**Designing Liquid-Crystalline Oligomers to Exhibit Twist-Bend Modulated Nematic Phases**

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**Abstract**

Arguably the most active area in liquid crystal research presently, the twist-bend modulated nematic phase (TB) exhibits a nanoscale helical structure and therefore exhibits bulk chirality despite being formed of typically achiral materials. After a short introduction we address the structure-property relationship that exists for this unique mesophase before introducing recent advances in strategies employed to prepare oligomeric materials that exhibit this state of matter. These methods afford fine control over the molecular substructure and potentially over the nanostructure of the exhibited mesophases.

**1.1 Introduction**

The term liquid crystal (LC) refers to a group of phases of matter with some degree of positional or orientational order. In addition to being widely exploited in display devices, LC phases are also formed by DNA,1-6 carbohydrates and lipids, 7-9 and peptides, 10-12 as well as suspensions of viral 13-16 and inorganic particles. 17-19 The nematic LC phase possesses an average orientational order of its constituent molecules along a vector termed the director lacks positional order (Figure 1a). The addition of a chiral additive to a nematic LC leads to a chiral nematic (cholesteric, N\*) phase in which the director rotates through space to give a periodic, helical structure (Figure 1b).

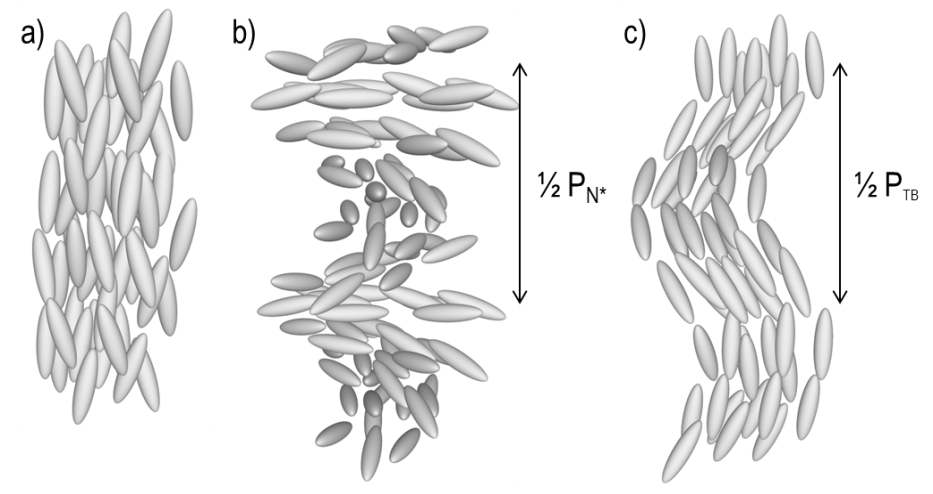


Figure 1: Cartoon depictions of the local structures and director arrangement in (a) the uniaxial nematic phase, (b) the chiral nematic (cholesteric, N\*) phase, and (c) the helicoidal twist-bend (TB)phase. Note that the pitch depicted in (c) is much smaller than that of (b); the former being ~10 nm while the latter can be over 1 μm and even into the millimetre to meter range.

The twist-bend modulated nematic phase (TB, Figure 1c) was predicted by Dozov and is a type of nematic phase with a modulated structure. 20 The TB phase possesses a short helical pitch and is therefore locally chiral, even when formed from achiral materials; this is therefore an example of spontaneous breaking of mirror symmetry in soft matter. The molecules are tilted away from the helix axis but lack positional ordering and thus the TB phase is ‘nematic’. 20 Similarly, other nematic-like mesophases have been predicted to occur (splay-bend nematic (N­SB), 21-22 and screw nematic (NS\*) 23-24 as well as polar ‘nematic’ phases with transverse (NTP­) and longitudinal (NLP) polarisation), 25 while other nematic or nematic-like phases whose structure is presently unknown have also recently been reported. 26-28 In the twist-bend modulated phase the helical pitch length (*PTB*) has been measured by freeze-fracture transmission electron microscopy, 29-31 by resonant small angle X-ray scattering at the carbon 32 33 and selenium K-edges. 34 All three methods give quantitative measurement of the pitch length, which is of the order of several nanometers. *In situ* 2H NMR spectroscopy conducted on samples doped with a suitable spin probe has also been interpreted as supporting the presence of a local helix with a nanoscale pitch (*i.e.* several molecular lengths), 35 although other models have been used to interpret these results. 36-37 Order parameters for the twist-bend modulated nematic phase have been determined by 2H NMR, 38 polarised Raman spectroscopy (PRS) 39 and wide-angle X-ray scattering (WAXS), 40 the values being of a similar magnitude to the nematic phase suggesting that the TB phase itself is structurally very similar to the nematic.

