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The twist-bend phases: structure–property relationships, chirality and hydrogen-bonding

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ABSTRACT

This article will review some of our recent work concerning the relationships between molecular structure and the observation of the fascinating twist-bend nematic, N_{TB} , phase. From a chemist's perspective, understanding the molecular features influencing the formation and stabilisation of the N_{TB} phase is of paramount importance, and allows for the design of new materials that have targeted properties. As such, recent work in Aberdeen has had the primary aim of enhancing our current understanding of these relationships in dimeric liquid crystals, through the synthesis and characterisation of a diverse range of materials, including a selection of supramolecular liquid crystals. A second aim has been to explore the intriguing question as to how the N_{TB} phase, having spontaneous structural chirality, would respond at a microscopic level to the presence of intrinsic molecular chirality – the inclusion of chiral fragments in the dimers – and to obtain examples of the 'chiral' twist-bend nematic phase (N_{TB}^*) for comparative study alongside the conventional N_{TB} phase. We also show that bent achiral molecules form heliconical smectic phases, as predicted by Dozov in his seminal 2001 work.

KEYWORDS

liquid crystal dimers; twist-bend nematic phase; chirality; structure-property relationships; hydrogen-bonding

1. Introduction

The prediction [1,2] and subsequent experimental discovery [3] of the twist-bend nematic phase, N_{TB} , is undeniably one of the most significant recent developments in the field of liquid crystals. Dubbed the 'structural link' between the conventional nematic, N , phase, and its chiral counterpart, N^* , shown in Figure 1, in the N_{TB} phase the director is tilted at constant angle θ and forms a heliconical superstructure of nanoscale periodicity, while the molecules retain a random distribution of their centres of mass [4,5]. The chiral helix is formed despite the constituent molecules being chemically achiral, and indeed, the N_{TB} phase represents the first example of spontaneous chiral symmetry breaking in a fluid system with no spatial ordering. There exists an equal probability of the formation of either handedness of the helix and hence the N_{TB} phase consists of doubly degenerate locally chiral domains of opposite handedness, giving a globally achiral phase. However, the presence of intrinsic molecular chirality removes this degeneracy and the chiral N_{TB} phase is formed. Short-pitch heliconical smectic phases formed from achiral molecules were predicted together with the N_{TB} phase, and examples of these have recently been reported [6,7].

The N_{TB} phase was discovered through the comprehensive characterisation of the liquid crystal dimer

1,7-bis-4-(4-cyanobiphenyl) heptane, CB7CB, and its ability to exhibit this new phase was attributed to the bent shape of the molecule arising from the odd-membered spacer, resulting in an anomalously low bend elastic constant [3]. By far the greatest number of twist-bend nematogens reported are odd-membered liquid crystal dimers; however, the N_{TB} phase has also been observed for rigid bent-core materials [8], a hybrid bent-core-calamic dimer [9], trimers and tetramers [10–13], a hexamer [14], and main-chain polymers [15]. The common structural feature shared by these molecular architectures is curvature, not necessarily uniform, and it is now widely believed that this is a prerequisite to observe twist-bend nematic behaviour. This view has been reinforced by a generalised Maier–Saupe theory developed for rigid V-shaped molecules that has shown the twist-bend nematic–nematic phase transition temperature to be highly sensitive to the molecular bend angle [16].

Motivated by the discovery of the N_{TB} phase in CB7CB, much of our initial work focussed on revisiting a number of similar dimer series, originally synthesised some time ago as model compounds for polymers or as part of the still-ongoing quest to find the elusive thermotropic biaxial nematic phase [17–20]. Many of these materials had previously been reported to exhibit a smectic phase below the conventional nematic, assigned due to the former's

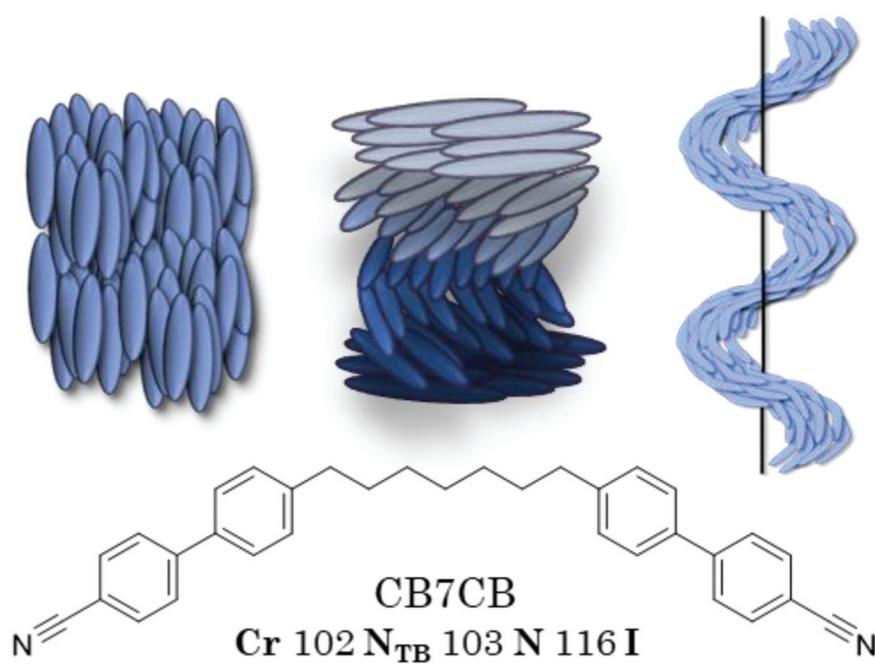


Figure 1. Top. Schematic representations of the (left to right) nematic, chiral nematic and twist-bend nematic phases. Bottom. CB7CB.[3].

polygonal and focal conic textures despite some unusual thermal behaviour. However, our studies were able to reassign a number of these designated smectic phases as N_{TB} phases [21–23]. This early work culminated in a detailed structure-property investigation of the cyanobiphenyl-based series $CBnOCB$, $CBnCB$ and their intermediate $CBnOCB$ [21], together with a comprehensive study on the latter series' hexyloxy member, $CB6OCB$ [24]. This was subsequently selected as a candidate for further modification to explore the effects of structural changes on the incidence of the N_{TB} phase and its properties. This particular structure was chosen because the methylene-ether link allows for the straightforward synthetic addition of different mesogenic units to the $CB6O$ 'backbone' while maintaining the ideal molecular curvature required for an enantiotropic, stable twist-bend nematic phase. This compares to the corresponding ether-linked dimers, for which the increased linearity raises the melting point and lowers T_{NTBN} such that the phases are typically highly monotropic and hence their study is difficult [21].

