Etheric bimesogens and the twist-bend nematic phase

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ABSTRACT
Despite the relationship between molecular structure and the occurrence of the twist-bend nematic phase being partially understood, very little is known about how these relationships are manifested for ether-linked bimesogens. In this article, we report several novel ether-linked bimesogens that exhibit the N\textsubscript{TB} phase and explore how the thermal properties of these materials are largely governed by the angle between the two aromatic, carbocyclic or rigid cyclic units.

Introduction

The twist-bend nematic phase (N\textsubscript{TB}) has proven to be one of the most active areas of liquid crystal research in recent years.[1–19] For some time, it was considered that the heliconical model of Dozov (also proposed by Meyer some time earlier) was an accurate descriptor of the N\textsubscript{TB} phase.[19,20] In particular, measurements of the electroclinic effect in 4',4''-(heptane-1,7-diyl)bis(((1,1'-biphenyl]-4-carbonitrile)) (CB7CB) were taken to support the idea of the twist-bend nematic phase having a pitch length of a few nanometres.[14]

However, the results from freeze-fracture transmission electron microscopy (FFTEM) and solid state deuterium nuclear magnetic resonance (\textsuperscript{2}H NMR) have been questioned recently. For example, the FFTEM method, often used to measure the N\textsubscript{TB}...
heliconal pitch length, has been called into doubt due to the existence of similar periodic length scales in the solid state of 4′,4″-(nonane-1,9-diyl)bis([1,1′-biphenyl]-4-carbonitrile) (CB9CB). It has been argued based on both $^3$H solid-state NMR and solution-based 2D $^1$H NOESY NMR that a heliconal structure is not present. Furthermore, the original model proposed by Dosov predicts that for the N$_{TB}$ phase, the bend elastic constant $K_{13}$ is negative, which is contrary to experimental data.

The number of compounds in the literature that are known to exhibit the N$_{TB}$ phase has increased vastly in the past year, and as such, the relationship between molecular structure and this unique state of matter is partially understood. In this article, we present a number of novel ether and mixed ether/ester-linked bimesogens that exhibit the N$_{TB}$ phase, expanding upon previous work in this area. The structural modifications to architectural design presented in Figure 1 are discussed in this article.

**Experimental**

Compound 1 was prepared as described previously. The syntheses of all other materials were performed via modifications of this route using appropriate starting materials either available in house or from commercial suppliers. Computational chemistry was performed in Gaussian G09 revision D.01 with output files rendered using QuteMol. Full experimental details, including synthetic procedures and chemical characterisation, are provided in the Supplemental data.

**Results and discussion**

Compound 1 was the first unsymmetrical ether-linked material demonstrated to exhibit the N$_{TB}$ phase. We opted to modify the molecular structure by changing the mesogenic units, and the spacer composition and parity. In the first instance, we sought to replace the 4-fluorobiphenyl unit of compound 1 with a number of other polar biphenyl groups. The transition temperatures of the resulting materials are given in Table 1.

Replacement of the 4-fluorobiphenyl unit of compound 1 with any of the polar mesogenic ‘R’ groups shown in Table 1 leads to loss of the N$_{TB}$-SmA polymorphism although the N$_{TB}$ phase is retained in all cases with the exception of compound 3, which exhibits a direct nematic to smectic A transition. The aromatic units (R) for compounds 2 and 4 are very similar in terms of polarity to 5 and 6, respectively; yet, large variations exist in the thermal stability of the N$_{TB}$ phase, whereas the clearing points for these materials vary significantly less. Replacement of the 4′-fluorobiphenyl oxyx group of 1 with a 4′-cyanobiphenyloxy group, for compound 7, gives a sharp rise in the clearing point with more modest increases in the melting point and nematic to N$_{TB}$ transition temperatures. The entropy associated with the nematic to N$_{TB}$ transition was, in all cases, significantly smaller than that associated with the clearing point indicating that for all of the materials in Table 1 the degree of change in the local structure is quite small at the N–N$_{TB}$ transition. Mesophase assignments were made by polarised light microscopy, with representative photomicrographs of the optical textures observed for the nematic, N$_{TB}$ and smectic A phases presented in Figure 2.

