leading to possible supramolecular oligomeric structures.[28,37] Whereas **2** has been demonstrated to exhibit nematic and twist-bend nematic phases,[26] **1** was found to exhibit a first order nematic to smectic C phase transition. Phase assignments were made initially by polarised optical microscopy (POM) and then by small angle X-ray scattering (SAXS) see Fig. 3, whereas the associated enthalpies and entropies of transitions were determined by differential scanning calorimetry (DSC) as shown in Table 1.

The defect texture observed for the nematic phase of **1** showed a classical *schlieren* texture composed of singularities possessing 2- and 4-brushes, whereas the smectic C phase exhibited a focal-conic texture that was unbroken, which at first sight could appear as a texture associated with the smectic A phase (Fig. 1a and b). However, X-ray diffraction clearly shows that the smectic phase is tilted (Fig. 1d), and with the combination of the POM studies the phase was unequivocally classified as smectic C. The tilt angle determined from X-ray diffraction was found to reach a maximum of 13°, although as the sample readily crystallises shortly after cooling into the smectic C phase this value is not saturated.

If we turn now to the properties of the dimers, we can compare those of unsymmetrical structure with the parent symmetrical bimesogen **2**, which was found to possess a melting point of 157.6 °C, and monotropic phase transitions from the liquid to the nematic phase at 146.6 °C, and from the nematic to the N_{TB} phase at 114.5 °C. In calamitic systems is well known that nitrile terminated materials have a strong tendency to exist as antiparallel correlated pairs or *n*-mers.[32,33] Contrast this with isothiocyanates, which do not exhibit as large a degree of antiparallel correlation as nitriles,[38] and with nitro terminated materials, which have a stronger tendency than nitriles to form antiparallel correlated pairs.[34] As noted in the introduction, moving from symmetrical bimesogens to unsymmetrical variants such as compounds **2–6** (Table 2) allows the possibility of engineering molecules and thus exerting a degree of control over the condensed phases they exhibit by controlling the strength and type of intermolecular interactions.

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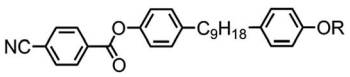
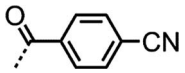
Table 1 Transition temperatures (°), associated enthalpies of transition [kJ mol^{-1}] and dimensionless entropies of transition {$\Delta S/R$} for compounds **1** and **2**.[26,29] Transitions in parenthesis () are monotropic



No.	R	Cr		SmC		N_{TB}		N		Iso
1	···H	●	109.5 [47.19] {14.85}	(●	61.6 [3.21] {1.15}	—	—	●	71.9) [1.32] {0.46}	●
2		●	157.6 [45.41] {12.68}	—	—	(●	114.5 [0.65] {0.20}	●	146.6) [1.50] {0.43}	●

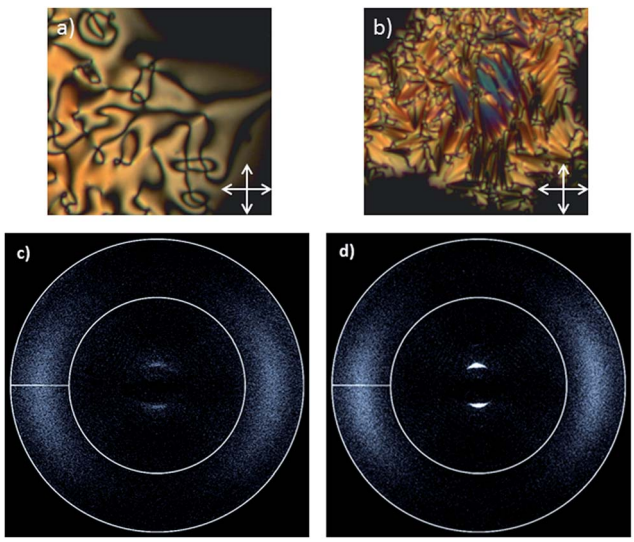
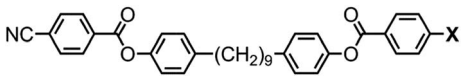


Fig. 1 The *schlieren* texture of the nematic phase of **1** shown by POM (×100, area approximately 100 μm) ((a), 65 °C) and the focal-conic texture of the smectic C phase of **1** ((b), 55 °C) showing numerous focal-conic defects. Small angle X-ray scattering pattern for the nematic phase of **1** ((c), 63 °C) and the smectic C phase ((d), 57 °C).