Here we will describe a selection of recent projects which explore the exchange of the ether-linked cyanobiphenyl moiety of $CB6OCB$ with a variety of mesogenic units, selected for reasons pertaining to the specific aim of the work, and these structures are illustrated in Figure 2.

The azobenzene moiety, Figure 2(a), undergoes photolytic isomerisation from its *trans* to *cis* form at certain wavelengths of light. This introduces the possibility of controlling molecular shape, and hence material

phase behaviour and elastic properties, through external stimuli [25–27]. Benzylideneaniline units Figure 2(b,c) have historically been paired with cyanobiphenyl due to their respective electron rich and electron deficient natures, which result in a specific intermolecular attraction – possibly a quadrupolar interaction – thought to drive the formation of intercalated smectic phases [19,28]. Local molecular intercalation was reported as a common feature of twist-bend nematogens, and hence this specific interaction appeared desirable. From a synthetic perspective, the imine link is a convenient and straightforward way to vary terminal alkyl and alkoxy groups to explore what happens when the terminal chain becomes longer than the hexyloxy spacer, assuming intercalation is no longer possible [23,29]. Moreover, those materials with long terminal chains have the potential to exhibit rare N_{TB} -smectic phase transitions and, as we will see, helical smectic phases with unique structures. To extend the asymmetry of these dimers an additional phenyl benzoate was introduced to the benzylideneaniline moiety to give a three-ringed mesogenic unit [6]. Use of a hydrogen-bond donor (such as benzoic acid, Figure 2(d)) or acceptor (e.g. stilbazole, Figure 2(e)) as the terminus of the mesogenic unit allows for an alternative construction of twist-bend nematogens, in the form of bent-shaped supramolecular complexes [30–33]. Finally, we use a simple phenyl benzoate-based mesogenic unit (f) to attach a chiral terminal chain to our bent-dimer and explore the relationship between molecular and structural chirality in

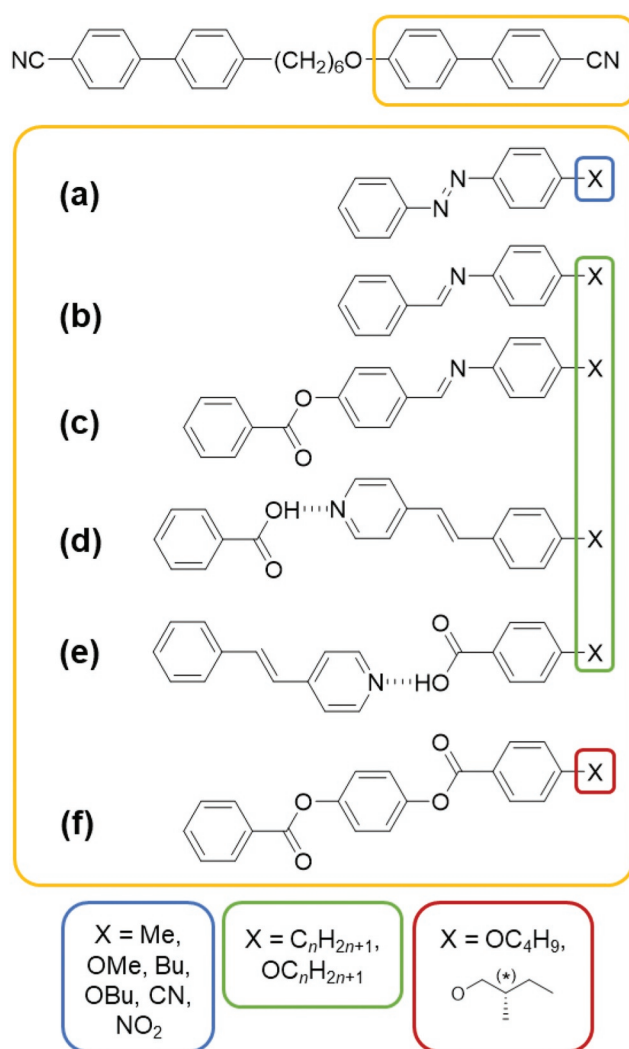


Figure 2. Structures of nonsymmetric dimers discussed in this work.

the context of the twist-bend nematic phase and its chiral counterpart, the chiral twist-bend nematic phase, N^*_{TB} [34].

2. Structural modifications

2.1 Azobenzenes

The *trans*-to-*cis* isomerisation of the azobenzene unit is well documented in the literature [25] and, in the context of liquid crystals, results in a lowering of the nematic-isotropic transition temperature – readily explained by considering the more elongated molecular shape of the *trans*-isomer

compared to that of the *cis*. This feature makes azobenzene-based compounds attractive candidates for use in applications such as liquid crystal displays, optical storage devices or nonlinear optics. To investigate the effect of *trans*-*cis* photoisomerisation on the primarily shape-driven N_{TB} phase, we prepared a series of azobenzene dimers CB6OABX , with $\text{X} = \text{Me}, \text{OMe}, \text{Bu}, \text{OBU}, \text{CN}$ and NO_2 (Figure 3).

All these dimers were enantiotropic nematogens bar the methyl-terminated, which showed a monotropic nematic phase. Conversely, only the butoxy-terminated dimer exhibited an enantiotropic twist-bend nematic phase while the N_{TB} phases shown by the other five were monotropic. Textures for these phases are shown in Figure 4(c). The enantiotropic N_{TB} phase of CB6OABOBu allowed for its further investigation and for this material we demonstrated the first example of an isothermal, photochemically driven twist-bend nematic-nematic phase transition. UV irradiation reduced both T_{NI} and T_{NTBN} , with a more significant effect on the latter. This was attributed to changes in the relative concentrations of the *trans*- and *cis*-forms of the azobenzene moiety, confirmed by UV-vis spectroscopy, see Figure 4(d). Hence, increasing the concentration of *cis* conformations destabilises first the N_{TB} phase in favour of a conventional nematic, then the nematic phase in favour of the isotropic phase. While the latter transition is expected, one might have thought the more strongly bent *cis* isomer would promote twist-bend behaviour, considering the dependence of the N_{TB} phase on molecular bend. However, it is important to consider that while the *trans* isomer has a spatially uniform bend, governed by the geometry of the alkyl spacer, bend deformations in the *cis* isomer occur at two different locations: the spacer and the azobenzene moiety (Figure 4(b)). This causes a reverse in the bend polarity on moving from one end of the molecule to the other, creating a spatially variable bend. Such a bend appears incompatible with the local packing requirements of the twist-bend nematic phase, and hence it is destabilised. CB6OABOBu has been shown to exhibit a fast and giant photorheological effect, giving this material considerable applicability with the potential to achieve a whole new performance level for mechanically responsive organic materials [35].