Compounds 1 and 3 were both studied by small angle X-ray scattering so that the subtype of smectic A phase could be determined. Unfortunately due to the minimal supercooling available for the X-phase of compound 1, it was not possible to obtain SAXS data for the X phase. Two dimensional diffraction patterns for the smectic A phases of 1 and 3 and the nematic phase of 3 are presented in Figure 3.

In the smectic A phases of compounds 1 and 3, the layer spacings were measured to be 19.99 and 19.96 Å, respectively, with the layer spacing found to be independent of temperature for both compounds. Using molecular lengths obtained at the B3LYP/6-31G level of theory (40.77 Å for 1 and 40.61 Å for 3) this corresponds to a d/l ratio of 0.49 for both 1 and 3. Hence, the phase can be identified as being an intercalated smectic A phase. This is perhaps unsurprising given that the two mesogenic units employed have different molecular lengths and opposite signs of dielectric anisotropy.

For some time it was thought that only methylene-linked dimers could exhibit the N$_{TB}$ phase; however,
Table 1. Transition temperatures (°C), associated enthalpies of transition [kJ mol$^{-1}$] and dimensionless associated enthalpies of transition ($\Delta S/R$).

| No. | R = | Cr | 'X' | SmA$_2$ | N$_{TB}$ | N | Iso |
|-----|-----|----|-----|---------|--------|---|-----|
| 1   | [●] | 79.8 | (●) | 58.3 | (●) | 66.7 | (●) | 68.4 | (●) | 162.1 | (●) |
| 2   | [●] | 37.9 | [35.00] | (13.53) | – – – – – | 61.7 | (●) | 160.0 | (●) |
| 3   | [●] | 75.3 | (17.94) | – – (●) | 74.7 | (1.90) | – – – | 133.1 | (●) |
| 4   | [●] | 98.4 | (57.87) | (22.38) | – – – – – | (●) | #) | 144.0 | (●) |
| 5   | [●] | 62.8 | (85.10) | (32.91) | – – – – – | (●) | 28.4 | (0.07) | 143.1 | (●) |
| 6   | [●] | 82.2 | (54.70) | (21.15) | – – – – – | (●) | 45.3 | (0.04) | 144.6 | (●) |
| 7   | [●] | 83.5 | (52.94) | (20.47) | – – – – – | (●) | 83.3 | (0.01) | 190.1 | (●) |

Notes: Transitions in parenthesis are monotropic, i.e. they occur below the melting point of the sample upon supercooling. #, the N$_{TB}$ phase could be observed during rapid uncontrolled cooling, however, this precludes accurate measurement of the transition temperature or associated enthalpy.

Figure 2. Photomicrographs (×100) of the schlieren texture of the nematic phase of compound 3 at 85°C (a), the ‘rope-like’ texture of the N$_{TB}$ phase of compound 6 at 41°C (b), the fan texture of the smectic A phase of compound 3 at 71°C (c) and the blocky texture of the N$_{TB}$ phase of 2, cooled to ambient temperature (20°C) (d).
this has since been demonstrated to be untrue. Thus, we sought to prepare materials containing both ether- and carboxylate-linking groups to see if such compounds could support the formation of the $N_{TB}$ phase. Compound 1, as the first ether-linked $N_{TB}$ material, presents a good starting point for such studies while both mixed ether/ester-linked dimers (8 and 9 in Table 2) are easily accessed synthetically. We also elected to vary the number of methylene units in the central spacer for materials based on compound 1. Therefore, homologues of 1 with both shorter (nona-methylene, 10) and longer (dodecamethylene, 11) spacers were prepared.

Replacement of the ether groups in compound 1 with carboxylate esters, to give 8 and 9, confers a modest increase in melting point and a small increase

![Figure 3. Small-angle X-ray diffraction patterns obtained for magnetically aligned samples of compound 1 in the smectic A phase at 64°C (a), compound 3 in the smectic A phase at 50°C (b) and compound 3 in the nematic phase at 100°C (c). A plot of intensity (counts, square root) vs. d spacing (Å) at a series of temperatures for compound 3 is given in (d), with scans corresponding to the nematic phase in red and those corresponding to the smectic A phase in blue.]