In terms of applications, the twist bend modulated nematic phase exhibits a fast electrooptic response. 41 Photopolymerisation of the TB phase 42 preserves the local nanohelical structure and potentially gives nanoscale materials which may find use in photonics. 43-46

**2.1. Outline of Structure Property Relations**

The twist-bend modulated nematic phase is commonly observed in liquid crystalline dimers, two rigid units joined with a flexible spacer. 47-49 The phase is exclusively observed for materials with odd- parity spacer; the resulting bent shape appears to be a prerequisite for TB phase formation. The optical textures of the twist-bend modulated nematic phase are somewhat reminiscent of smectic phases, 50 it is unsurprising that many materials that were reported to exhibit lamellar phases of unknown structure (SmX) have subsequently been demonstrated to exhibit the TB phase, 38, 51 or are suspected of doing so. 52-54 LC dimers can be subdivided into several distinct units: terminal groups, mesogenic units, linking groups and the central spacer (Figure 2). For example, the CBnCB materials have nitrile terminal groups, biphenyl mesogenic units, methylene linking groups and alkyl spacers (structure shown in Figure 3), and were the first materials in which the TB phase was definitively identified. 55

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Figure 2: Generalised structure of an LC dimer, showing the different subdivisions used in this account and examples of the chemical composition of each

Our initial foray into work on the TB phase was to synthesise the CBnCB materials as shown in Figure 3, and at the time one of only a handful of materials known to exhibit the TB phase. 55 The *bis* (4-hydroxyphenyl)alkanes can also be used to construct dimers containing ester groups such as the PCBnPCB compounds; given the large number of commercially available benzoic/carboxylic acids, we envisaged a large number of materials could be prepared, allowing the elucidation of a structure-property relationship. Initially we screened a number of polar terminal groups (CN, NO2, F, CF3, SF5), 56 followed by apolar terminal groups (H, H2n+1Cn, H2n+1CnO) 57 and mixed polar/apolar materials. 58-59 Materials with long (>C8) terminal chains have a tendency to exhibit tilted smectic C phases directly from the nematic phase, although a few examples of TB-SmC phase transitions exist. 57, 60-61 Replacing one phenyl ring with cyclohexyl usually leads to retention of the TB phase; however incorporation of a bicyclohexyl leads to smectic B phases. 62 Ahmed *et al.* demonstrated that a phenyl ring can be replaced with thiophene without loss of the twist-bend modulated nematic phase, 63 similarly selenophene can be incorporated whilst retaining the TB phase, 58 permitting measurement of *PTB* by resonant X-ray at the Se K-edge. 34

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Figure 3: Synthesis of the ‘CBnCB’ materials *via* *bis* (4-hydroxyphenyl)alkanes, and the related PCB*n*PCB materials.

