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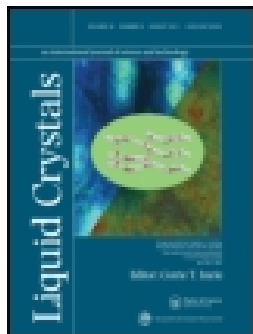
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## Developments in liquid-crystalline dimers and oligomers

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## Developments in liquid-crystalline dimers and oligomers

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### ABSTRACT

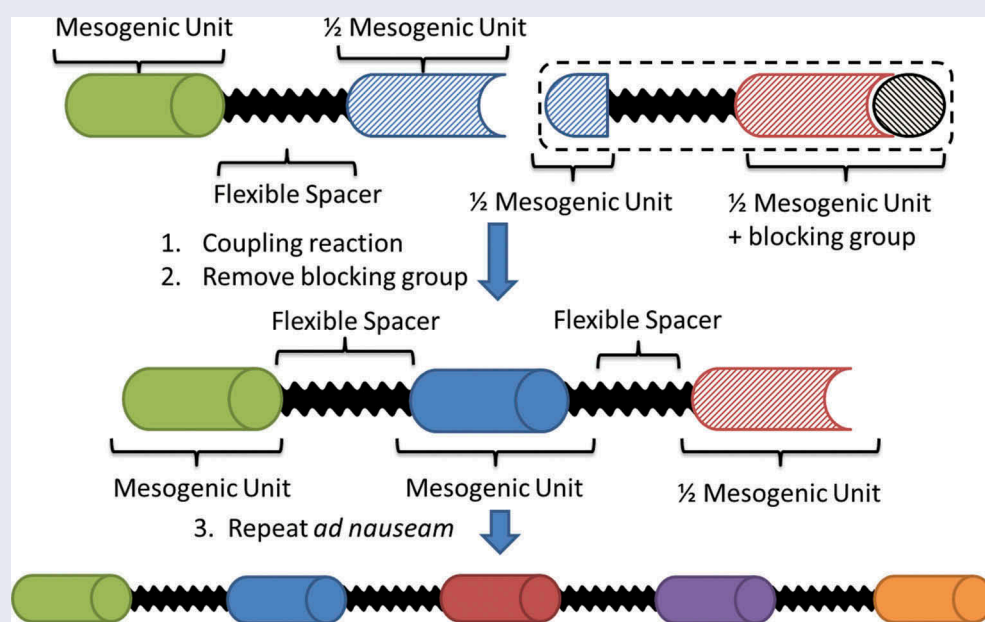
Liquid-crystalline dimers and bimesogens have attracted much attention due to their propensity to exhibit the spontaneously chiral twist-bend mesophase ( $N_{TB}$ ), most often by dimers with methylene spacers. Despite their relative ease of synthesis, the number of ether-linked twist-bend materials significantly lags behind those of methylene-linked compounds. In this work, we have prepared and studied a range of ether-linked bimesogens homologous in structure to the FFO9OCB; as with methylene-linked systems, it appears that it is molecular topology and the gross molecular shape that are the primary drivers for the formation of this phase of matter. Dimers and bimesogens are well studied within the context of the twist-bend phase; however, present understanding of this mesophase in oligomeric systems lags far behind. We report our recent efforts to prepare further examples of oligomeric twist-bend nematogens, including further examples of our 'n+1' methodology, which may allow the synthesis of high-purity, monodisperse materials of any given length to be prepared. We have observed that there is a tendency for these materials to exhibit highly ordered soft-crystalline mesophases as opposed to the twist-bend phase.

### ARTICLE HISTORY

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### KEYWORDS

Liquid crystals; oligomeric;  $N_{TB}$ ; dimer; twist-bend nematic



### Introduction

Presently, the majority of known low-molar-mass liquid crystals have calamitic (rod-like) molecular structures. Joining two *identical* rod-like units together affords a dimer, three units afford a trimer and  $n$  units afford an oligomer [1–4]. However, if we join together  $n$  mesogenic units that are not identical, such as rod-

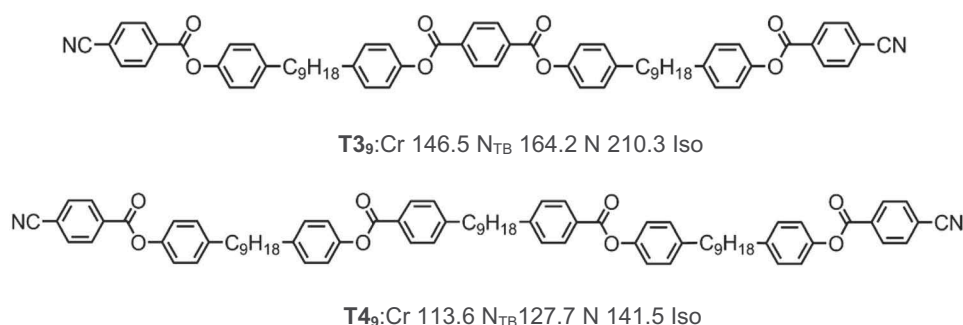
disc systems [5], then it is preferable to use the terms bimesogen ( $n = 2$ ), trimesogen ( $n = 3$ ), tetramesogen ( $n = 4$ ) and oligomesogen. There has been something of resurgence in interest in liquid crystal dimers in recent years, due largely to the observation of thermodynamically stable twist-bend phases in these systems [6–38]. This has motivated the synthesis of a number of novel compounds, and present experimental results

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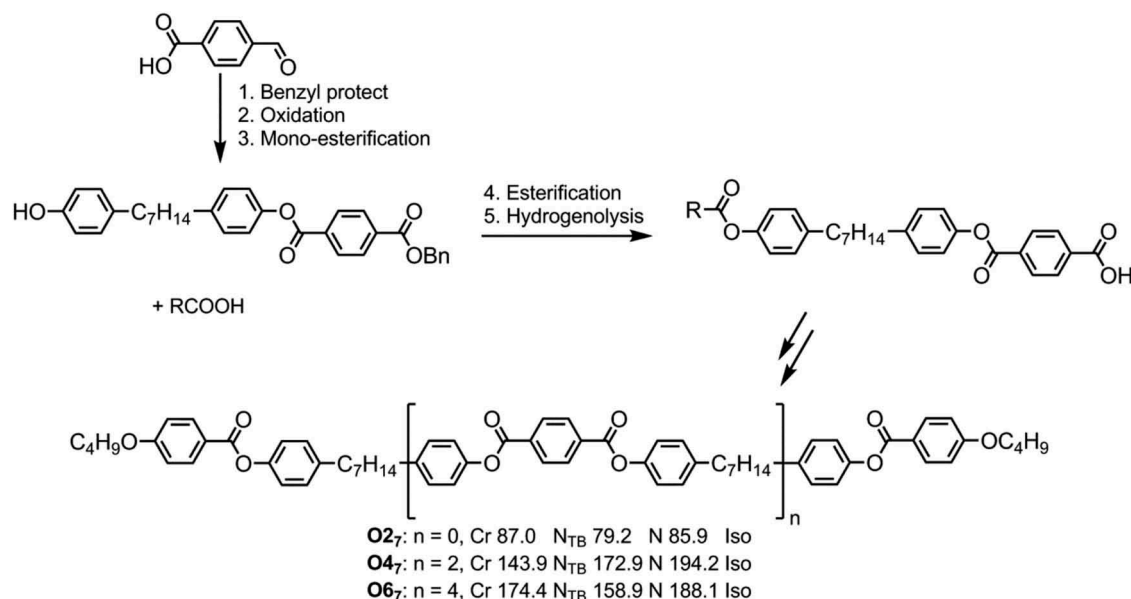
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**Figure 1.** The molecular structures and transition temperatures (°C) of the trimer **T<sub>3</sub>**, (top) and the tetramer **T<sub>4</sub>**, (bottom) [53,54].