The nature of the terminal group is clearly influential in determining the stability of both the N and N_{TB} phases, as illustrated by the variation of T_{NI} and T_{NTBN} shown in Figure

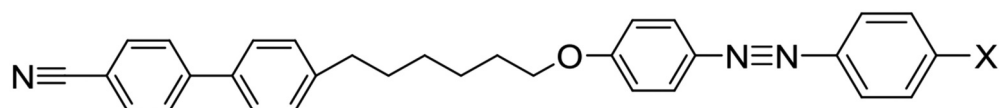


Figure 3. CB6OABX , with $\text{X} = \text{Me}, \text{OMe}, \text{Bu}, \text{OBU}, \text{CN}, \text{NO}_2$.

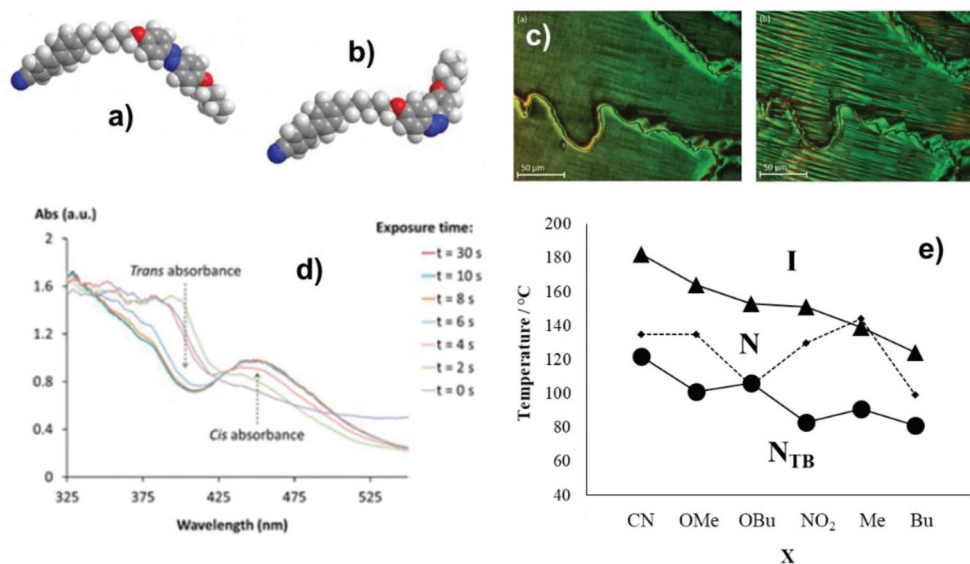


Figure 4. Space filling models showing (a) *trans*- and (b) *cis*-forms of CB6OABOBU; (c) Textures of (left) the N phase (85°C) and (right) the N_{TB} phase (80°C) exhibited by CB6OABNO₂ [27]; (d) UV-vis spectrum showing the decrease and increase of *trans*- and *cis*-forms of CB6OABOBU on UV irradiation respectively; (e) Dependence of T_{NI} and T_{NTBN} on varying the terminal group. (a), (b) and (d) Adapted with permission from [26], Copyright 2016 American Chemical Society.

4(e) [27]. The nitrile group ranks as the most efficient in stabilising both the N and N_{TB} phases, while the butyl terminal chain is the least effective. The observed order may be accounted for in terms of subtle changes in the average molecular shape, steric factors, and the strength of the mixed mesogen interaction on varying the terminal group; however, this work reinforced the general view that there is not a clear and simple relationship between the electronic properties of the mesogenic units and T_{NI} or T_{NTBN} [36–38].

Additional structural modifications to our azobenzene-based dimers included exchange of the hexyloxy spacer with its diether analogue, oxypentyloxy (O5O), replacement of the cyanobiphenyl mesogen with methoxybiphenyl, and formation of symmetric azobenzenes-based dimers connected by the O5O spacer [27,39]. T_{NI} is elevated and T_{NTBN} reduced for the diether-linked dimers compared with the CB6OABX series, with the N_{TB} phase seen only for the butyl and butoxy-terminated materials. These observations are attributed mainly to the influence of the spacer on molecular shape, a trend well documented for liquid crystal dimers [18,21,36,40] and completely in accord with the predictions of theoretical models [41,42]. In the symmetric materials, the N_{TB} phase is lost and these are exclusively nematogenic, with the exception of the butyl-terminated dimer for which a conventional monolayer smectic A phase was observed [27].

Investigations into the photocontrolable azobenzene-based twist-bend nematogens remain ongoing, with intriguing aspects such as the effect of irradiation

on the elastic constants and the possibility of light-controlled selective reflection in a chiral material yet to be fully addressed.

2.2 Benzylideneanilines

In addition to the N_{TB} phase, Dozov's seminal 2001 work also predicted the existence of heliconical smectic phases formed from bent-shaped, achiral molecules [2]. This has been a particularly difficult prediction to verify as the majority of twist-bend nematic phases either crystallise or vitrify on further cooling and hence N_{TB}-smectic phase transitions are only rarely observed. We sought to establish and understand how these bent molecules pack into smectic phases and the properties such phases exhibit. To this end, we prepared several dimer series combining the molecular curvature required to exhibit the N_{TB} phase with selected structural features known to promote smectic phase behaviour, Figure 5(a–c). The cyanobiphenyl and Schiff's base moieties are known to exhibit a favourable specific interaction thought to drive smectic phase formation in mixtures of conventional low molar mass mesogens and in non-symmetric dimers. For this study, it was critical that the length of the terminal chain *m* could be readily varied given the role of microphase separation in smectic phase formation. The inclusion of phenyl benzoate in the benzylideneaniline mesogenic unit to give the series shown in Figure 5(c) was to enhance

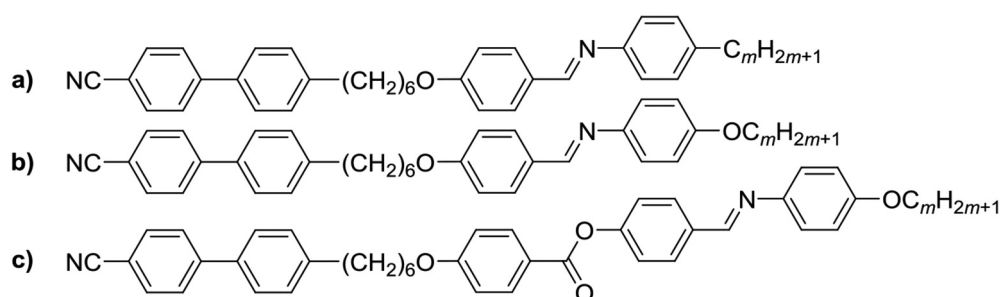


Figure 5. Benzylideneaniline-based dimer series (a) CB6O.*m*, (b) CB6O.O*m*, (c) CB6OBelO*m*.

intermolecular interactions between these units in order to further drive smectic behaviour.