Table 2 Transition temperatures (°C) and scaled N_{TB}–N transition temperatures ($T_{N_{TB}-N}/T_{N-I}$) for compounds **2**–**7**. Transitions in parenthesis () are monotropic, *i.e.* they occur below the melting point of the material



No.	X=	Cr		N_{TB}		N		Iso
2	–CN	●	157.6	(●	114.5	●	146.6)	●
3	–SCN	●	95.6	●	100.0	●	123.8	●
4	$-NO_2$	●	115.4	(●	100.5)	●	124.9	●
5	–F	●	86.2	(●	78.2)	●	95.9	●
6	$-CF_3$	●	110.0	(●	69.6	●	78.3)	●
7	$-SF_5$	●	102.2	(●	61.1	●	72.8)	●

Compounds **2**–**7** were studied by a combination of POM and DSC and as with the symmetrical parent compound **2** all were found to exhibit nematic and twist-bend nematic mesophases. Representative photomicrographs of both the nematic and N_{TB} phases are given in Fig. 2 for compounds **2** and **4**. In both cases the nematic phase exhibits a classical nematic *schlieren* texture, whereas the texture of the N_{TB} phase in both cases shows long-range correlations, described as blocks, indicating that the phase is substantially more ordered than the nematic phase that it was derived from paramorphotically.

For compounds **3** and **4** both the nematic to isotropic and nematic to N_{TB} transition temperatures are close to being an average of those of the two symmetric parent materials that we reported previously, whereas for the unsymmetrical compounds **5** to **7** only one of the symmetrical parent materials (*i.e.*, compound **2**) was mesogenic.[26]

The associated enthalpies and entropies of transition for the N_{TB}–N and N–Iso transitions for compounds **3**–**7** were

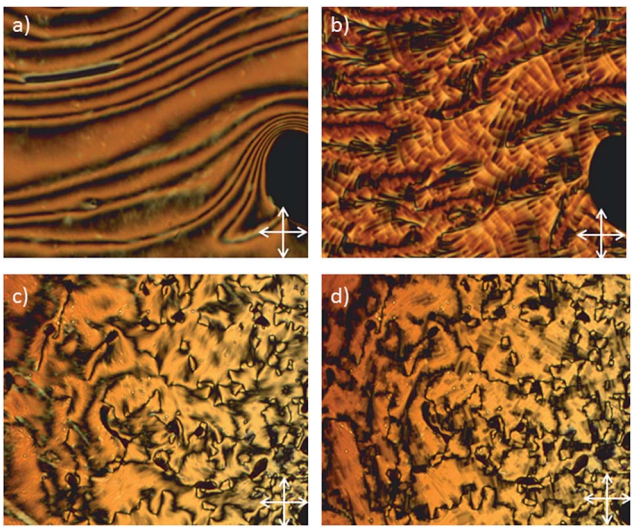


Fig. 2 Photomicrographs (×100, area approximately 100 μm) of the *schlieren* texture of the nematic phase of compound **4** at 122° (a), the block-texture of the N_{TB} phase of compound **4** at 95 °C (b), the *schlieren* texture of the nematic phase of compound **2** at 105 °C (c) and the block-texture of the N_{TB} phase of compound **2** at 95 °C (d). Both pairs of photomicrographs (a and b, c and d) present approximately the same region of the sample.