Table 2. Transition temperatures ($^\circ$C), associated enthalpies of transition [kJ mol$^{-1}$] and dimensionless associated enthalpies of transition ($\Delta S/R$).

| No. | L1  | L2  | n  | Cr | $\chi'$ | SmA | $N_{TB}$ | N  | Iso |
|-----|-----|-----|----|----|--------|-----|---------|----|-----|
| 1   | -O- | -O- | 11 | ●  | 79.8   | [40.79] | [0.04] | 66.7 | [0.74] | 68.4 | [0.02] | 162.1 | [1.14] |
| 8   | -COO- | O  | 10 | ●  | 89.0   | [15.77] | [0.01] | (●) | #   | 166.7 | [1.60] | 167.4 | [3.60] |
| 9   | -O- | -COO- | 10 | ●  | 89.3   | [65.30] | [25.25] | (●) | #   | 167.4 | [0.44] | 167.2 | [0.98] |
| 10  | -O- | -O- | 9  | ●  | 92.9   | [64.10] | [24.79] | (●) | #   | 167.2 | [0.44] | 167.2 | [0.44] |
| 11  | -O- | -O- | 12 | ●  | 108.7  | [47.27] | [18.28] | (●) | 99.9 | [0.04] | 0.02] | 158.2 | [4.37] |

Notes: Transitions in parenthesis are monotropic, i.e. they occur below the melting point of the sample upon supercooling. #, the $N_{TB}$ phase could be observed during rapid uncontrolled cooling, however, this precludes accurate measurement of the transition temperature or associated enthalpy.
in the clearing point; however, the materials now only exhibit the $N_{TB}$ phase when subjected to rapid cooling which precludes accurate determination of the $N-N_{TB}$ transition temperature. Both compounds can be supercooled to around 55°C before crystallisation occurs with the $N-N_{TB}$ transition occurring somewhere between this temperature and 60°C, hence the $N_{TB}$ phase is destabilised by the incorporation of carboxylate esters.

Next we opted to vary the length of the aliphatic spacer to give compound 10, which has a nonamethylene spacer, and compound 11, which has a dodecamethylene spacer. The removal of two methylene units from compound 1 (to give compound 10) gives a small increase in the clearing point, whereas the nematic to $N_{TB}$ transition temperature drops by 40°C. Such behaviour is not mirrored in the CBNCB series of materials in which the $N_{TB}-N$ transition temperature does not vary greatly as a function of spacer length (103°C, 105°C and 108.6°C for CB7CB, CB9CB and CB11CB respectively). One possible explanation is that the $N_{TB}$ phase is only observed in these materials due to the relatively long spacer lengths nullifying the unfavourable angle constraints imposed by the ether-linking groups. Conversely, it could be that the C9 is the first example in the homologous series. The former view is also supported by the reduction in thermal stability that occurs upon incorporation of a carboxylate ester; however, the synthesis of additional homologues would need to be undertaken to confirm this hypothesis. Additionally, compound 10 no longer exhibits the SmA or ‘X’ phases. Compound 11 exhibits both a nematic and smectic A phase; however, due to its likely overall linear shape, a consequence of the even number of methylene groups in the spacer, the material does not exhibit the $N_{TB}$ phase. To determine the subtype of the smectic A phase, compound 11 was subjected to analysis by small-angle X-ray scattering. A two-dimensional diffraction pattern obtained for the smectic A phase of 11 is given in Figure 4.

The layer spacing in the smectic A phase of compound 11 was found to be temperature independent and measured to be 20.75 Å. The all trans minimum energy conformer of 11, as obtained at the B3LYP/6–31G level of theory (shown in Figure 5), has a molecular length of 42.72 Å, which corresponds to a $d/l$ ratio of 0.48. As was also found for compounds 1 and 3, the smectic A phase of 11 is also intercalated. From the optimised geometries obtained for 1 and 11, it is trivial to calculate the angle between the individual mesogenic units in the gas phase, this yields angles of 146.0° for 1 and 170.2° for 11. It should be cautioned that this approach does not present a picture of the distribution of conformers that are likely to exist in the bulk phase.[2,32]

The angle between the two mesogenic units in 1 is significantly larger than that for the well known CBNCB materials, calculated previously by us for CB11CB to be 111° at the B3LYP/3–21G level of theory.[8] This appears to support our earlier explanation that the occurrence of the $N_{TB}$ phase in compounds such as 1

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**Figure 4.** Small-angle X-ray diffraction patterns obtained for a magnetically aligned sample of compound 11 in the smectic A phase at 95°C.