CB6O.*m* dimers with $m = 1-10$ (Figure 5(a)) show N and N_{TB} phases, see Figure 6(a). X-ray diffraction measurements shown in Figure 6(b) revealed that for short chain lengths ($m = 1-6$) the local packing in both nematic phases is an intercalated arrangement; for intermediate chain lengths ($m = 7-9$) there exists a frustrated local structure, with competition between intercalated, monolayer and interdigitated arrangements, and for the longest chain length ($m = 10$) a new, bilayer arrangement is observed. This was the first time such a change in the local structure on increasing m had been seen in a dimer series exhibiting the N_{TB} phase. Surprisingly, this has no apparent effect on the stability of either nematic phase, and T_{NTBN} and T_{NI} show a regular dependence

on m (Figure 6(c)). Specifically, T_{NTBN} and T_{NI} decrease on increasing m and superimposed upon this is a weak odd-even effect in which the odd members show the higher values, typical behaviour for such dimer series. These results suggest that previous reports may have overstated the importance of local molecular intercalation in driving the formation of the N_{TB} phase. A smectic mesophase with a lamellar bilayer arrangement ($d = 2l$) is exclusive to the dimer with $m = 10$ and is discussed later.

Exchange of the alkyl terminal chain for an alkoxy chain gave the CB6O.O*m* series, Figure 5(b). N and N_{TB} phases are again observed in all 10 dimers, and X-ray measurements found a somewhat similar local packing progression in the nematic phases on increasing m to that observed in the CB6O.*m* series. Thus, local molecular

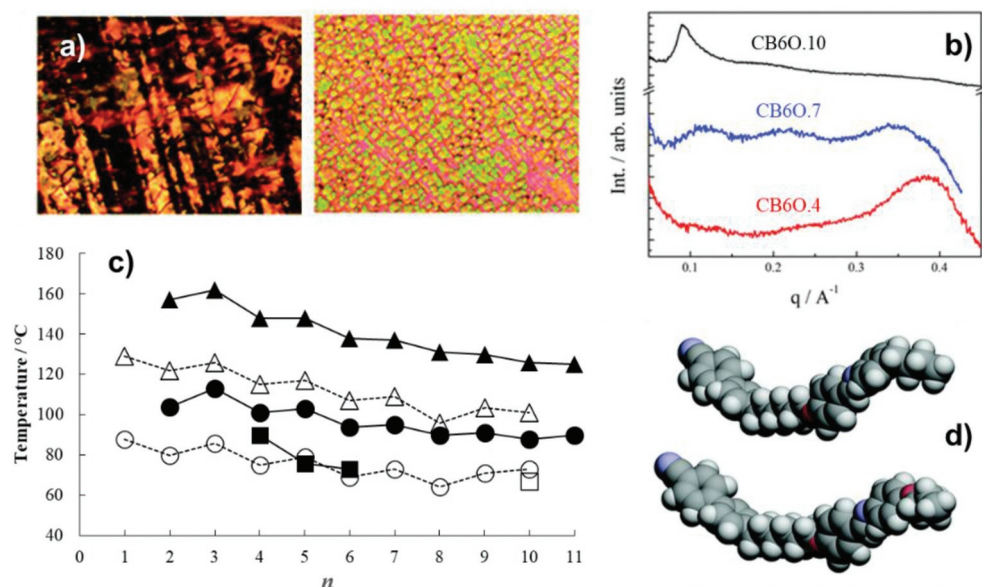


Figure 6. (a) Textures of CB6O.4 in the (left) N and (right) N_{TB} phases; (b) X-ray measurements in the N_{TB} phase representative of long (top), intermediate (middle) and short (bottom) terminal chain lengths, showing evidence of a local structure with bilayer, competition between different packing arrangements and intercalation, respectively; (c) Dependence of T_{NI} (▲) and T_{NTBN} (●) on the number of atoms, n , in the terminal chain. For the CB6O.O*m* series (filled symbols) $n = m + 1$, and for CB6O.*m* (empty symbols) $n = m$. Sm phases in each series are denoted with squares; (d) The shapes of CB6O.4 (top) and CB6O.03 (bottom) with the spacers in the all-*trans* conformation. Reproduced from [23] by permission of The Royal Society of Chemistry.

intercalation is seen for short chain lengths, and frustration/monolayer packing for longer chains. Intercalated smectic phases are observed only in dimers with $m = 3-5$, and the higher temperature of these is suggested to be a new type of heliconical smectic phase, discussed later. The lack of smectic behaviour for longer terminal chain lengths suggests that intercalation has been destabilised, and the absence of a strong driving force for the formation of a monolayer smectic phase precludes its observation.

It is well documented for both conventional low molar mass and dimeric mesogens that replacement of an alkoxy terminal chain by an alkyl group results in a lowering of the melting and clearing points, as well as the other liquid crystal phase transition temperatures. A contributing factor to these reductions is the respective orientations of the terminal chains with respect to the mesogenic unit to which they are attached. Specifically, an all-*trans* alkyl chain protrudes at some angle from the plane of the unit, and hence disrupts the packing efficiency of the molecules (Figure 6(d)). In contrast, an alkoxy terminal chain lies more-or-less in the plane of the mesogenic moiety and enhances the shape anisotropy. This is indeed what we observe here, with the CB6O. m dimers having consistently lower melting, clearing and T_{NTBN} temperatures than the corresponding member of the CB6O.O m series, see Figure 6(c). These lower transition temperatures may also account for the lack of intercalated smectic behaviour in CB6O. m dimers with short chains.

The phase behaviour of the CB6OBeO m series with $m = 1-10$ (Figure 5(c)) is illustrated in Figure 7(a) [6]. All 10 dimers were nematogenic, and those with short terminal chains exhibited the intercalated N_{TB} phase. For $m > 6$, a sequence of up to four monolayer-lamellar phases is seen below the N phase. Unique to homologues with $m = 7$ and 8 is a tilted, smectic C phase, the details of which are discussed in the next section. The lowest temperature smectic phase, common to all homologues, was identified as a hexatic-type phase, HexI, with unique multi-level chirality. AFM studies of the morphology of this phase revealed mesoscopic helical filaments with uniform twist over micron-size areas, see in Figure 7(b), resembling that of the B_4 phase but without an internal crystal structure [43,44].