**Figure 2.** Truncated synthetic pathway to **O<sub>4</sub>** ( $n = 2$ ) and **O<sub>6</sub>** ( $n = 4$ ) via the use of a phenolic intermediate bearing a masked carboxylic acid [55]. Transition temperatures are given in °C, and the related dimer 'O<sub>2</sub>' is given for comparison [56].

indicate that the twist-bend phase is primarily driven by topology [39], with the thermal stability having a dependency on the intermesogen angle [40,41]. Several aspects of the N<sub>TB</sub> phase have been reviewed recently [28,32,42,43]. It has been demonstrated for materials with nonamethylene and heptamethylene central spacers that there is a linear relationship between T<sub>N<sub>TB</sub>-N</sub> and T<sub>N-Iso</sub> [39]. It has been observed that many functional groups – including the SF<sub>5</sub> group – can be incorporated into the structure of a suitable dimer without loss of the N<sub>TB</sub> phase. Last, the twist-bend nematic phase – in dimers and bimesogens at least – is found mostly for methylene-linked materials, although a number of other linking groups are known to yield materials that afford this mesophase [7,21,22,33,44–49]. In the first part of this paper, we present the latest part of our study into the structure–property relationships of *bis* ether-linked dimers and bimesogens that exhibit the twist-bend phase.

Following the identification of the N<sub>TB</sub> phase in dimers [10], and bent-core materials [50], Jansze et al. reported in 2014 on a novel hydrogen-bonded liquid-crystalline trimer that also exhibited the twist-bend nematic phase [51]. This material, known as CB5OBA, has an odd-parity spacer unit – the homologous even-parity material does not exhibit the N<sub>TB</sub> phase, mirroring trends seen for dimers and bimesogens. Shortly after this Wang et al. reported a hybrid calamitic/bent-core trimesogen that exhibited the N<sub>TB</sub> phase [52]. This material has two cyanobiphenyl mesogenic units appended to a central resorcinol-derived bent-core-type mesogenic unit. In 2015, a methylene-linked tetramesogen (**T<sub>4</sub>**, Figure 1) was reported by us group; this material exhibits enantiotropic nematic and twist-bend nematic mesophases [53], as does the related linear trimesogen (**T<sub>3</sub>**, Figure 2) [54]. Both **T<sub>3</sub>** and **T<sub>4</sub>** are prepared in the same manner; an intermediate with one complete mesogenic unit and

one 'half-complete' mesogenic unit bearing a phenol is esterified with an appropriate dicarboxylic acid to yield a trimer/tetramer.

Unfortunately, this method is ill suited to the preparation of higher oligomesogens due to the lack of available dicarboxylic acids that will yield pentamesogens, hexamesogens, etc. The aspiration to prepare higher oligomesogens than tetramesogens was later realised using chemistry inspired by a simple polyester condensation; a chemical intermediate (prepared in three steps from 4-carboxybenzaldehyde) was devised (Figure 2), which bears a free phenol and a carboxylic acid masked with a benzyl group. The phenol is esterified with a suitable carboxylic acid; hydrogenolysis liberates the carboxylic acid group, which is then free to partake in another esterification reaction. Finally, esterification of the free acid with a suitable *bis* (4-hydroxyphenyl) alkane affords the symmetrical dimers. To date this has been used to prepare a tetramesogen (**O4<sub>7</sub>**) and a hexamesogen (**O6<sub>7</sub>**), with the synthesis of higher oligomers currently ongoing; both **O4<sub>7</sub>** and **O6<sub>7</sub>** exhibit nematic and twist-bend mesophases.

This approach is not without drawbacks; the use of *bis* phenyl terephthalate mesogenic units is especially problematic due to transesterification. We therefore sought to prepare materials with biphenyl mesogenic units which for obvious reasons do not undergo this unwanted side reaction, if possible avoiding the obvious and laborious lithiation/borylation/cross-coupling stratagem. In the second part of this paper, we present a novel synthesis of liquid-crystalline oligomers with mixed ether/methylene-linking groups using a derivative of the 'n+1' methodology used by us to prepare the hexamesogen **O6<sub>7</sub>** [55].

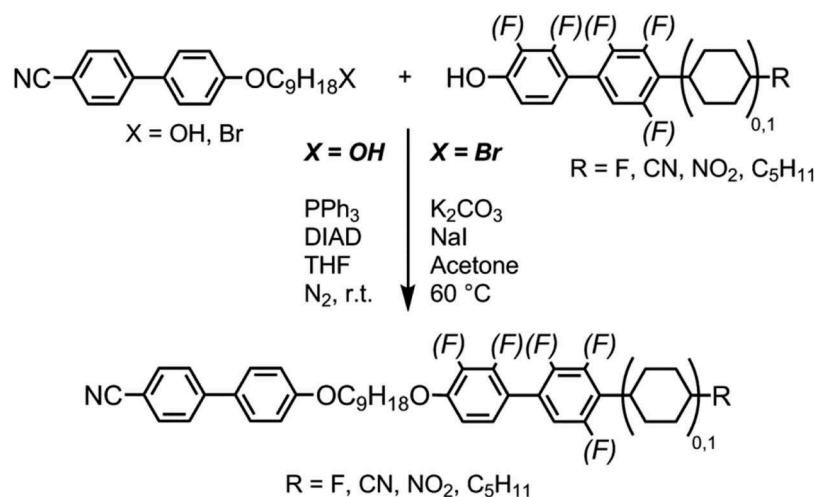
## Experimental

Materials were characterised by nuclear magnetic resonance (NMR) ( $^1\text{H}$ ,  $^{13}\text{C}\{^1\text{H}\}$  and where appropriate  $^{11}\text{B}\{^1\text{H}\}$ ,  $^{19}\text{F}$ ), mass spectrometry and Fourier-transform infrared (FT-IR), with purity of dimers assessed by either combustion analysis and reverse-phase high performance liquid chromatography (HPLC). Computational chemistry was performed in Gaussian G09 revision e.01 [57]. The experimental set-up used for X-ray scattering experiments has been described previously [58,59]. Details of chemical synthesis and characterisation are given in the supplementary information to this article. Compounds were synthesised as depicted in Schemes 1-4.