After much synthetic effort we concluded that the TB phase was not especially sensitive to the composition of the mesogenic units, 56-57 similar conclusions also being reached by others, 64-65 although the use of non-linear mesogenic groups such as cyclophanes can render the resulting materials non-mesogenic. 66 We next considered the role of the linking groups and the spacer. Adlem *et al*. demonstrated the first material with ether-linking groups to exhibit the TB phase, 67 albeit in a multicomponent mixture. Separately to this we had prepared a large number of fluorinated, ether-linked dimers, finding many of them to exhibit the twist-bend phase. 68-70 Many materials with imine linking groups have been reported to exhibit the twist-bend modulated nematic phase, 53-54 61, 71-72 including materials that exhibit direct isotropic to TB phase transitions without an intervening nematic phase. 73-74 Most recently the role of torsion in the central spacer has been studied by Lesac *et al*. 75

**2.2. Dependency on Molecular Bend, Flexibility and Shape**

Theoretical treatments had suggested the TB phase should display some dependency upon the gross molecular bend-angle. 76 As an experimental study we synthesised several new materials with cyanobiphenyl mesogenic units, various linking groups and nonamethylene (or equivalent) spacers. 77 The change in linking group leads to a change in bend-angle which we estimated from DFT calculations and 1D 1H NOESY NMR. 77 The use of a single conformer to describe flexible systems such as LC dimers is an obvious weakness; we later improved upon this earlier study by using large libraries of conformers for each material, allowing us to obtain Boltzmann weighted average bending angles as well as to quantify how broad the distribution of bend angles is for each material. 78 This computational approach is in good, albeit not perfect, agreement with experimental conformational data obtained *in situ* in the twist-bend phase 79 and that inferred from dielectric measurements. 80 Results from our two studies strongly imply a link between the gross molecular bend angle and the incidence of the twist-bend phase. In particular bend angle in the region of 105-115 ° appears to confer a large increase in the TB transition temperature, as shown in Figure 4. Simply taking an average bend neglects molecular flexibility, a point that will be returned to shortly.

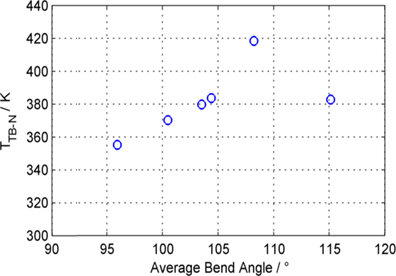


Figure 4: Plot of the TB-N transition temperature as a function of the average molecular bend angle as reported by Archbold *et al* 78

We observed that for methylene-linked dimers the TB-N transition temperature (TTB-N) and clearing point (TN-Iso) exhibit a linear relationship. 58, 81 This linear relationship is obeyed the oligomeric materials 82 and polymers that exhibit twist-bend modulated nematic phases. 51 Similar relationships are found for materials with mixed ether/methylene linking groups, 83 and unpublished results point to a similar relationship for other linking group combinations. The fact that the two transition temperatures are interdependent on one another, irrespective of the chemical makeup of the material, indicates that the TB phase is driven by steric factors, *i.e.* the gross molecular shape. This outcome was first described in a theory work by Greco *et al.* 76 and later Vaupotic *et al.* proposed that *“…the internal structure of the TB is driven mainly by steric interactions.”* 84 A plot of TTB-N versus TN-Iso for materials with nonamethylene and octamethyleneoxy spacers is given in Figure 5a. This plot includes materials with extremely polar terminal groups (NO2, SF5, CN), apolar terminal groups (H2n+1Cn, H2n+1CnO), lateral groups (F, CH3, OH), hydrogen bond donors/acceptors (CN, OH, COOH, NO2); the lack of deviation from linearity - despite the range of functional groups included – is remarkable and as far as is known, not observed for any other combination of phase transitions. Different linking groups give near identical slopes, only the intercept values vary.