2.2.1 The twist-bend smectic phases

Arguably the most exciting result to emerge from these studies is the discovery of new short-pitch, tilted smectic phases formed by achiral molecules, as were predicted by Dozov along with the N_{TB} phase [2]. Such a phase was first seen in CB6OBeO7 and CB6OBeO8 preceded by non-tilted SmA and SmAb phases [6], and we termed

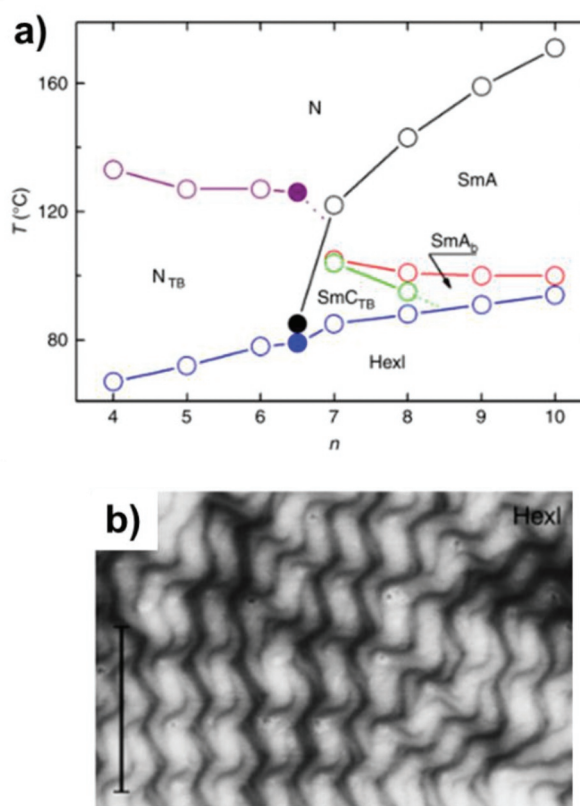


Figure 7. (a) Phase diagram for the CB6OBeO m series ($m = 4-10$). Filled points correspond to a 50:50 mixture of $m = 6$ and $m = 7$; (b) AFM image of CB6OBeO7 in the HexI showing twisted entangled filaments. Reproduced with permission from [6] under a Creative Commons Attribution 4.0 International Licence <https://creativecommons.org/licenses/by/4.0/>.

this phase the twist-bend smectic C phase, SmC_{TB}, proposing the structure illustrated in Figure 8(a). A variant of this phase, having apparent structural differences (discussed later), was subsequently observed in CB6O.10, formed directly from the N_{TB} phase [7,23].

Although calorimetric studies of CB6O.10 clearly reveal the enthalpy change associated with the transition between the N_{TB} and this phase, in optical studies the phase transition is not easy to detect. In planar aligned cells, the stripe texture of the N_{TB} phase persists into the lower temperature SmC_{TB} phase (Figure 8(b)) and in cells with homeotropic anchoring, both phases appear black and hence are optically uniaxial. This suggests that in both phases there is an averaging of molecular orientation in space due to the formation of the helix. Similar textural observations were made also for the CB6OBeO m dimers. However, a lack of this optical uniaxiality need not discount the possibility of a SmC_{TB} phase, and for a helical structure in which the molecular orientations are not fully averaged over the helix – *ie.*

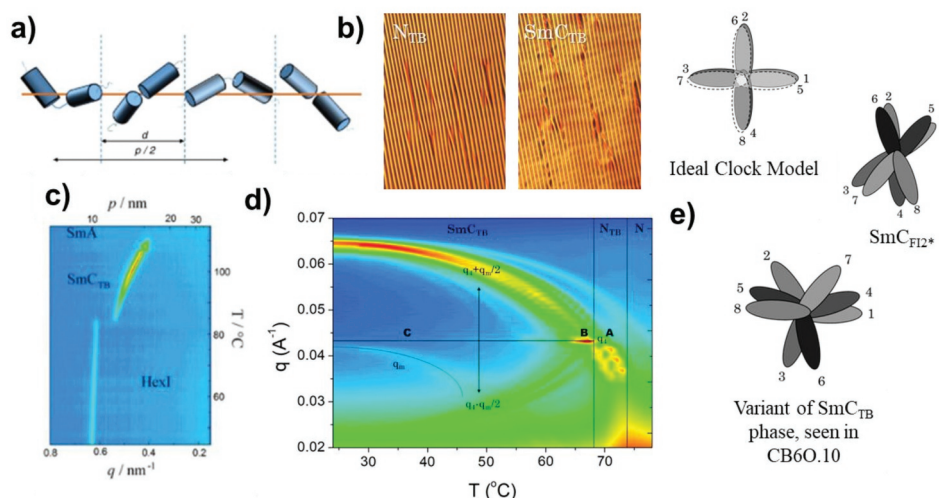


Figure 8. (a) Schematic representation of the proposed model for the SmC_{TB} phase of CB6OBel07; (b) Stripe textures seen for CB6O.10 in the N_{TB} (left) and SmC_{TB} (right) phases; (c) RSoXS pattern obtained for CB6OBel07; (d) Complex RSoXS pattern obtained for CB6O.10; (e) (top) Ideal clock model, with azimuthal rotation of 90° between consecutive molecules 1–4 and no rotation between layers; (middle) $\text{SmC}_{\text{F12}}^*$ phase, with rotation between consecutive molecules $\neq 90^\circ$ and very small rotation between layers (weak additional modulation) (bottom) proposed ‘distorted’ clock model of the SmC_{TB} phase in CB6O.10, with an azimuthal rotation $\neq 90^\circ$ and strong additional modulation, *ie.* the rotation between layers is significantly larger than in the $\text{SmC}_{\text{F12}}^*$ phase.

a ‘distorted’ clock structure – a schlieren texture may be observed. This is the case for CB6O.05, for which resonant soft X-ray measurements in the SmC phase reveal a helicoidal structure despite its optical resemblance to a conventional SmC_A phase [45]. This suggests the phase seen in CB6O.05 may be a second structural variant of the SmC_{TB} phase.

The key technique for identifying these helicoidal smectic phases, and importantly, to distinguish between a conventional SmC_A phase and a distorted-clock type smectic C_{TB} phase, is resonant soft X-ray diffraction (RSoXS). This method reveals periodic structures related to orientational order and has in the past been used to study the structure of helical phases which have a uniform electron density but differ with respect to the orientation of the molecules, such as the N_{TB} phase, the blue phases and subphases of the ferroelectric chiral smectic C^* phase [46]. The twist-bend nematic phase, and indeed the SmC_{TB} phases of CB6OBel07, CB6OBel08 and CB6O.05, show simple RSoXS patterns containing a single signal associated with the helical pitch (which typically corresponds to just a few smectic layers). In contrast, RSoXS measurements of CB6O.10 revealed the potential complexity of a SmC_{TB} -type phase, see Figure 8(c) [7]. The pattern consists of a large symmetrical splitting of the RSoXS signal and the simultaneous appearance of a weak harmonic signal, suggesting an additional nanoscale helical modulation is superimposed onto the basic, layered helical structure. Such an RSoXS pattern resembles that observed for the