## Results and discussion

The unsymmetrical bimesogens were prepared via one of the two methods, either the Williamson etherification of 4-(9-bromononyloxy)-4'-cyanobiphenyl with an appropriate phenol, or the Mitsunobu etherification of 4-(9-hydroxynonyloxy)-4'-cyanobiphenyl with an appropriate phenol as shown in Scheme 1. Both 4-(9-bromononyloxy)-4'-cyanobiphenyl and 4-(9-hydroxynonyloxy)-4'-cyanobiphenyl were available in house, having been prepared previously [60]. Most phenols were available in house; however, 4-hydroxy-4'-nitrobiphenyl was prepared as described previously [61], and 4-fluoro-4'-hydroxybiphenyl was purchased from TCI.

The liquid-crystalline properties of all materials were analysed by a combination of polarised optical microscopy (POM) and differential scanning calorimetry (DSC) (Table 1). Of the compounds presented in Table 1, both **1** (CBO9OCB) and **8** (FFO9OCB) are



Scheme 1.

**Table 1.** Transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpies of transition ( $\text{kJ mol}^{-1}$ ) for **1–13** as determined using a Mettler Toledo DSC822e at a heat/cool rate of  $10^{\circ}\text{C min}^{-1}$ . Phase identification was made by POM as described in the text.

$\text{RC}_9\text{H}_{18}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{CN}$

No.	R =	Cr		$\text{N}_{\text{TB}}$		N		Iso
<b>1</b>		•	143.4 [53.9]	#	–	•	171.8 [2.7]	•
<b>2</b>		•	110.3 [76.8]	(•	99.2) [0.06]	•	150.4 [2.4]	•
<b>3</b>		•	123.6 [49.4]	(•	96.3) [0.05]	•	150.7 [3.8]	•
<b>4</b>		•	98.3 [30.0]	(•	97.6) [0.07]	•	152.0 [1.5]	•
<b>5</b>		•	86.3 [33.6]	(•	71.6) [0.01]	•	134.0 [2.5]	•
<b>6</b>		•	72.7 [40.6]	(•	31.2) [0.03]	•	98.0 [1.30]	•
<b>7</b>		•	87.7 [47.1]	(•	61.5) [0.05]	•	116.8 [4.8]	•
<b>8</b>		•	81.1 [42.6]	(•	50.0 <sup>a</sup> )	•	112.5 [2.0]	•
<b>9</b>		•	73.9 [38.6]	(•	45.0 <sup>a</sup> )	•	107.9 [1.6]	•
<b>10</b>		•	83.8 [41.7]	–	–	•	91.3 [0.4]	•
<b>11</b>		•	81.0 [43.1]	•	89.2 [0.05]	•	194.2 [3.7]	•
<b>12</b>		•	103.2 [15.3]	•	127.1 [0.03]	•	238.3 [0.9]	•
<b>13</b>		•	101.4 [21.6]	•	136.9 [0.01]	•	235.8 [2.3]	•

Phase transitions in parenthesis are monotropic, i.e. they occur below the melting point of the sample.

<sup>a</sup>The  $\text{N}-\text{N}_{\text{TB}}$  transition temperature was taken from microscopy as both compounds **8** and **9** readily crystallised during DSC experiments at  $\sim 55^{\circ}\text{C}$  and  $\sim 48^{\circ}\text{C}$ , respectively.

#The  $\text{N}_{\text{TB}}$  phase could be observed by ejecting the sample into liquid nitrogen to facilitate rapid cooling without crystallisation; however, this method is unsuitable for determination of a transition temperature.

already known in the literature; the former exhibits a nematic phase whereas the latter exhibits an additional monotropic twist-bend ( $\text{N}_{\text{TB}}$ ) phase [48]. Knowing that replacement of one of the 4-cyanobiphenyl mesogenic units of **1** with the 2'-4-difluorobiphenyl unit leads to the formation of the twist-bend phase serves as a starting point for our present study into structure–property relationships.

Compound **2**, in which a fluorine atom has been positioned *ortho* to the nitrile group of one mesogenic unit, exhibits a monotropic twist-bend phase and, relative to the parent material, reduced melting and clearing points. Compound **3** is an isomer of **2** in which the position of the fluorine atom has been varied, and although this leads to a change in the melting point both the clearing point and  $\text{N}-\text{N}_{\text{TB}}$  transition temperatures are virtually unchanged. For compound **4** a nitro group has replaced the cyano group of one mesogenic unit; this leads to a reduced melting point; however,

both the  $\text{N}-\text{I}$  and  $\text{N}_{\text{TB}}-\text{N}$  transition temperatures are comparable to those of **2** and **3**. Replacement of a single nitrile with a fluoro-group affords compound **5**; this leads to significantly lower melting and clearing points than **1**, whereas the  $\text{N}_{\text{TB}}-\text{N}$  transition temperature is around  $25^{\circ}\text{C}$  lower than for **2–4**. Although the  $\text{N}-\text{I}$  phase transition was invariably found to be first order the  $\text{N}_{\text{TB}}-\text{N}$  transition was only weakly first order, with the associated enthalpies of transition being significantly smaller for the latter than the former. Compound **8** was reported previously to exhibit both nematic and  $\text{N}_{\text{TB}}$  mesophases; we opted to resynthesise it to use as a standard for comparative purposes. The transition temperatures we obtain are essentially identical, albeit with a marginally higher melting point, to those reported previously (Cr  $72.5$   $\text{N}_{\text{TB}}$   $49.9$   $\text{N}$   $112.4$  Iso). When studied by DSC, the material was invariably found to recrystallise prior to the  $\text{N}-\text{N}_{\text{TB}}$  transition (see thermogram in Figure 3). However, it was possible to



observe by microscopy that the transition occurs around 50°C. Similarly, for compound **9** we observed the material readily crystallised during DSC study, but it was possible to obtain a reproducible temperature value of 45°C for the N<sub>TB</sub>-N transition by microscopy, although this often occurred simultaneously with crystallisation.