**Figure 5.** The minimum energy geometries of compound 1 (top) and compound 11 (bottom) as obtained at the B3LYP/6–31G level of theory for an isolated molecule at 298 K.
is due to the relatively long spacer length annulling the unfavourable angle constraints that the ether-linking groups impart. This hypothesis also accounts for the destabilisation encountered when carboxylate esters are used. In this scenario, it is more energetically unfavourable to attenuate the bend angle due to the increased rigidity of the spacer, hence the depression in the thermal stability of the twist-bend nematic phase. The angles between the two aromatic/carbocyclic units of 8 and 9 (using the B3LYP/6–31G minimum energy geometry, presented in Figure 6) were found to be 123.9° and 122.5°, respectively. Given that these two angles are nearly identical, it is unsurprising that the two materials also have almost identical thermal behaviour. This serves as further evidence that it is the gross topology of bimesogens that dictates their thermal behaviour rather than the dipole moment of the individual aromatic/carbocyclic units, which in the case of compounds 8 and 9 are quite different due to the relocation of the electronegative carboxylate ester group.

So far, all of the ether-linked dimers studied have possessed the 2,3-difluorobiphenyl-4′-(4-propylcyclohexane) mesogenic unit. Given that this group has a fluorine atom ortho to the ether-linking unit, the Ar–O–CH₂– bond angle is different from the non-fluorinated analogue. We sought to confirm that the occurrence of the N_{TB} phase was therefore not dependent on this structural unit in ether-linked systems. The transition temperatures and associated enthalpies of the resulting compounds are given in Tables 3 and 4.

When the trans 4′-(4-propylcyclohexyl)-2,3-difluorobiphenyl group for compound 1 was replaced with a fluorinated biphenyl unit, the resulting materials typically exhibited significantly lower clearing points, whereas, with the exception of compounds 15, the N_{TB}, SmA and ‘X’ phases were not observed. However, when 4-hydroxy-4′-cyanobiphenyl (17) was used, there was a significant increase in the thermal stability of the N_{TB} phase with only a small reduction in clearing point. Thus far, in a given series of materials, those that incorporate a terminal nitrile in one of the aromatic/carbocyclic units (compounds 7 and 17) have higher clearing points and nematic to N_{TB} transition temperatures. In the cases of both 15 and 17, the entropy associated with the nematic to twist-bend nematic transition is of the same magnitude as the parent compound 1. Owing to this propensity of cyano-terminated compounds to exhibit the twist-bend nematic phase, we opted to prepare analogues of compound 1 where the 4-fluorobiphenyl unit was replaced with 4-cyanobiphenyl. The thermal behaviour of these materials is presented in Table 4.

It is perhaps unsurprising that compound 20 exhibits the N_{TB} phase given that Sebastián et al. showed the nonamethylene homologue of this material (termed FFO9OCB) exhibited the N_{TB} phase.[25] Indeed, the transition temperatures of 20 are not remarkably different to those of FFO9OCB (Cr 72.5 (N_{TB} 49.9) N 112.4 Iso). Of the three structural isomers of compound 20, it was found that both 18 and 19 exhibit the N_{TB} phase whereas 21 does not, even when subjected to rapid uncontrolled cooling. In all cases, the associated entropy of the nematic to N_{TB} transition is an order of magnitude smaller than that associated with the nematic to isotropic transition, this being indicative that the degree of change in the local structure is quite small at the N–N_{TB} transition.

For the compounds shown in Tables 1, 3 and 4, the bend angle is expected to be largely consistent with the

![Figure 6](colour online) The minimum energy geometries of compound 8 (top) and compound 9 (bottom) as obtained at the B3LYP/6–31G level of theory in an isolated molecule at 298 K.
exception of compounds where a fluorine atom is in the ortho position with respect to the ether group(s). Hence, any differences in the thermal properties of these materials are due to the propensity of the individual mesogenic units to form given liquid crystal phases, itself a consequence of dipole moments, polarisabilities, steric considerations and the specific nature of the intermolecular interactions. Although some differences do exist, the difluorobiphenyl systems typically having much reduced clearing points compared to monofluorobiphenyl and cyanobiphenyl systems, but the thermal behaviour of these materials is