chiral smectic C subphase $\text{SmC}_{\text{F12}}^*$, seen in highly chiral systems in a temperature range between the anticlinic and synclinic forms of the smectic C^* phase. In the $\text{SmC}_{\text{F12}}^*$ phase, molecules in four consecutive layers form a distorted helix, represented by a clock model. The ‘ideal’ clock model (with the azimuthal angle between consecutive molecules $\varphi = 90^\circ$) is shown in Figure 8(e) along with the distorted structure of $\text{SmC}_{\text{F12}}^*$, for which $\varphi \neq 90^\circ$. The additional helical modulation arises due to interactions between the chiral molecules – the whole 4-molecule ‘unit cell’ is rotated by some angle with respect to the next. We therefore propose a similar structure for our SmC_{TB} -type phase exhibited by CB6O.10, see Figure 8(e). However, our material is achiral. Therefore, if the structure of the phase does indeed resemble that of the $\text{SmC}_{\text{F12}}^*$ phase, the interactions driving its formation must be different and are presumably related to the molecular bend and resulting low bend elastic constant of the material. It is also notable that the additional helical modulation in the SmC_{TB} phase is on the nanoscale, while in the $\text{SmC}_{\text{F12}}^*$ it is within the optical range.

Helicoidal lamellar mesophases have also been observed in achiral, semi-rigid bent-core molecules with long terminal alkyl chains ($\text{C}_n\text{H}_{2n+1}$, where $n = 12$ –22), either spontaneously formed on cooling from preceding smectic phases ($n = 12$ –16) or induced by application of an electric field [8,47]. It is notable that these polar smectic phases have an even shorter pitch (<3 smectic layers) than our SmC_{TB} -type phases [47].

It is clear that the investigations into these twist-bend smectic phases are still in their preliminary stages, and the preparation of a large number of new materials is required to elucidate structure–property relationships for this class of phases, and specifically to establish the molecular features that drive their subtly different microstructures. Moreover, it will be intriguing to discover whether the structural similarity of these phases to the ferroelectric SmC* subphases will be matched in their physical properties.

3. Chirality and the N_{TB} phase

Mesophases exclusive to chiral liquid crystals arise because of molecular chirality – most commonly the presence of a chiral centre in a molecule but also through chiral axes or planes (axial chirality) – or are induced by the presence of a chiral dopant. Many of these chiral mesophases have a twisted or helical structure, for example, the chiral nematic N* or smectic C* phases, and hence have very different physicochemical properties compared to their achiral counterparts. The N_{TB} phase was the first example of such a heliconical superstructure formed in the absence of intrinsic molecular chirality in a system with no spatial ordering. As this formation of chirality is spontaneous, the probability of either handedness of helix forming is equal; thus, the N_{TB} phase consists of doubly degenerate locally chiral domains of opposite handedness and hence is a globally achiral phase. Our particularly intriguing research question was therefore how the N_{TB} phase, having spontaneous structural chirality, would respond at a microscopic level to the presence of molecular chirality. Meyer extended the elastic instability model of the N_{TB} phase to consider the effect of a chiral field introduced by chiral doping and predicted the removal of the double degeneracy of the chiral domains, with the new ground state of the N_{TB} phase being those domains with the same handedness as the dopant [48]. With increasing chiral doping the conical angle in this favoured helical state increases, while that in the unfavoured helical state decreases, and eventually the more favoured handedness dominates. The helical pitch is predicted to be essentially unchanged. Chiral doping is therefore predicted to increase the stability of the N_{TB}

phase. Longa and Tomczyk used minimum coupling Landau-de Gennes theory to reveal the possibility of a polar, chiral N_{TB} phase [49]. Only a handful of chiral nematic-twist-bend nematic transitions have been observed experimentally. These have included mixtures of twist-bend nematogens with a chiral dopant [11,50] as well as intrinsically chiral materials, with the latter being particularly rare and prior to our studies exclusive to cholesterol-based dimers [51].

Molecular chirality is most easily introduced to a liquid crystal dimer by the addition of a methyl branch to a carbon atom in a terminal chain. It became apparent in earlier work, however, that such branching destabilises nematic behaviour, by disrupting the interactions between the mesogenic units [36]. Thus, our design strategy for new chiral dimers was to begin with a liquid crystal dimer confirmed to exhibit the N_{TB} phase, 4-butoxyphenyl 4-[[6-(4'-cyano[1,1'-biphenyl]-4-yl)hexyl]oxy]benzoate, CB6OPEPO4 [36], and extend one of the mesogenic units by the addition of a phenyl benzoate fragment, with the aim of raising the liquid crystal transition temperatures such that the subsequent addition of the branch would not remove N_{TB} behaviour. This approach proved successful and we recently reported the first example of the chiral twist-bend nematic phase, N*_{TB}, below the N* phase in a material with a single chiral centre, (S)-CB6OPEP(2-Me)4, Figure 9 [34]. Moreover, we made the first direct comparison between the conventional N_{TB} and its chiral equivalent, the N*_{TB} phase, through the synthesis of the racemic version of CB6OPEP(2-Me)4, which exhibits an N_{TB}-N transition.

The N*_{TB} phase exhibits optical textures with lower birefringence than those observed for the achiral N_{TB} phase, suggesting an additional mechanism of averaging the molecular orientations. Textural features include stripes/'ropes', as seen in the N_{TB} phase formed by achiral molecules, but also several unique patterns, the origins of which are unclear. These include 'jagged' stripe textures, uniform areas with a faint 'diamond-like' pattern and chain-like defects, see Figure 10(a). A particularly intriguing observation is that although $T_{N^*1} \approx T_{N1}$, the N*_{TB} phase is consistently seen at a higher temperature than N_{TB} when comparing the chiral and racemic versions of CB6OPEP(2-Me)4 in mixtures with

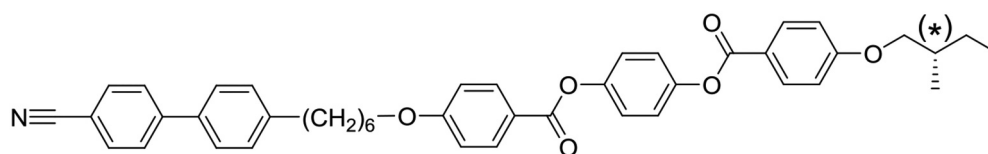


Figure 9. Molecular structure of (S)-CB6OPEP(2-Me)4.