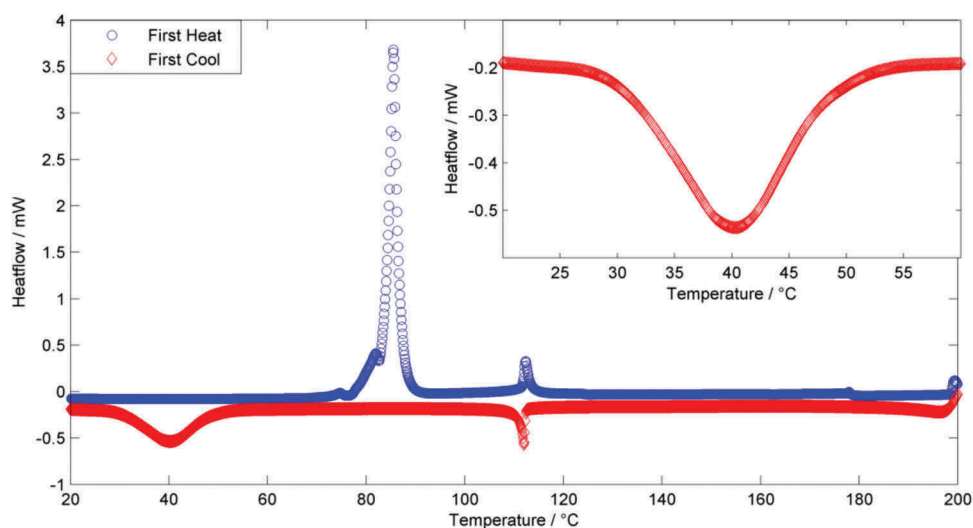
The incorporation of a third fluorine atom into the structure of **6** leads to compound **10**; this material has a comparable melting point to the parent. However, the clearing point is dramatically reduced and the twist-bend phase is not observed because even with rapid cooling the sample crystallises directly from the nematic phase. Representative photomicrographs are given in Figure 4.

Thus, we opted to prepare a material incorporating the 2,3-difluorobiphenylcyclohexyl (DFBC) unit employed in the first ether-linked bimesogen to exhibit the N<sub>TB</sub> phase, FBO<sub>11</sub>ODFCB<sub>3</sub> [62]. We have found previously that dimers and bimesogens incorporating the DFBC unit have a strong tendency to exhibit the twist-bend nematic phase [63]. Increasing the aspect ratio of the mesogenic units of a dimesogen/bimesogen has been demonstrated previously to confer large increases to both the clearing point and, if present, the N<sub>TB</sub>-N transition temperature [31,39,64,65], and with this in mind, we prepared the two mixed biphenyl/terphenyl bimesogens **12** and **13**. Compounds **11**, **12** and **13** were found to exhibit enantiotropic nematic and N<sub>TB</sub> mesophases. Representative photomicrographs are given in Figure 5. In the case of the biphenyl/terphenyl bimesogens **12** and **13** the clearing points are significantly higher than the analogous biphenyl/biphenyl dimers **1** and **2**. The thermal behaviour of

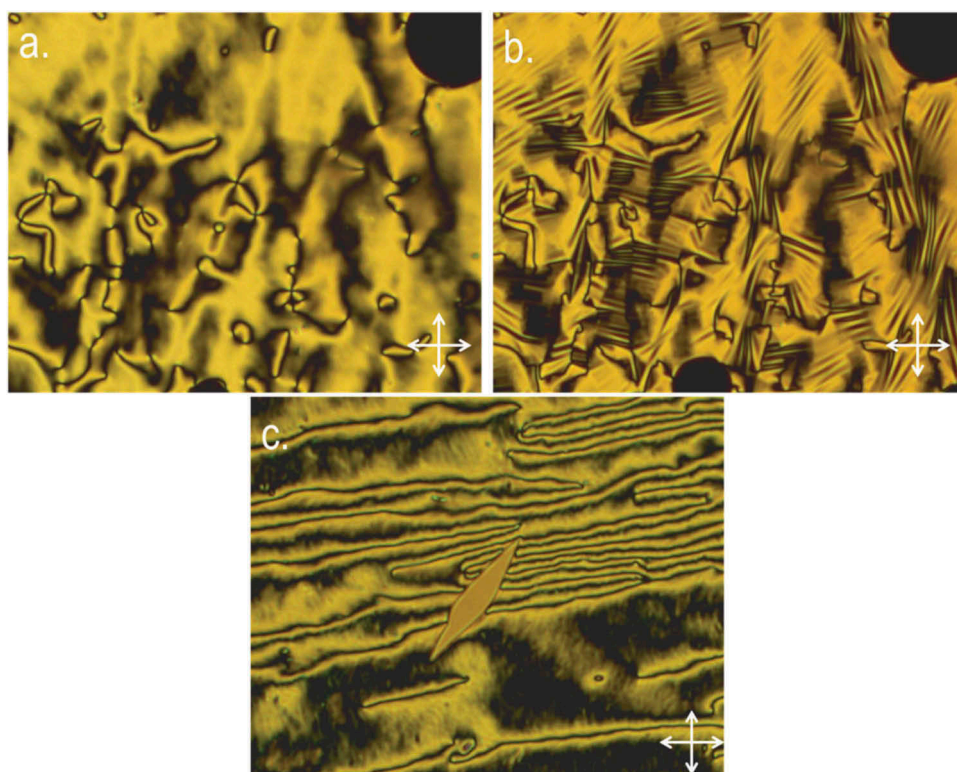
compound **11**, which has a nonamethylene spacer and a pentyl terminal chain, is remarkably close to that of the homologous dimer reported by us previously with an undecamethylene spacer and a propyl terminal chain (Cr 83.5 N<sub>TB</sub> 83.3 N 190.1 Iso) [63].

The ability of ether-linked dimers and bimesogens to exhibit the twist-bend nematic phase has once again been firmly demonstrated. We next turned our attention to incorporating ether linkages, as well as either alkyne or methylene linkers, into tetramesogenic materials with a view to obtaining further examples of oligomeric twist-bend materials. The two hydroxyl-terminated alkoxybiphenyls (**i1** and **i2**) used in Scheme 2 were prepared as described previously [58], and the preparation of 1,9-bis(4-bromophenyl)nona-1,8-diyne (**i6**) was reported in a previous publication [40]. Palladium on carbon (5%) poisoned with diaminoethane (denoted as Pd/C{En} in the text) was prepared by us previously [40,66].