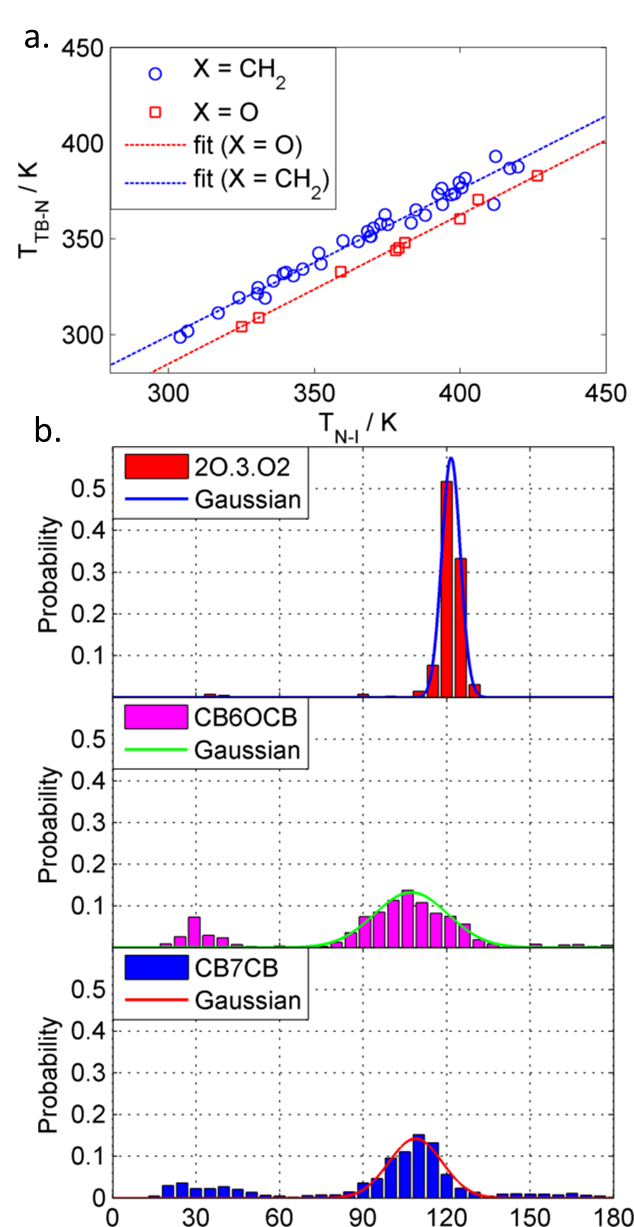


Figure 5: (a) Plot of TTB-N / TN-Iso (K) for dimers with two methylene linking groups (circles) and dimers with mixed ether/methylene linking units (squares). Linear fits take the form y = 0.766x + 69.67 for X = O and y = 0.7788x + 51.27 for X = -CH2-. Data was taken from ref 81, 83 (b) Histogram plot of bend angle probabilities for the dimers 2O.3.O2, CB7CB and CB6OCB along with Gaussian fits (solid lines).

Recent results suggest that the TB phase is promoted by a narrow distribution of bend angles centred at ~ 110 °, when this is sufficiently tight direct isotropic to TB transitions can occur (*i.e.* the intercept of the linear fit is >1). In the case where the distribution is broadened, the intercept value reduces; swapping one methylene for an ether leads to a wider distribution and a lower intercept value (Figure 5b). 83 The dimer 2O.3.O2 exhibits a direct TB to isotropic phase transition, and is therefore a suitable case study for this hypothesis. 73-74 Using the conformational analysis technique described by Archbold *et al*, 78 a libraries of conformers for the dimers CB7CB, CB6OCB and 2O.3.O2 were constructed by allowing rotation about each dihedral of the spacer of both compounds using the AM1 semi empirical method as implemented in Gaussian G16. 85 The Boltzmann weighted average bending angles are 119 ° for 2O.3.O2, 108 ° for CB6OCB and 107 ° for CB7CB. We determine the breadth of the bend-angle distribution by fitting a histogram plot of probability versus bend-angle with a Gaussian centred at the average bend angle; the FWHM for CB7CB is 21.7 °, for CB6OCB it is 32.7 ° and for 2O.3.O2 it is 11.1 °. These FWHM values correlate well with TB phase stability, and suggest this hypothesis has some validity. The incidence of the TB phase in bimesogens and dimers is therefore a product not only of the molecular bend, but also the flexibility and distribution of bend angles. It is unclear how flexibility and bend influence the pitch length (and other properties) of the TB phase as there is a real lack of experimental data for both pitch length and conformer distribution. It seems a reasonable hypothesis that the most flexible molecules would have the longest pitch, whereas those with a relatively tight distribution of bend-angles would have relatively short pitches. The pitch of CB7CB (7.8 Å) 32 is shorter than that of the more flexible CB6OCB (8.9 Å), 86 and this is consistent with the presented hypothesis.