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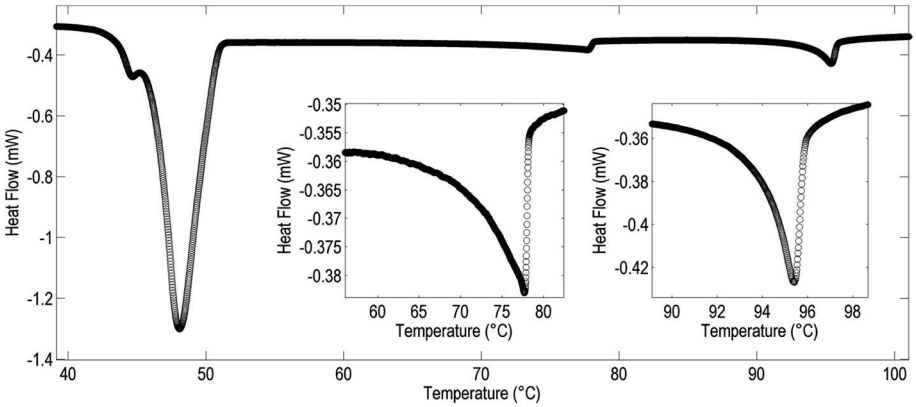
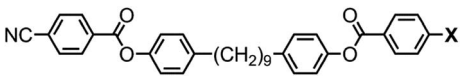


Fig. 3 DSC thermogram (1st cool, 10 °C min^{-1}) of compound **5** with expansions showing the isotropic to nematic (right) and nematic to N_{TB} phase transitions (left).

determined by DSC at a heat/cool rate of 10 °C min^{-1} (see Table 4). Although the nematic to isotropic transition was found to be invariably first order the nematic to N_{TB} phase transition was only weakly first order, as reported previously.[13] The DSC thermogram of **5** on cooling is presented in Fig. 3; thermograms for other compounds are similar and are presented in the ESI.†

Curiously for compounds **5** to **7**, which bear fluorine or fluorine containing terminal groups, the associated enthalpy (and thus associated entropy) of the N_{TB} to nematic transition is higher than that of the nematic to isotropic (Table 3). This is at odds with all of the other dimeric twist-bend materials that we are aware of, although similar behaviour has been reported in an oligomeric system.[29] Conversely, compounds **2** to **4** display classical behaviour, with the associated enthalpy/entropy of the N_{TB}–N transition being smaller than that of the N–I transition. The scaled transition temperature, $T_{N_{TB}-N}/T_{N-I}$, for compounds **2** to **7** were shown to be not particularly diagnostic, with each material having values of similar magnitude.

Table 3 Associated enthalpies of transition (ΔH, kJ mol^{-1}) and dimensionless entropies of transition ($\Delta S/R$) for compounds **2–7**

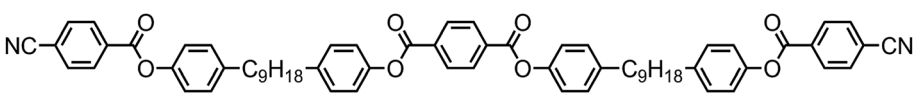


No.	X	$\Delta H_{N_{TB}-N}$	ΔH_{N-Iso}	$\Delta S_{N_{TB}-N}$	ΔS_{N-Iso}	$T_{N_{TB}-N}/T_{N-I}$
2	–CN	0.65	1.50	0.20	0.43	0.923
3	–SCN	0.18	0.80	0.06	0.24	0.940
4	–NO_2	0.09	1.10	0.03	0.33	0.939
5	–F	0.45	0.22	0.15	0.22	0.952
6	–CF_3	0.89	0.42	0.31	0.15	0.975
7	–SF_5	0.50	0.40	0.18	0.14	0.966

With a great deal of chemical space concerning dimers and bimesogens now explored in the context of the N_{TB}/N_X phase[25–27,30,31] it is perhaps inevitable that future synthetic work will shift beyond simple mesogenic dimers. Trimers are the logical progression from dimers, and it is already known that these systems can exhibit the N_{TB}/N_X phase; Jansze *et al.* described a novel hydrogen bonded trimer,[28,39,40] whereas Wang *et al.* reported a trimer composed of two cyanobiphenyl units appended to an oxadiazole bent core.[41] In this study trimer **8** was formed by the esterification of **1** and terephthalic acid, and is the first covalently bonded, linear trimer to exhibit the N_{TB} phase. The transition temperatures, associated enthalpies and entropies of compound **8** of transition are given in Table 4.