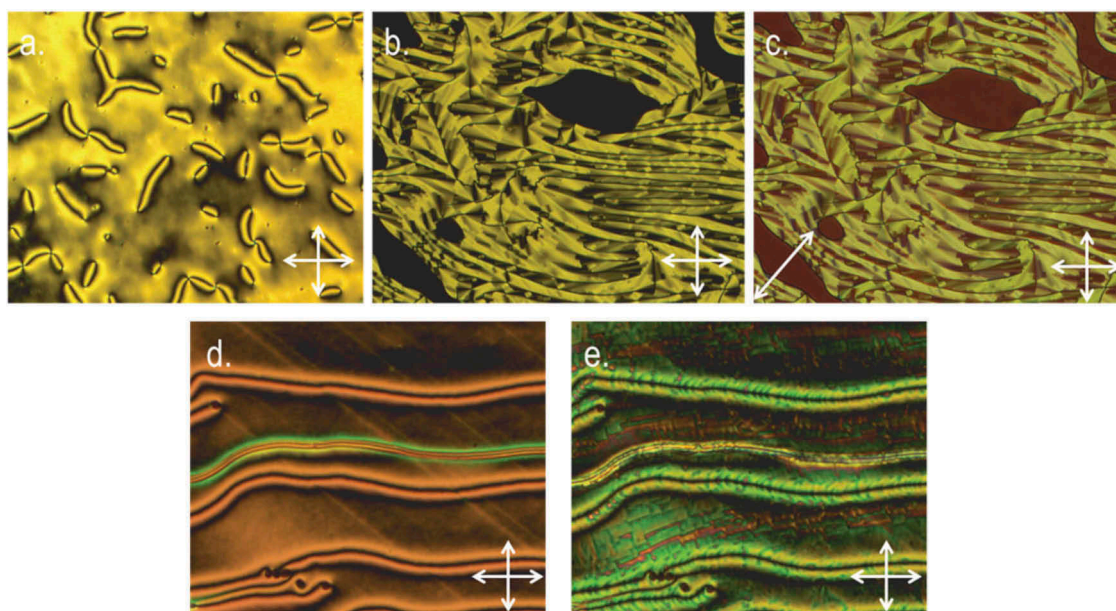
As shown in Scheme 2, the Mitsunobu etherification of **i1** and **i2** with the pinacol ester of 4-hydroxyphenyl boronic acid (**i3**) afforded **i4** and **i5**. The Suzuki coupling of both **i4** and **i5** with **i6** proceeded smoothly to afford the tetramesogens **14** and **15**, respectively. Using biphenyl mesogenic units rather than the phenylbenzoate or *bis* teraphthaloyl benzoate effectively eliminates the problem of transesterification. The hydrogenation of **1** and **2** with palladium on carbon poisoned with diaminoethane afforded the tetramesogens **3** and **4**, respectively. The reaction proceeded smoothly without hydrodefluorination or reduction of the nitrile to a benzylamine and was complete within 2 h in all cases. The products (**16/17**) and the starting materials (**14/**



**Figure 3.** (Colour online) DSC thermogram for compound **8** (FFO9OCB) obtained at 20°C min<sup>-1</sup> with an expansion showing the region between 20°C and 60°C during which the sample recrystallises; however, with rapid uncontrolled cooling we can observe a N<sub>TB</sub>-N transition occurring simultaneously with crystallisation at around 50°C.

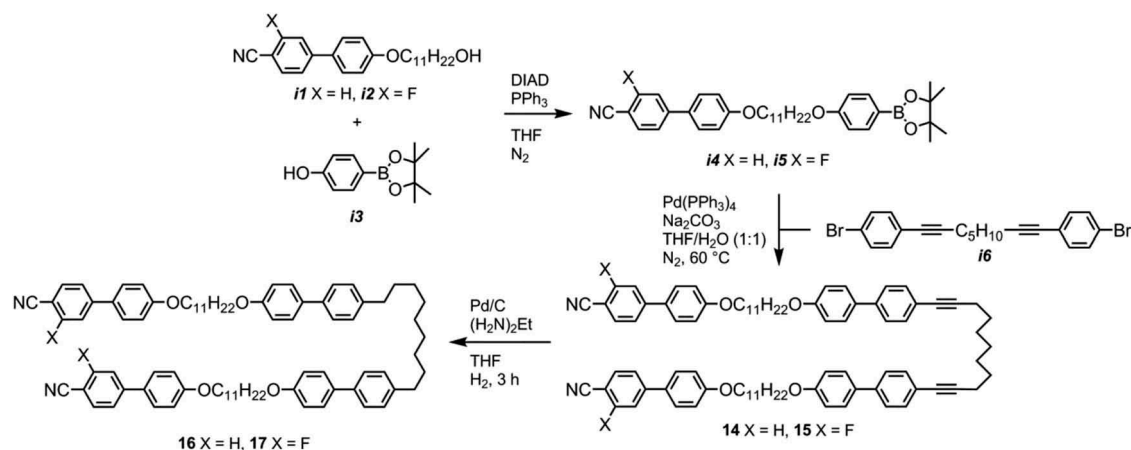


**Figure 4.** (Colour online) Photomicrographs (100 $\times$ , crossed polarisers) of (a) the *schlieren* texture of the nematic phase of **7** at 71 $^{\circ}$ C, (b) the same region showing the blocky texture of the twist-bend phase of **7** at 56 $^{\circ}$ C and (c) the nematic phase of **8** (FFO90CB) at 56 $^{\circ}$ C, cooled at 10 $^{\circ}$ C min $^{-1}$  showing crystallisation of the sample when not rapidly cooled.



**Figure 5.** (Colour online) Photomicrographs (100 $\times$ , crossed polarisers) of (a) the *schlieren* texture of the nematic phase of **11** at 180 $^{\circ}$ C, (b) various optical textures of the N<sub>TB</sub> phase at 75.8 $^{\circ}$ C, (c) the same region with a  $\frac{1}{4}$  waveplate inserted, (d) the *schlieren* texture of the nematic phase of **13** confined in a 9  $\mu$ m cell with surfaces treated for homeotropic alignment and (e) the same region of **13** cooled into the N<sub>TB</sub> phase at 121 $^{\circ}$ C.





Scheme 2.

**15**) could be easily distinguished by <sup>1</sup>H NMR spectroscopy due to the difference in chemical shift of a CH<sub>2</sub> adjacent to an aromatic ring versus a CH<sub>2</sub> adjacent to an alkyne, as well as differences in two of the aromatic proton environments as shown in Figure 6. Furthermore, workup of the hydrogenation was trivial and chromatography free; the reaction mass was filtered through a packed bed of celite, dried *in vacuo*, redissolved in DCM onto which ethanol was layered, affording the tetramesogens **16** and **17** as microcrystalline solids.

The liquid-crystalline behaviour of the tetrameso-gens **14**–**17** was determined using a combination of POM and DSC. Given the high viscosity of these materials, even in the isotropic liquid, we were unable to load the samples into the capillary tubes required for small angle X-ray scattering (SAXS) analysis, and so the phase identification was made solely on optical microscopy. Representative photomicrographs are presented in Figure 7.