**3. Beyond Dimers: *n*-mers and Polymeric Systems**

If a dimer is composed on two mesogenic units then more broadly we can define liquid-crystalline *n*­-mers are composed of *n* interconnected mesogenic units, *e.g.* n = 3 trimer, n = 4 tetramer and so on. The individual units need not be the same and the manner of linking need not be linear; the amount of chemical space occupied by such structures is incalculable. 48 Whereas polymers typically have a degree of polydispersity, liquid crystalline *n*-mers are monodisperse by definition. The hydrogen-bonded trimer formed spontaneously by CB6OBA (Figure 6) was the first quasi *n*­-mer reported to exhibit the TB phase. 87 The analogous material with even spacer parity, CB5OBA, does not exhibit the twist-bend phase due to its linearity. 87 Wang *et al* also reported the TB phase to be exhibited by a trimer containing a 2,5-disubstituted 1,3,4-oxadiazole. 88

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Figure 6: Transition temperatures (°C) of the hydrogen-bonded trimers (CB5OCB, linear) and (CB6OBA, bent). 87

We considered that if the helical structure of the twist-bend phase is correct then this phase should be readily formed by *n*-mers as well as simple dimers/bimesogens as the phases formed by these two materials structurally differing materials are basically degenerate. During the synthesis of the dimer **T29** small quantities of the monoesterified product were isolated; following optimisation of this reaction we could isolate multigram quantities and we used these to prepare the trimer (**T39**) and the tetramer (**T49**) as shown in Figure 7. 59, 89

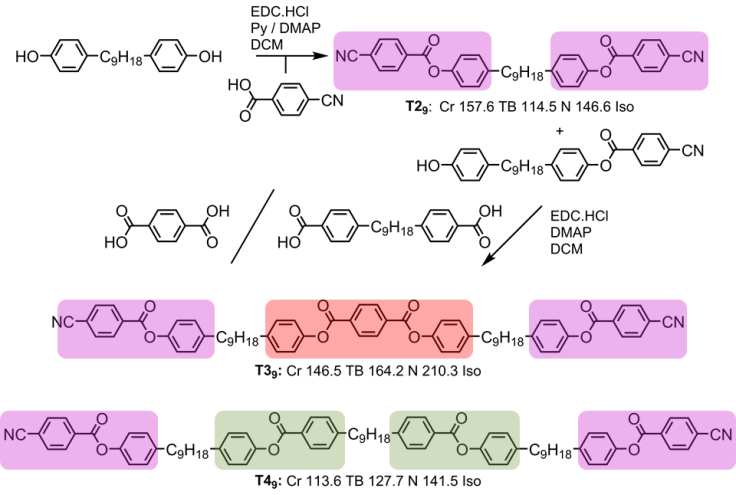
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Figure 7: Chemical synthesis of the dimer T29, 56 the trimer T39, 59 and the tetramer T49. 89 Transition temperatures are given in °C

While **T39** and **T49** demonstrated conclusively that the TB phase could be observed systems beyond simple dimers, the synthetic route to these materials is not well suited to the preparation of higher *n*-mers. We devised the ‘N+1’ synthetic strategy to overcome this; this is loosely defined as a synthesis of a liquid crystal incorporating *n* number mesogenic units which are installed sequentially, giving a high degree of control over the molecular sub structure. In principle this allows the synthesis of perfectly monodisperse materials incorporating any number of similar/dissimilar mesogenic units (Figure 8a). This concept was applied in the synthesis of the second generation of *n*-mers designed to exhibit the TB phase. We devised a chemical intermediate containing two ‘half’ mesogenic units, one bearing a phenol and the other a protected carboxylic acid; this allows complete mesogenic units to be formed by successive esterification/deprotection, in principle allowing any number of mesogenic units to be incorporated. This method was used to afford the tetramer **O47** and the hexamer **O67**, 82 with both materials found exhibit nematic and TB phases. Comparing the transition temperatures of the tetramer and hexamer to the analogous dimer (**O27**) we find the linear relationship described in Figure 5a is obeyed. Molecular structures and transition temperatures are given in Figure 8b.