On cooling compound **8** from the isotropic liquid a clean schlieren texture could be observed by POM (Fig. 4a). Further cooling into the N_{TB} phase yielded a transition to the classical blocky texture (Fig. 4b and c). The degree of supercooling was rather short, with the material recrystallizing in the region of 130–135 °C. In both phases the material was highly viscous and a large amount of manual force was required to shear the

Table 4 Transition temperatures (°C), associated enthalpies of transition (kJ mol^{-1}) and dimensionless entropies of transition for compound **8**



	Cr–N_{TB}	N_{TB}–N	N–Iso
T (°C)	146.5	164.2	210.3
ΔH (kJ mol^{-1})	41.58	0.29	2.56
$\Delta S/R$	11.92	0.08	0.64

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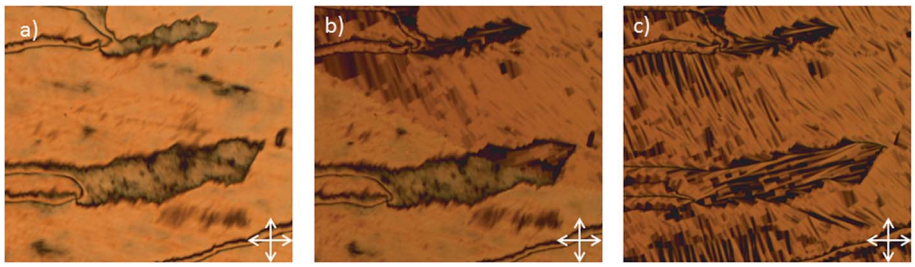
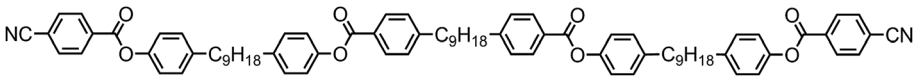


Fig. 4 Photomicrographs (×100, area approximately 100 μm) of the *schlieren* texture of the nematic phase of compound **7** at 179 °C (a), the nematic to N_{TB} transition at 164 °C (b) and the blocky-texture of the N_{TB} phase of compound **8** at 160 °C. (c) All photomicrographs present approximately the same region of the sample.

Table 5 Transition temperatures (°C), associated enthalpies of transition (kJ mol^{-1}) and dimensionless associated entropies of transition of compound **9** (ref. 29)



	Cr–N_{TB}	N_{TB}–N	N–Iso
T (°C)	113.6	127.7	141.5
ΔH (kJ mol^{-1})	51.02	3.36	3.06
$\Delta S/R$	15.87	1.01	0.89