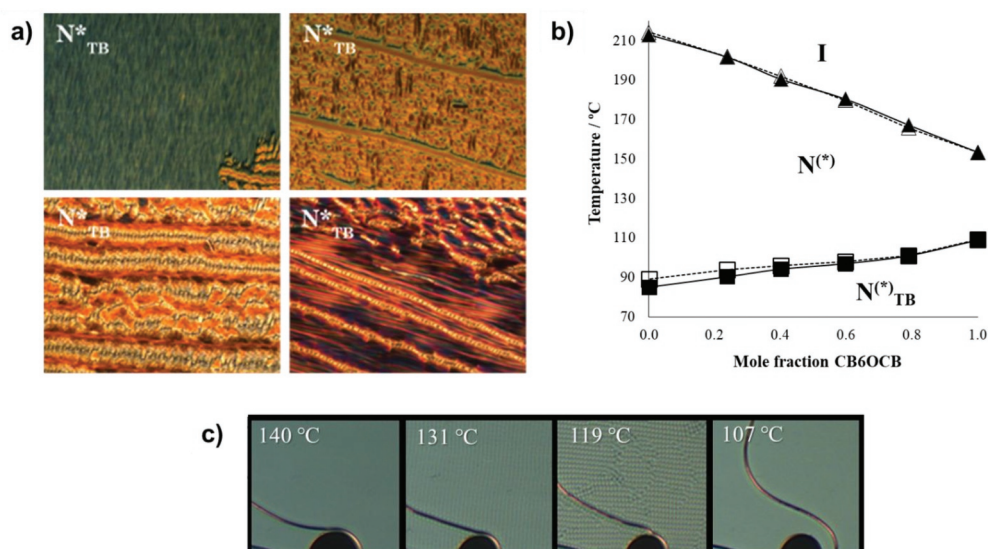


Figure 10. (a) Example textures of the N^*_{TB} phase; (b) Binary phase diagram of chiral (S)-CB6OPEP3PO(2-Me)₄ (unfilled shapes, dashed lines) and racemic CB6OPEP3P(2-Me)₄ (filled shapes, solid lines) in mixtures with CB6OCB; (c) Progression of square lattice pattern in the N^* phase prior to $T_{N^*_{TB}N^*}$ in a 40/60 mixture of (S)-CB6OPEP3PO(2-Me)₄/CB6OCB.

CB6OCB, see Figure 10(b), and currently the largest observed difference is $\sim 10^\circ\text{C}$ [52]. This is in accord with Meyer's elastic instability model [48], and indeed suggests that the double degeneracy of the helical twist sense in the N^*_{TB} phase is removed by the intrinsic molecular chirality and the favoured twist sense becomes more stable. This may be a consequence of differences in the mechanism in forming the heliconical structure of the N^*_{TB} phase, and depends on the structure of the preceding phase. A second curiosity is the formation of a square lattice pattern in the N^* phase over a temperature range of several degrees above, before disappearing prior to, the N^*_{TB} - N^* phase transition, see Figure 10(c). A similar phenomenon had been reported for chirality-doped bent-core materials and may be attributed to a non-monotonic dependence of the bend elastic constant [53].

There is considerable application potential for materials combining the properties of the chiral and twist-bend nematic phases. An electrically tunable helical pitch may be used in, for example, tunable lasers or energy-saving smart-windows. It has been demonstrated in a proof-of-concept study that mixtures containing chirally doped nematogens with a sufficiently low bend elastic constant (ie. twist-bend nematogens) do indeed possess an electrically tunable pitch in their cholesteric phase [54,55]. However, use of such mixtures in liquid crystal applications can introduce numerous problems including phase separation of the mixture components and incompatibility issues, and thus it would be desirable to use a less complex mixture, or

indeed, a single component capable of exhibiting both the N^* and N^*_{TB} phases.

4. Hydrogen-bonding and the N_{TB} phase

The majority of twist-bend nematogens are covalently bonded oligomeric or bent-core materials, but we have also reported the observation of both the N_{TB} and the N^*_{TB} phases in supramolecular liquid crystals (SLCs), specifically, bent-shaped complexes created through hydrogen bonding (H-bonding). The preparation of supramolecular mesogens *via* H-bonding is a flexible and efficient alternative to covalent bonding, and a convenient way of adding functionality to a molecule in an effective and controllable manner. Moreover, it is useful for introducing chirality to a system as it avoids the risk of partial racemisation during the synthetic process. H-bonding emerged as a means of constructing liquid crystal systems in the early 1950 s, with one of the earliest reports detailing the phase behaviour of the *n*-alkoxybenzoic acids (*n*OBA)s [56]. Their mesogenic behaviour was attributed to the formation of calamitic-like, symmetric homomeric complexes of two equivalent benzoic acid fragments with a supramolecular core formed *via* hydrogen bonding. We extended this approach, reporting the formation of the first supramolecular twist-bend nematogen, CB6OBA, in which two acid dimers hydrogen-bond to form a bent supramolecular trimer, see Figure 11 [31].

The first heterodimeric rod-like complexes formed *via* hydrogen bonding between unlike hydrogen-bond donors

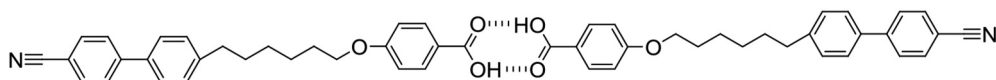


Figure 11. The first supramolecular twist-bend nematogen, CB6OBA.

and acceptors – for example, benzoic acid and pyridyl-based fragments – were described by Kato and Frechet in the late 1980s [30]. In 2018, we reported the first example of spontaneous chiral symmetry breaking through the mixing of achiral components; specifically, the induction of the N_{TB} phase through molecular recognition in mixtures containing unlike H-bond donors and acceptors: the n OBA ($n = 4,5$) and 1OB6OS, respectively, **Figure 12** [57].

We later extended this study to include more members of the n OBA series ($n = 1-10$) and a second H-bond acceptor, CB6OS, to create two homologous series of new supramolecular liquid crystals, see **Table 1** [32,33]. By analogy with the covalently assembled systems discussed earlier, extending the terminal chain attached to the hydrogen-bond donor aimed to drive the formation of smectic phases.

Several members of the 1OB6OS: n OBA and CB6OS: n OBA series show N_{TB} phases over a broad temperature range despite the H-bond acceptor not being liquid crystalline and the donor exhibiting only the conventional

N phase. Those with short values of n exhibit N and N_{TB} phases and for longer chains the N_{TB} phase is lost and a series of up to four smectic phases is seen below the N phase. In the CB6OBA: n OS mixtures (where n OS are short, non-mesogenic stilbazole-based materials, see **Table 1**), considered to be the ‘reverse’ of the CB6OS: n OBA complexes, the N_{TB} phase is exhibited up to $n = 7$, whereas mixtures with $n > 7$ again show a Sm-N transition. Selected mixtures also exhibited N_{TB} -smectic transitions, for example, CB6OBA: n OS with $n = 4-7$ cooled from the N_{TB} phase into a SmC phase, although unfortunately, the monotropic nature of this phase precluded study by RSoXS. This is true also for CB6OS: n OS mixtures with $n = 7-10$ which exhibit an SmC-SmA transition.