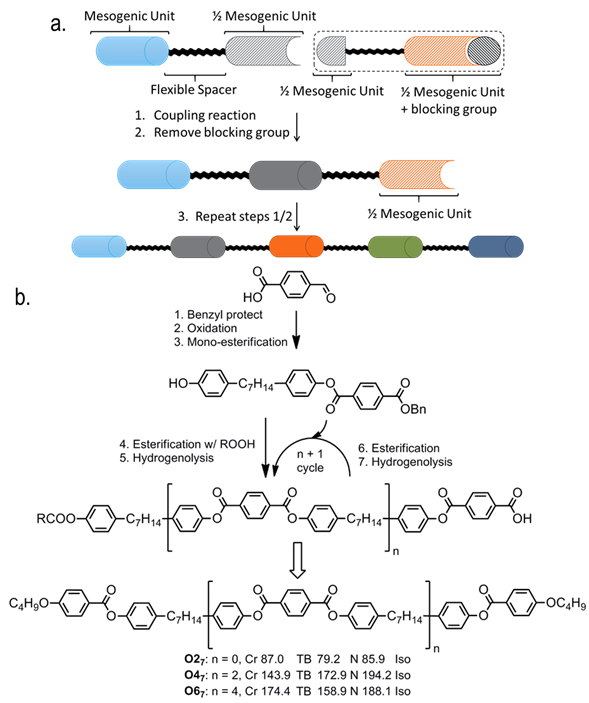


Figure 8: (a) conceptual route to n-mers *via* stepwise insertion of mesogenic units, the ‘N+1’ approach; (b) a truncated synthesis of O27, O47 and O67, transition temperatures are given in °C.

The synthetic route employed to synthesise the **O*n*7** materials is poorly suited to higher generation *n*-mers due to low yields resulting from transesterification and the resulting difficulties in chromatographic separation of the desired material from reaction side products. Replacement of the phenyl benzoate mesogenic units present in the **T*n*9** and **O*n*7** n-mers with biphenyls should improve chemical stability, whilst substituting one methylene linking group with an ether group simplifies the preparation of these materials. The ‘N+1’ in this synthetic approach is a two-step deprotection/etherification, allowing each mesogenic unit to be installed in turn. As shown in Figure 9 the target of this synthetic approach is the **A6n** materials, where *n* is the number of mesogenic units in the *n*-mer, these being homologous in structure to the well-known dimer CB6OCB. 86The key intermediate in this approach is derived from 1-bromo-4-iodobenzene in 3 steps and incorporates a free phenol and a benzyl protected primary alcohol; the ‘n+1’ cycle in these materials encompasses etherification via the Mitsunobu protocol followed by hydrogenolysis of the benzyl ether to afford a free alcohol. 90 Unfortunately despite screening a range of different catalysts and poisons we were unable to affect hydrogenolysis of the benzyl group without accompanying nitrile reduction, although we were able to obtain quantitative reduction of the alkyne without reduction of the nitrile using palladium on carbon poisoned with diaminoethane (Figure 9). 90-91 Nevertheless, the obtained material exhibits the twist-bend phase despite possessing a terminal benzyl ether (Cr 93.1 TB 48.3 N 67.1 Iso). 90