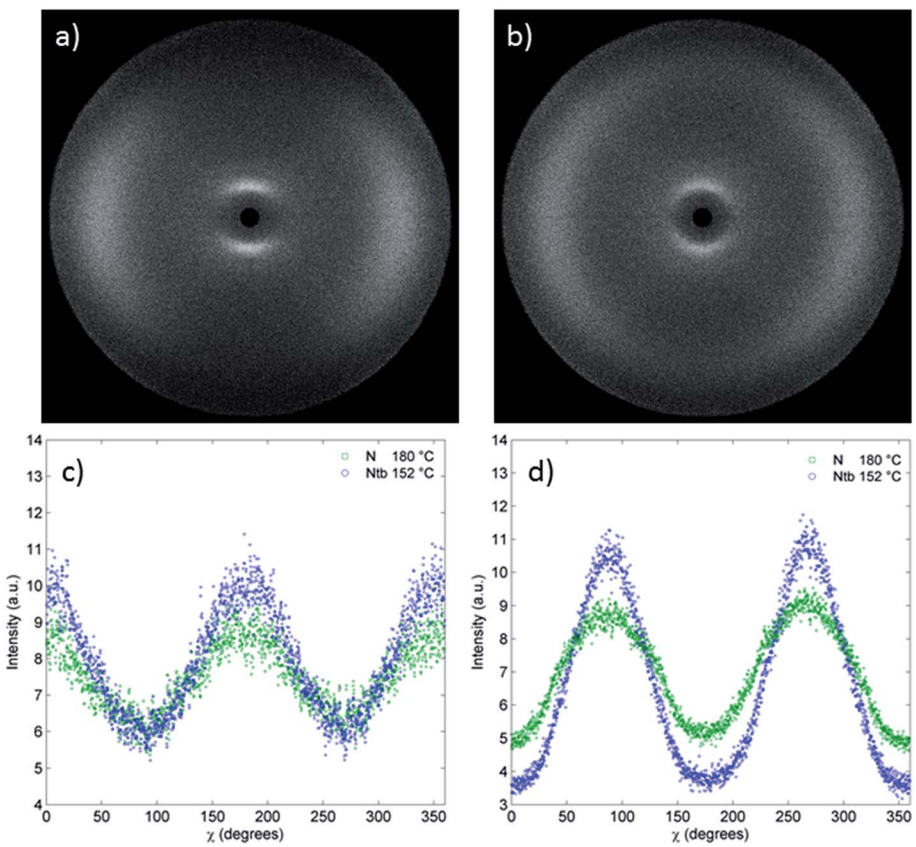


Fig. 5 Two dimensional small angle X-ray scattering (SAXS) patterns for compound **8** in the nematic phase ((a), 180 °C) and the N_{TB} phase ((b), 152 °C) along with the distribution of the small angle χ scan ((c), $2\theta = 3$–15) and the wide angle χ scan ((d), $2\theta = 15$–25).

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sample. This qualitatively high viscosity is a consequence of the material being intercalated, as reported for other dimers.[13]

Extending the oligomeric form resulted in the preparation of compound **9**, which is the first tetramer to exhibit the twist-bend nematic phase; a full account of its behaviour has recently been given.[29] However, unlike oligomeric materials such as compound **9** (Table 5), for compound **8** the entropy and enthalpy associated with the twist-bend nematic to nematic phase transition was found to be around an order of magnitude lower than that for the nematic to isotropic liquid transition. Thus, the transitional behaviour of **8** appears to be closer to that of dimeric materials than that of the oligomer **9**.

The nematic and twist-bend nematic phases of compound **8** were studied by small angle X-ray scattering (Fig. 5) over a temperature range of 207–141 °C with data collected in 3 °C steps, the experimental setup for which is described in the ESI.† Two dimensional X-ray scattering patterns for compound **8** in the nematic phase at 180 °C and the N_{TB} phase at 152 °C are presented in Fig. 5a and b respectively.

In the small angle region (2θ = 3–15) a moderate reduction (<0.5 Å) was observed in the *d*-spacing at the nematic to N_{TB} phase transition. Tabulated values of *d*-spacings are given in the ESI.† This reduction in *d*-spacing is accompanied by a decrease in the scattered intensity at small angles relative to the nematic phase (Fig. 5c). Previously such a reduction in *d*-spacing has been reported to be a consequence of the molecules tilting away from the helix axis of the N_{TB} phase.[9] Although the nematic phase of **8** is well aligned by the magnetic field employed during SAXS studies the N_{TB} phase is only partly aligned, this results in the reduction in scattered intensities at $\chi = 90°$ and 270° and the increase in scattered intensities at $\chi = 0°$ and 180° (Fig. 5c and d).

The wide-angle peak corresponding to the average lateral molecular separation is more defined in the nematic phase than in the N_{TB} phase. On entering the N_{TB} phase there is a small reduction in the *d*-spacing (<0.2 Å) of this peak, however the definition is actually reduced relative to that in the nematic phase, as shown by the distribution of the wide angle scattering peak (2θ = 15–25) about χ in Fig. 5d.