As shown in Table 2 all three tetrameric materials exhibited smectic C and X phases, with **15**, **16** and **17**

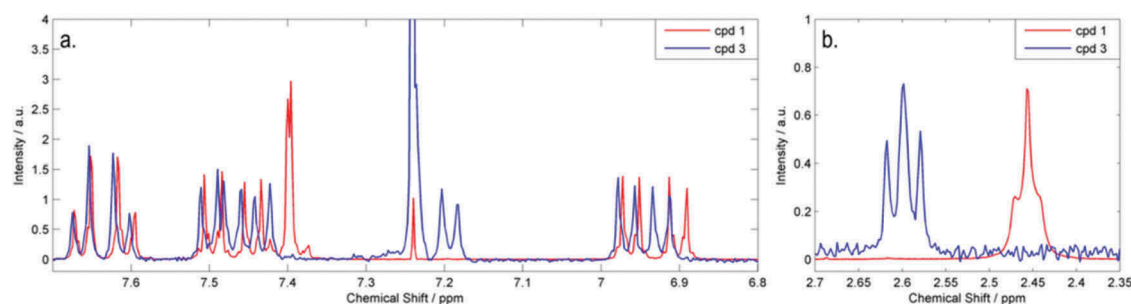


Figure 6. (Colour online) Overlaid <sup>1</sup>H NMR spectra (400 MHz, CDCl<sub>3</sub>) of compounds **14** (red) and **16** (blue) showing the change in multiplicity in the aromatic region ((a) 6.8–7.8 ppm) and in the chemical shift in the 'aliphatic' region ((b) 2.3–2.7 ppm).

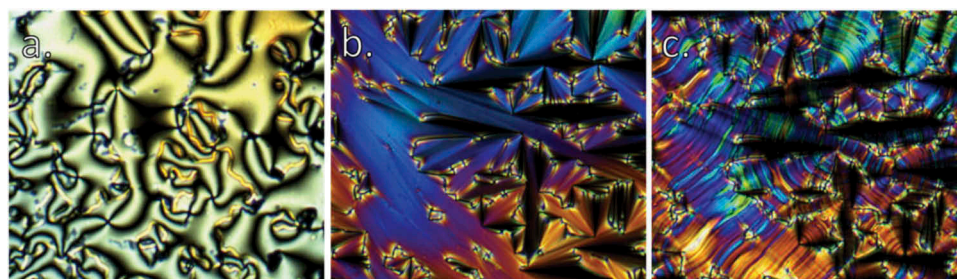


Figure 7. (Colour online) Photomicrographs (100×) of compound **16** on an untreated glass slide in (a) the nematic phase at 175 °C, (b) the smectic C phase at 165 °C and (c) the unknown 'X' phase at 135 °C. All photomicrographs are of approximately the same region of the sample.

**Table 2.** Transition temperatures (°C) and associated enthalpies of transition (kJ mol<sup>-1</sup>) for compounds **14–17**, as determined by DSC with a heat/cool rate of 10°C min<sup>-1</sup>.

No.	R	X	Cr		X		SmC		N		Iso
<b>14</b>	H	...	•	157.4 [52.2]	•	164.6 [22.0]	•	188.1 [8.2]	–	–	•
<b>15</b>	F	...	•	153.2 [64.4]	(•)	117.0 [17.6]	•	160.7 [6.4]	•	165.2 [2.6]	•
<b>16</b>	H		•	97.9 [33.2]	•	143.1 [15.9]	•	173.7 [8.2]	•	177.7 [4.7]	•
<b>17</b>	F		•	95.9 [15.9]	•	144.7 [8.1]	•	155.5 [8.7]	–	–	•

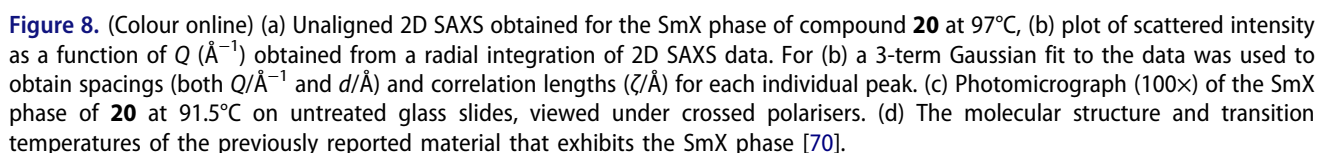
Values in parenthesis are monotropic, i.e. they occur below the melting point. X refers to a smectic mesophase whose structure is not currently known, see the text for discussion.

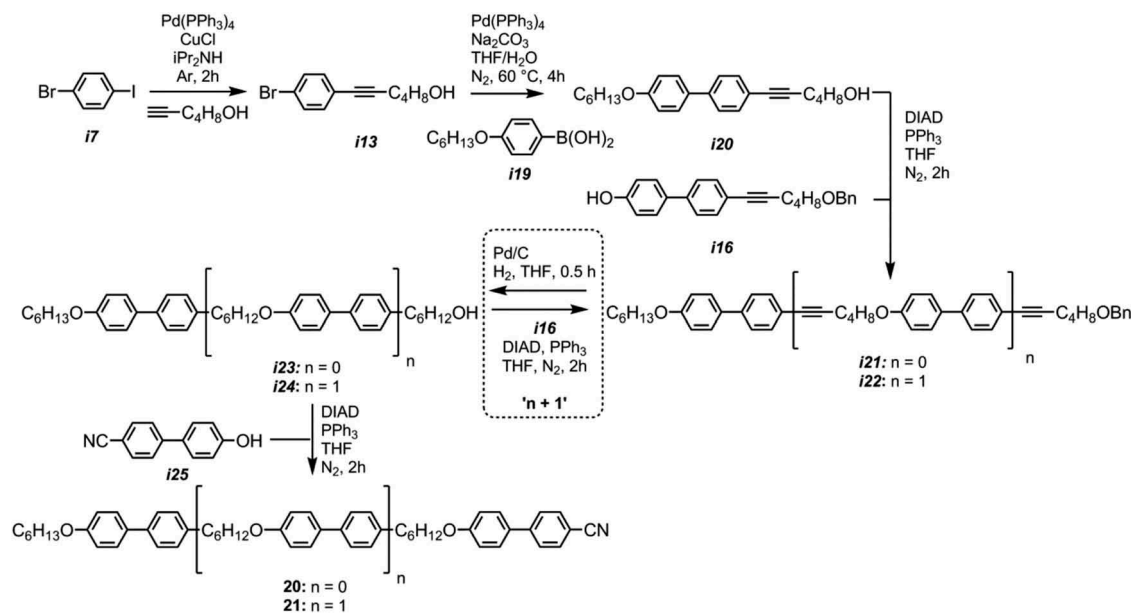
exhibiting additional nematic phases. We were surprised that compounds **14–17** did not exhibit N<sub>TB</sub> phases, given that they satisfy the prerequisite bent shape and in the case of **16** and **17** possess methylene-linking groups. The identification of the nematic and smectic C phases was trivial from their defect textures, the former exhibiting a *schlieren* texture and the latter exhibiting both focal-conic defects and a *schlieren* texture. The magnitude of the enthalpy associated with the X-SmC transition suggests that the lower temperature phase is soft-crystalline in nature rather than liquid-crystalline. The optical textures of this unknown smectic are primarily comprised of broken banded focal conics (which are presumably paramorphic from the smectic C phase); in this regard, the X phase is reminiscent of the crystal E phase. Photomicrographs are given in Figure 7.