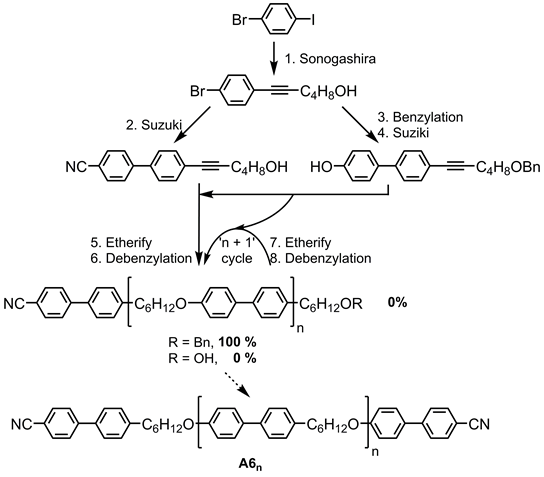


Figure 9: Attempted synthesis of the A6n materials. 90

As workaround to the problem of debenzylation in the presence of a nitrile we replaced the benzyl ether protecting group with tert butyldimethylsilyl ether (TBDMSO), which is cleavable using tetrabutylammoniumfluoride (TBAF). This enabled us to synthesise the two isomeric trimesogens **A63** and **B63** as a proof of concept to this approach. The trimer **A63** exhibits the TB phase whilst its isomer **B63** displays a phase of matter that we could not be definitively identified as being the TB. 92 In a later paper, Tuchband *et al* reported resonant X-ray studies on this material and find it has a nanoscale periodicity of 66 Å which, unlike normal TB materials, is temperature invariant. 93 The synthetic route devised for the preparation of **A63** and **B63** can also afford higher *n*-mers such as **A64**, demonstrating the power of our synthetic approach shown in Figure 10a. Replacing one of the nitriles of **A63** with a hexyloxy chain (**6OA63**, Figure 10b) prevents the resulting material from exhibiting the TB phase, instead forming a highly ordered smectic phase of unknown structure. 90

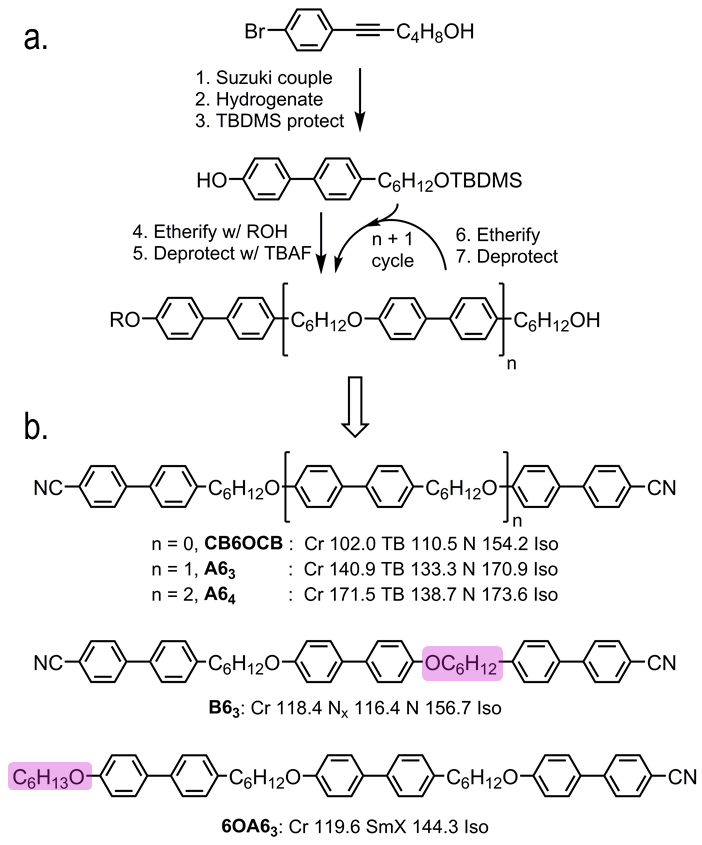


Figure 10: (a) Truncated synthetic route incorporating an ‘N+1’ cycle used in the synthesis of the A6n *n*-mers; (b) molecular structure and transition temperatures (°C) of the dimer CB6OCB, 86 the trimer A63, 92 the tetramer A64, the trimer B63 92 and the trimer 6OA63. 90 For B63 and 6OA63 the structural differences with A63 are highlighted.