Table 3. Transition temperatures (°C), associated enthalpies of transition [kJ mol\(^{-1}\)] and dimensionless associated enthalpies of transition {\(\Delta S/R\)}.

| No. | R = | Cr | N<sub>Tb</sub> | N | Iso |
|-----|-----|----|--------------|---|-----|
| 12  | ●   | 128.6 | – | – | (●) 111.6 | ● |
|     |     | [49.42] | (19.11) |     | [1.19] |     |
| 13  | ●   | 77.9  | – | – | (●) 72.6  | ● |
|     |     | [36.31] | (14.04) |     | [1.84] |     |
| 14  | ●   | 84.3  | – | – | (●) 81.4  | ● |
|     |     | [39.42] | (15.24) |     | [2.34] |     |
| 15  | ●   | 70.1  | – | – | (●) 81.9  | ● |
|     |     | [47.91] | (18.53) |     | [2.05] |     |
| 16  | ●   | 96.0  | – | – | (●) 81.2  | ● |
|     |     | [59.51] | (23.01) |     | [2.05] |     |
| 17  | ●   | 86.7  | – | – | (●) 131.7 | ● |
|     |     | [54.99] | (21.27) |     | [2.73] |     |

Note: Transitions in parenthesis are monotropic, i.e. they occur below the melting point of the sample upon supercooling.

Table 4. Transition temperatures (°C), associated enthalpies of transition [kJ mol\(^{-1}\)] and dimensionless associated enthalpies of transition {\(\Delta S/R\)} for compounds 7 and 17–21.

| No. | R = | Cr | N<sub>Tb</sub> | N | Iso |
|-----|-----|----|--------------|---|-----|
| 17  | ●   | 86.7 | – | – | (●) 77.7 | ● |
|     |     | [54.99] | (21.27) |     | [0.004] |     |
| 18  | ●   | 68.7 | – | – | (●) 47.9 | ● |
|     |     | [35.34] | (13.66) |     | [0.002] |     |
| 19  | ●   | 85.6 | – | – | (●) 65.4 | ● |
|     |     | [49.34] | (19.08) |     | [0.12] |     |
| 20  | ●   | 72.8 | – | – | (●) 46.7 | ● |
|     |     | [43.28] | (16.97) |     | [0.08] |     |
| 21  | ●   | 93.4 | – | – | – | ● |
|     |     | [45.52] | (17.60) |     | [0.03] |     |
| 7   | ●   | 83.5 | – | – | (●) 83.3 | ● |
|     |     | [52.94] | (20.47) |     | [0.02] |     |
not as radically different as when modifications are made to the spacer and linking groups.

Conclusion

Starting from the previously reported ether-linked bimesogen 1, we have prepared a number of new compounds that incorporate ether-linking groups, and which exhibit the twist-bend nematic phase. Ultimately, and in keeping with earlier reports, [22,24,26] we find that the occurrence and absence of the N\textsubscript{TB} phase is not strictly dependent on the type of mesogenic unit. This means that the ability to use molecular properties such as polarisability and dipole moment to rationalise the observation of this phase may be limited to groups of materials with highly similar molecular structure.

We hypothesise that ether-linked materials exhibit the N\textsubscript{TB} phase only when the spacer length is long, as this allows the unfavourable angular constraints imposed by such a linking group to be nullified. This seems to be a reasonable argument and is supported by the large drop in the thermal stability of the N\textsubscript{TB} phase when shortening the central spacer from eleven methylene units to nine. Furthermore, it was found that systems containing mixed ether/ester-linking groups can also exhibit the twist-bend nematic phase, albeit at reduced thermal stabilities compared to the ester-linked analogues. Most interestingly, the thermal properties of the two mixed ester/ether-linked materials (8 and 9) are almost identical, suggesting a strong link between the inter-aromatic/carbocyclic angle (which is also identical) and thermal properties of a given family of materials. In this work, it has been demonstrated that changes to this angle are detrimental to the thermal stability of the twist-bend nematic phase; however, this need not be the case. Through subtle changes to molecular structure, perhaps the incorporation of a dimethylsilyl unit in lieu of a methylene group in the spacer, or the loss of one CH\textsubscript{2}-linking unit in favour of a ketone, it may be possible that a change can be affected in the intermesogen angle that is actually beneficial to the stability of the N\textsubscript{TB} phase.

Disclosure statement

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