We hypothesise that the lack of the N<sub>TB</sub> phase in **14–17** can be attributed to two distinct structural features. First, the length of the ether-linked spacer is rather long and may favour the formation of smectic phases in an analogous manner to how the length of terminal chain dictates the incidence of either the N<sub>TB</sub> or SmC<sub>A</sub> phase in apolar dimers [67]. It is known that the bend-angle dictates the incidence of the twist-bend nematic phase; this is demonstrated by comparing CB9CB (which exhibits the N<sub>TB</sub> phase) to the *bis* ether-linked CBO7OCB (which does not). The material CB8OCB (Figure 9) is ‘halfway’ between these two materials, having one methylene- and one ether-linking group, and this also exhibits the N<sub>TB</sub> phase, having been reported by us previously [40] and more recently by others [21]. It has been observed that as the number of ether linkages increases, the scaled N<sub>TB</sub> transition

temperature (T<sub>N<sub>TB</sub>-N</sub>/T<sub>N-Iso</sub>) decreases irrespective of the actual values of T<sub>N<sub>TB</sub>-N</sub>. We therefore opted to reduce the number of ether-linking groups and prepare materials that can be thought of, in crude terms, as oligomeric analogues of CB6OCB, reported by Paterson et al. [33], with our synthetic approach outlined in Scheme 3. We hypothesised that the reduction in the number of ether linkages would increase the scaled N<sub>TB</sub> transition temperature and therefore afford further examples of oligomeric twist-bend nematogens.

The useful alcohol-terminated cyanobiphenyl **i14** was prepared via a Sonogashira coupling followed by a Suzuki–Miyaura reaction in high yield. Benzyl protection of the hydroxyl group of **i13** followed by a Suzuki–Miyaura coupling with 4-hydroxyphenyl boronic acid afforded **i16**, with a subsequent etherification via the Mitsunobu protocol affording **i17**. We envisioned performing a selective heterogeneous hydrogenation/hydrogenolysis using palladium on carbon poisoned with diaminoethane (Pd/C{En}) so as to avoid unwanted reduction of the nitrile, affording the alcohol-terminated dimer **19**, which was then, in turn, etherified with 4-cyano-4'-hydroxybiphenyl to afford a trimer. By etherifying **19** with **i16**, followed by selective hydrogenation, we believed it would be possible to obtain monodisperse oligomeric materials of virtually any given length in a complimentary manner to the ‘n + 1’ method reported by us recently [55], affording the CB6O[B6O]<sub>n</sub>CB series of materials (Scheme 3). Although we could obtain quantitative reduction of the alkyne groups, we were unable to obtain the debenzylated material **19**, instead obtaining quantitative conversion to the saturated, benzyl-protected material **18**. Despite screening a range of conditions, we are yet to





Scheme 4.

find a suitable combination of catalyst and poison that affects debenzoylation without accompanying nitrile reduction.

When studied by POM and DSC, we observed that compound **18** exhibits both nematic and twist-bend mesophases, although at greatly reduced temperatures to the ‘parent’ material CB6OCB. The related dialkyne **i17** was found to be non-mesogenic, melting directly to the isotropic liquid and exhibiting no monotropic mesophases on supercooling. The contrast in thermal behaviour between **18** and **i17** mirrors our previous observations of alkyne- and methylene-linking groups in dimers, namely that the former exhibits reduced transition temperatures relative to the latter [40,41]. We believe that it could be possible for a ‘calamitic’ material to exhibit the

twist-bend phase via the formation of supramolecular oligomers formed via non-covalent interactions (hydrogen bonds, halogen bonds, etc.). For instance it is well known that alcohols form moderately strong hydrogen bonds to nitriles [68], and for this reason we studied **i14** and its saturated analogue (**i18**, obtained via Pd/C {En} catalysed selective hydrogenation) by POM and DSC. Neither material exhibits the  $N_{TB}$  phase: with **i14** exhibiting nematic and an unknown smectic (SmY) mesophases and **i18** exhibiting only a nematic phase. In the case of **i18** the material was supercooled to  $-60^{\circ}\text{C}$  and remained in the nematic phase with no further phase transitions observed. With **i14**, identification of the smectic phase (SmY) was hindered by the fact that the phase transition occurred simultaneously with crystallisation. The transition temperatures of materials from Scheme 3 are given in Table 4.

As a workaround to the problem of o-debenzylation in the presence of an aromatic nitrile, we opted to prepare oligomesogenic materials with one ‘apolar’ 4-alkoxybiphenyl mesogenic unit and one ‘polar’ cyano-biphenyl mesogenic unit, with multiple biphenyl groups interspersed between. As the aromatic nitrile group is introduced last the problems of selective hydrogenation were avoided. We elected to use a hexyloxy chain at one end of the molecule for two reasons: first, this is the same length and parity as the spacer unit; second, in our previous work on apolar bimesogens we observed this chain length to be the cross-over point from twist-bend nematic to smectic behaviour [65].

**Table 3.** Transition temperatures ( $^{\circ}\text{C}$ ) and associated enthalpies of transition ( $\text{kJ mol}^{-1}$ ) for compounds **20** and **21** as determined by DSC with a heat/cool rate of  $10^{\circ}\text{C min}^{-1}$ .

$\text{C}_6\text{H}_{13}\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\left[\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{C}_6\text{H}_4-\text{O}-\text{C}_6\text{H}_4-\text{CN}\right]_n$									
No.	n	Cr	SmX	SmC	N	Iso			
20	0	•	107.0 [29.9]	(•) 100.7 [2.5]	• 101.8 [1.0]	• 123.1 [0.7]	•		
21	1	•	119.6 [12.4]	• 144.3 [18.7]	–	–	–	–	•

Values in parenthesis are monotropic. SmX refers to a smectic mesophase whose structure is presently unknown.