A previously unreported trimer from the York group, **C6/83**, can be considered homologous in structure to **A63** except with an alkyne inserted into one methylene spacer. This structural modification has minimal impact on transition temperatures (**A63**: Cr 140.9 TB 133.3 N 170.9 Iso), and this result can be taken to support the idea of the TB phase being a shape driven phase. However, materials such **6OA6** suggest that the formation of the TB modulated phase in *n*-mers exhibits sensitivity to molecular structure that is not observed for simple dimers/bimesogens. The increased molecular complexity of *n-*mers over dimers necessitates longer synthetic routes; therefore the delineation of a structure property relationship for *n*-mers exhibiting the twist-bend phase poses a greater difficulty than for dimers, which are trivial to synthesise by comparison. The fine control over molecular substructure afforded by using the ‘n+1’ cycle allows oligomers of any length, any composition and any repeating sequence of mesogenic units to be constructed, simplifying the synthesis of higher oligomers.



Figure 11: The molecular structure and transition temperatures (°C) of the trimer C6/83. Synthesis and characterisation details are given in the SI.

**Summary and Outlook**

When our studies on structure-property relationships began only 7 materials were known to exhibit the TB phase; at the time of writing this is figure now over 250. The understanding of the molecular factors that influence the occurrence of this phase is not quite complete; however present results imply that the molecular shape (gross bend angle, flexibility) dictates this phase of matter and not any particular combination of functional groups. The number of structures that satisfy the shape requirements, and therefore might be considered possible candidates for exhibiting the TB phase, is probably inestimable.

Oligomeric materials that exhibit the TB phase are the next frontier in this area. Already there is some evidence to suggest that the structure-property relationships in these systems are more complex than in dimers. Our ‘N+1’ concept, in which individual mesogenic units are installed in turn, allows the synthesis of large materials (the hexamer **O67**) as well as unsymmetrical materials (the trimers **A63**, **6OA63**, and **C6/83**). The observation of TB phases in polymer systems 51 and – potentially - lyotropic suspensions of micron sized particles 94 - indicate this phase of matter is not confined to any one length scale, and it is probable that higher oligomers (decamers, dodecamers etc.) will be found to exhibit the TB phase. Provided the bend and flexibility requirements are satisfied, it may be possible to incorporate branched sections, either Y-shaped or λ-shaped, into an *n*-mer whilst retaining the heliconical TB phase. Tuchband *et al* recently expanded on the earlier idea of Goodby *et al*, 57 suggesting that the structure of the TB phase is a more complex than a single helix, instead having a duplex double-helical chain; 95 it is possible to envisage therefore that two *n*-mers, laterally appended to give an elongated ‘H’ shaped or ‘X’ shaped material, as candidates for exhibiting this unusual state of matter.

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**Biographical Sketch**

Richard J. Mandle is currently a postdoctoral researcher in the Department of Chemistry at the University of York, UK. He completed BSc (2007) and MSc degrees (2008) in Chemistry at the University of Hull UK, before completing a PhD (2012) in Chemistry at the University of York under the supervision of Professor John W. Goodby FRS. Some of Dr. Mandle’s current research interests include liquid crystal and OLED materials for optoelectronic devices, soft matter, mesophases with modulated structure, as well as novel dyes and dye-doped liquid crystals. To date he has published over 50 peer reviewed works, and was the winner of the 2017 BLCS Young Scientist Award.

**TOC Entry**

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Arguably the most active area in liquid crystal research presently, the twist-bend modulated nematic phase (TB) exhibits a nanoscale helical structure and therefore exhibits bulk chirality despite being formed of typically achiral materials. Recent advances and developments in strategies employed to prepare oligomeric materials that exhibit this state of matter afford fine control over the molecular substructure and potentially over the nanostructure of the exhibited mesophases.

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