Thus when studied by SAXS compound **8** behaves similarly to other bimesogenic materials that exhibit the N_{TB} phase. However the behaviour of **8** is in contrast to the oligomeric compound **9**, which lacks the discrete reduction in *d*-spacing associated with the small angle scattering peak at the N–N_{TB} transition, and instead exhibits a continuous increase with decreasing temperature.[29] Furthermore, for compound **9** there is almost no change in the intensity in the χ scan in either the small angle (2θ = 3–15) or wide angle (2θ = 15–25) regions of the scattering pattern (Fig. 6c and d) which is a consequence of both the nematic and N_{TB} phases being well aligned by the external magnetic field.

Molecular modelling was used to try to rationalise how the observed *d*-spacing of the small angle peak, 21 Å, relates to the

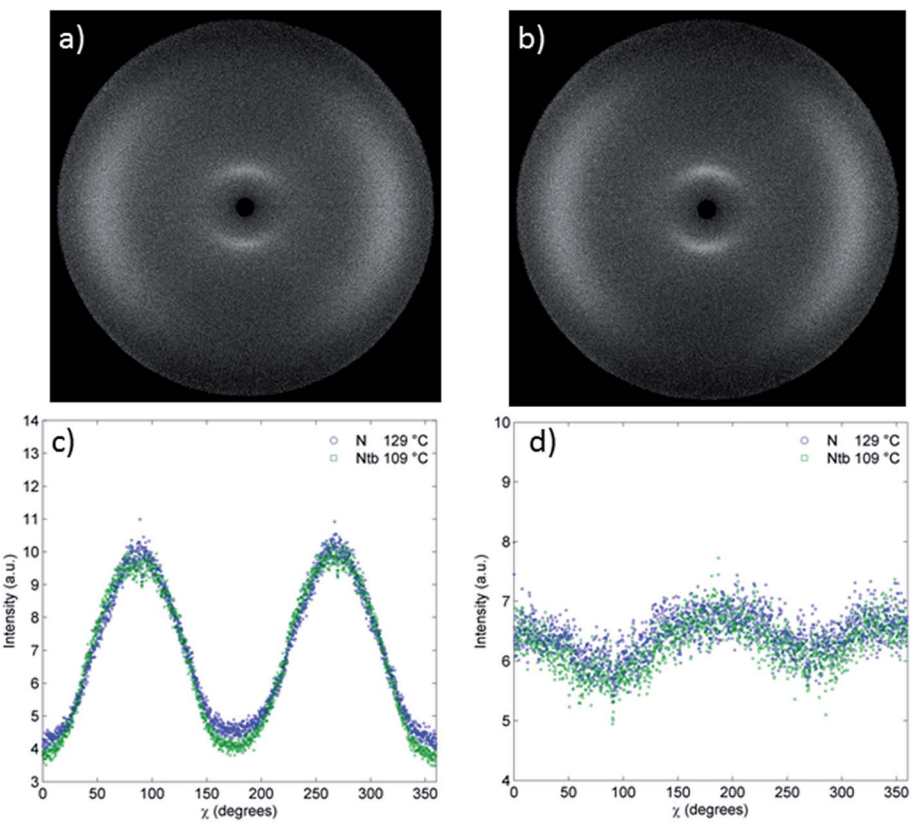

Fig. 6 Two dimensional small angle X-ray scattering patterns for compound **9** in the nematic phase ((a), 129 °C) and the N_{TB} phase ((b), 109 °C) along with the distribution of the wide angle χ scan ((c), 2θ = 15–25) and small angle χ scan ((d), 2θ = 3–15).

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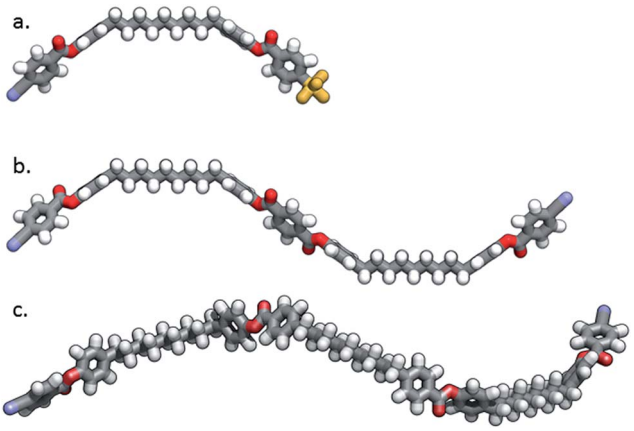