**Table 4.** Transition temperatures (°C) and associated enthalpies of transition (kJ mol<sup>-1</sup>) for compounds **i17** and **19** as determined by DSC with a heat/cool rate of 10°C min<sup>-1</sup>.

No.	Cr	SmY	N <sub>TB</sub>	N	Iso
CB6OCB	•	103.1	–	•	154.2
<b>i14</b>	•	62.3 [11.3]	•	–	51.9 [0.2]
<b>i18</b>	•	48.6 [9.1]	–	•	43.3 [0.4]
<b>i17</b>	•	93.5 [34.3]	–	–	–
<b>18</b>	•	93.1 [56.1]	–	•	67.1 [0.4]

Values in parenthesis are monotropic, i.e. they occur below the melting point. Values for CB6OCB were taken from a forthcoming paper by Archbold et al. [41]; however, these values are only marginally different to those reported by Paterson et al. [33].

<sup>a</sup>If rapidly cooled, a monotropic, unidentified smectic phase (SmY) is observed at roughly 25°C for **i14**; however, the sample crystallises before this point during DSC study.

A Mitsunobu etherification of **i16** and **i20** afforded the o-benzylated compound **i21**. Hydrogenation saturated the alkynes and cleaved the benzyl ether, affording an alcohol. The length of the oligomesogen can then be extended via a Mitsunobu coupling of the debenzylated material, **i23**, with **i16** or the oligomer could be ‘capped’ with 4-hydroxy-4'-cyanobiphenyl (**i25**). A full account of these materials, their intermediates (many of which are liquid-crystalline in their own right) and higher oligomers will be given in a future paper. We note that the reactions used to prepare these materials occur with minimal side-products and are much higher in yield than the methods used to prepare oligomers by us previously (the hexamesogen **O6<sub>7</sub>** was prepared in a ~13% yield, compared to ~60–80% for the present oligomeric materials) [55].

Although the related material CB6OCB exhibits nematic and twist-bend nematic mesophases, the homologue **20** (where  $n = 0$ ) exhibits nematic and SmX mesophases. Extending from the dimer to the trimer, **21**, the material no longer exhibits a nematic phase and instead has a direct Iso-SmX transition, as in Table 4. The SmX phase exhibited by **20** and **21** displayed similar optical textures (see Figure 9(c)) to the SmX phase exhibited by compounds **14–17**, shown in the photomicrographs in Figure 9. Due to the reduced viscosity of **20** relative to the trimeric (**21**) and tetrameric (**14–17**) materials, it was possible to study the SmX phase by SAXS (Figure 10). Although the nematic phase of **20** was well aligned by the external field ( $B \approx 0.6$  T at sample) perpendicular to the incident X-ray beam, this alignment was lost on entering the SmX phase. The SmX mesophase is characterised by having two Bragg scattering peaks at small angles ( $Q = 0.19 \text{ \AA}^{-1}$  and  $Q = 0.38 \text{ \AA}^{-1}$ ) as well as two more diffuse peaks at wide angles ( $Q = 1.40 \text{ \AA}^{-1}$  and  $Q = 1.54 \text{ \AA}^{-1}$ ). The two Bragg scattering peaks correspond roughly to the molecular length ( $Q = 0.19 \text{ \AA}^{-1}$ ) and one half of the molecular length ( $Q = 0.38 \text{ \AA}^{-1}$ ),

which was calculated to be  $33 \text{ \AA}$  at the DFT(B3LYP/6-31G(d,p)) level in Gaussian G09 [57]. The diffuse wide angle peaks correspond to lateral separation of the molecules within the smectic layers; our interpretation is that the differing mesogenic units (4-cyano and 4-hexyloxy-biphenyls) have differing side-to-side packing distances because of differences in polarity. Due to the lack of alignment attained for the SmX phase of **20**, it is not yet possible to give definitive phase identification; however, the SAXS pattern appears consistent with an unaligned soft-crystalline E mesophase [69]. The observed scattering pattern is nearly identical to that reported by us previously for what was then referred to as the ‘SmX’ mesophase [70]. Given the similarity in molecular structure between this previous material (Figure 9(c)) and compound **20**, it is perhaps unsurprising that both apparently exhibit the same intercalated, soft-crystalline mesophase.

## Conclusions and outlook

We have prepared and characterised several novel ether-linked dimers to exhibit the N<sub>TB</sub> phase, and within this homologous series the linear relationship between  $T_{N_{TB-N}}$  and  $T_{N-Iso}$  – recently observed for methylene-linked dimers – appears to be obeyed. Extending the aspect ratio of one mesogenic unit from 2- to 3-rings confers a predictable increase in both  $T_{N-I}$  and  $T_{N_{TB-N}}$ . Over the past few years, the number of dimeric materials known to exhibit the N<sub>TB</sub> phase has increased rapidly, and this work significantly increases the number of ether-linked dimers known to exhibit this intriguing state of matter.

The discovery of trimesogenic, tetramesogenic and hexamesogenic materials that exhibit the twist-bend nematic phase presents fresh impetus to prepare novel liquid-crystalline oligomeric compounds. It has been noted that the synthesis of higher linear oligomers



(i.e.  $n \geq 4$ ) is often challenging due to low reaction yields due to side- and by-products during synthesis and difficult chromatographic separation. By excluding carboxylate esters and preparing oligomeric materials featuring biphenyl-derived mesogenic groups, we find that reactions proceed significantly 'cleaner' and the synthesis of these materials is greatly simplified. Compounds **14–17** were found not to exhibit the  $N_{TB}$  phase, instead variously exhibiting nematic, smectic C and crystal E mesophases. With this in mind we have attempted to combine the advantages of both approaches, namely employing a short spacer with both one methylene- and one ether-linking unit to promote the formation of the  $N_{TB}$  phase and using biphenyl mesogenic units rather than phenyl benzoates to improve yield and reduce side reactions (predominantly transesterification).

The onus is shifting to understanding how, if at all, changes to molecular structure in dimers impact on the properties of the  $N_{TB}$  phase such as conical angle, pitch length, etc., whereas for oligomers the synthesis of further materials that exhibit the  $N_{TB}$  phase is essential for advancing understanding of these systems to the same level as that of dimers. Ether-linked oligomers are synthetically accessible but do not appear to exhibit the  $N_{TB}$  phase [71], whereas methylene-linked oligomers present more of a challenge to synthesise but do exhibit this mesophase. Further developments to the stepwise 'n+1' synthetic methods presented by us here (and in previous work [55]) should allow the synthesis of high-purity, monodisperse oligomeric materials of any length and help to increase understanding of these systems within the context of the  $N_{TB}$  phase.

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## Disclosure statement

No potential conflict of interest was reported by the authors.

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