Temperature-dependent FT-IR spectroscopy confirmed the presence of strong hydrogen bonding in the mixtures and revealed the existence of a complex equilibrium between various species, **Figure 13(a)** [32,58]. The amounts of the various H-bonded species present and how these shift on cooling from the

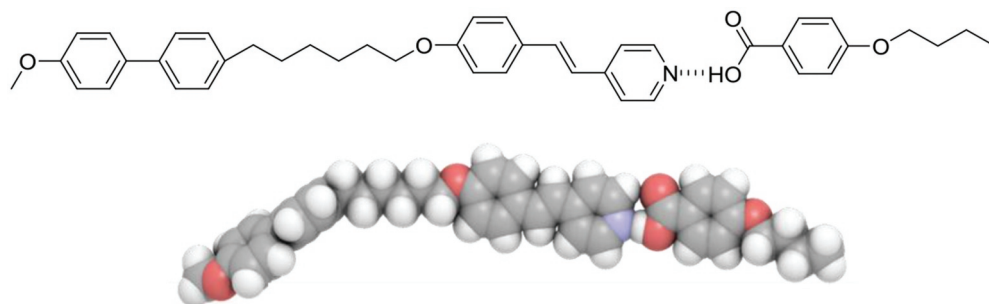


Figure 12. Heterocomplex formed by H-bonding between 1OB6OS and 4OBA.[57].

Table 1. Hydrogen-bond acceptors and hydrogen-bond donors discussed here.

H-bond Acceptors	H-bond Donors
<p>1OB6OS</p>	<p>CB6OBA</p>
<p>CB6OS</p>	<p>nOBA ($n = 1-10$, (S)-(2-Me)4)</p>
<p>nOS ($n = 1-10$, (S)-(2-Me)4)</p>	

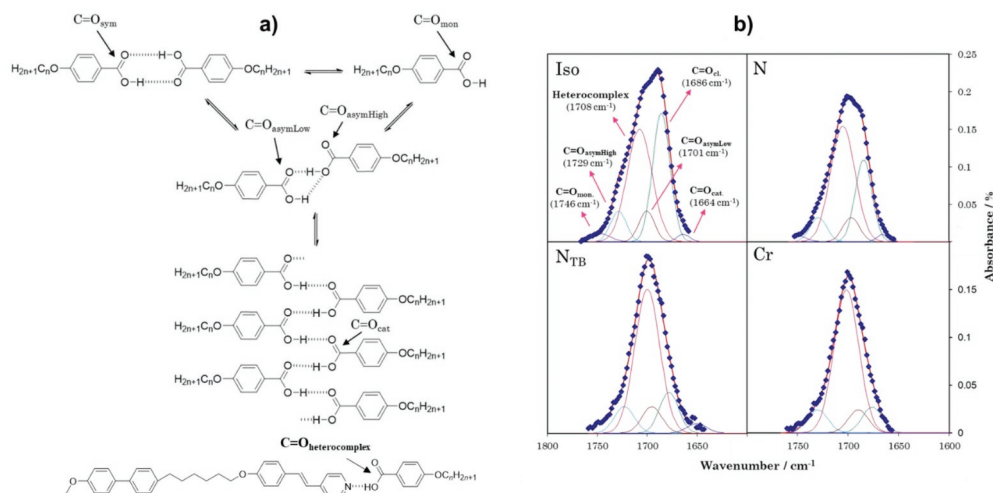


Figure 13. (a) Various acid species present in a complex equilibrium with the heterocomplex; (b) Deconvolution of the C = O stretching region in the FT-IR spectrum for 10B6OS:4OBA (50:50 mixture).

isotropic liquid through the liquid crystal phases were measured semi-qualitatively by the deconvolution of the complex C = O stretching region ($1650\text{--}1740\text{ cm}^{-1}$) into six Gaussian peaks representing the different individual contributions of each species to the overall band shape, see Figure 13(b) [59,60]. The bent-shaped heterocomplex formed between the unlike benzoic acid and stilbazole fragments is the dominant species in the observed mesophases, but various homomeric acid dimers are also present in significant amounts and thus may play a role in the stabilisation of these phases [32,57].

In general, we find that the behaviour of these supramolecular liquid crystals is reminiscent of that of their covalently bonded analogues. Similar to the CB6O(O) *m* series discussed earlier, X-ray diffraction studies revealed a progression of the local molecular packing from intercalated, to frustrated, to monolayer with no effect on the stability of either nematic phase, further evidence that intercalation is not key in forming the N_{TB} phase. Smectic phases are favoured by long terminal chains, a common observation in non-symmetric liquid crystal dimers, and indeed this is also seen for the CB6OBeIom series. Birefringence measurements strongly resemble those for CB6OCB: namely, a departure from critical dependence several degrees above T_{NTBN} caused by the instantaneous formation of local heliconical states and a decrease in birefringence at T_{NTBN} as a consequence of the tilting and averaging of the molecular positions around the helical axis.

Additional studies on H-bonded materials have included the supramolecular trimers CB6OBA:CB6OS and CB6OBA:10B6OS, which exhibit N and N_{TB} phases. These are the first H-bonded trimers consisting of unlike donor and acceptor fragments which exhibit

N_{TB} behaviour [32]. Most recently, we have explored complexes in which the H-bonded donor or acceptor is chiral. CB6OS:(S)-(2-Me)4OBA and CB6OBA:(S)-(2-Me)4OS both exhibit an N* to N*_{TB} phase transition and are the first examples of the chiral N*_{TB} phase driven by H-bonding [61].

5. Summary

Summarising, it is evident that our investigations into relationships between molecular structure and the incidence of the twist-bend nematic phase have revealed many unique and unprecedented features. Particularly notable observations include the first twist-bend nematic-nematic transition controlled by light, the first example of spontaneous symmetry breaking driven by molecular recognition, and the first series of twist-bend nematogens to show a change in local packing structure from intercalated to bilayer. In addition, we have reported the first dimers to exhibit short-pitch heliconical smectic phases – the SmC_{TB} phases – and new examples of the chiral twist-bend nematic phase, N*_{TB}, in both covalently and hydrogen-bonded materials. In general, these projects have reaffirmed previous conclusions that the main structural feature required for the observation of the twist-bend phases is molecular curvature; while the dimeric structure need not be symmetric, the bend must be spatially uniform. However, with some of our dimers exhibiting monolayer, partially- and fully-bilayer N_{TB} phases, we have shown that local molecular intercalation does not appear to be as important a feature in driving its formation as previously thought.

While our understanding of the N_{TB} phase has progressed significantly over the past decade, it is clear that

each advance introduces many new questions and there remains much to discover about these fascinating twist-bend phases.

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Disclosure statement

No potential conflict of interest was reported by the author(s).

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