Fig. 7 The B3LYP/6-31G(d) minimised geometry of compound **7** (a), of compound **8** (b) and of compound **9** (c).

molecular length of **8** which was estimated to be significantly larger than this figure. The B3LYP/6-31G(d) minimised geometry of **8** is shown in Fig. 7. The end-to-end molecular length, as determined from the minimised geometry, of compound **8** is 58 Å, predictably larger than a simple dimer such as **7** (32 Å). The measured *d*-spacing for **8** corresponds to 0.37 times the full molecular length, indicating that, unsurprisingly, there is extensive intercalation of the molecules in both the nematic and N_{TB} phases. This manifests in the sample having a qualitatively high viscosity, which was evident during microscopy when attempting to mechanically shear the sample. Similarly, the *d*-spacing observed for the small angle peak in compound **9** is around $1/4^{th}$ of the molecular end-to-end length,[29] indicating that both the nematic and N_{TB} phases are also extensively intercalated. This is in analogy to behaviour observed in other tetrameric and trimeric materials.[42,43]

As shown in Fig. 7, the minimum energy geometry of **9** is helical due to the non-linearity of the phenylbenzoate mesogenic units. In contrast to this, the minimum energy geometry of **8** is linear due to the presence of a phenyl terephthalate mesogenic unit in the centre of the molecule. The linear shape of **8** is only preserved in the conformer where all methylene groups in both spacers are *trans*; any deviation from this breaks the plane of symmetry and results in left- and right-handed helical conformers that are degenerate.

Conclusions

For the unsymmetrical bimesogens, we have demonstrated that it is possible to incorporate functional groups that are normally detrimental to mesomorphic properties for dimers while retaining the twist-bend nematic phase. The pentafluorosulphanyl group ($-SF_5$) is highly polar, yet gives notoriously low clearing points due to its sheer bulk and polarity.[44,45] Yet the SF_5 group can be incorporated into an unsymmetrical bimesogen and retain the mesomorphic state. The thermal stability of the twist-bend nematic phase is highest when the polar group is conjugated to the core (–CN > $-NO_2 \gg$ –F). However, non-conjugated groups can also support the N_{TB} phase albeit with reduced thermal stability (–SCN $\gg$ $-CF_3$ > $-SF_5$). It is worth noting that in symmetrical systems all polar groups other than nitrile and isothiocyanates resulted in the materials being non-mesogenic (NO_2, F, CF_3, SF_5).[26]

The twist-bend nematic phase has been observed in both polar and non-polar symmetrical dimers.[25,26] It therefore seems probable that unsymmetrical bimesogens with one polar and one non-polar group will exhibit this phase. The ability to incorporate the bulky $-SF_5$ group whilst still retaining the twist-bend nematic phase has implications for the experimental study of the local structure of the N_{TB} phase as it raises the possibility of incorporating specific molecular features as probes to aid investigations of the local structure of the mesophase. Possible examples include materials that are unsymmetrically deuterated for ^2H NMR, reactive mesogens for polymer stabilised twist-bend nematics and incorporating fluorescent dyes for imaging.

Secondly, for the oligomeric twist-bend materials, it appears that the driving force behind the formation of the N_{TB} phase is molecular shape and the minimisation of free volume.[46,47] Based on this we hypothesise that higher oligomers and even polymers are highly likely to exhibit the N_{TB} phase, provided they retain a gross bent or twisted structure between consecutive mesogenic units. Indeed, there has been suggestion and much discussion that the twist-bend phase may have originally been observed in polymers long before its discovery in simple dimeric materials.[48] However, as with dimers and bimesogens, the specific angle between subsequent mesogenic units may dictate the incidence or absence of the twist-bend nematic phase in such materials and may explain its absence until recently in linear oligomers.[28,41]

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