**The effect of the structural architecture of the spacer unit on the incidence of the twist-bend nematic phase in liquid crystal dimers.**

**Could we the title change to:**

**Effect of the Linking Unit on the Twist-Bend Nematic Phase in Liquid Crystal Dimers: A Comparative Study of Two Homologous Series of Methylene and Ether Linked Dimers.**

**And if so, make sure to change it in the SI too!**

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**Abstract**

It has been reported that bimesogens composed of rigid aromatic units linked together by methylene spacers of odd parity are more likely to exhibit the twist bend nematic phase in comparison to their analogues in which the spacer chain is linked to the aromatic units by ether moeities. In order to investigate this structure-property correlation bimesogens were prepared consisting of phenyl-benzoate aromatic units and either a heptamethylene or pentamethylene-1,5-dioxy linking group. The nematic to twist-bend nematic phase transitions of these materials were determined either directly or by extrapolation of binary phase diagrams with the standard NTB material CB9CB.It was found that when comparing methylene linked materials to their ether linked analogues, the N-NTB transition temperatures were, in most cases, higher in the ether linked materials. This is contrary to reported theories which predict that the incorporation of ether linkages serves to destabilise the NTB phase.

Two series of bimesogens with rigid phenyl benzoate mesogenic units were prepared: one series having a heptamethylene spacer and the other a pentamethylene spacer with two ether linking groups. These materials were prepared to provide experimental backing to the widely held hypothesis that methylene-linked bimesogens are more likely to exhibit the twist-bend nematic mesophase than their ether-linked counterparts. Several of the methylene linked materials exhibited nematic and NTB mesophases, whereas the analogous ether linked materials gave only nematic phases albeit with significantly higher clearing points. Virtual N-NTB transition temperatures for both methylene and ether-linked bimesogens were extrapolated by constructing binary phase diagrams with the well-studied twist-bend material CB9CB. Contrary to our expectations these virtual transition temperatures were in most cases higher for the ether-linked bimesogens than in the analogous methylene compounds, contrary to reported theories and hypotheses that the incorporation of ether linking groups should serve to destabilise the NTB phase.

**NOTE – is that ok? Just tried to make it more abstract-y**

**Keywords:** Liquid crystals, bimesogens, twist-bend nematic.

**Introduction**

The study of liquid crystal bimesogens, referred to as dimers in the case of symmetrical materials, has seen a large increase in popularity in recent years, primarily due to the propensity of these materials to form the so called "twist-bend nematic" (NTB)phase.1–6 This phase, first postulated by Dozov in 2001 7 has been the subject of much debate in current research, with its structure and properties yet to be conclusively determined despite the fact that the nature of this phase has been probed *via* various analytical techniques including polarised and conoscopic optical microscopy; differential scanning calorimetry, X-ray diffraction (XRD), freeze-fracture transmission electron microscopy (FFTEM), electron spin resonance (ESR), dynamic light scattering (DLS), variable temperature 2H NMR spectroscopy and Raman spectroscopy. 8–23 The most widely accepted model of this phase is the heliconical model presented by Dozov, 7 in which a spontaneous twist bend deformation of the nematic director results in a heliconical local structure. Recently an elegant resonant small-angle X-ray scattering experiment has provided the first *in situ* measurement of the pitch length of the twist-bend phase, 24 although several alternative models proposed for the structure of the NTB phase stemming from experimental evidence that has arisen in opposition to the heliconical model.25–27

The vast majority of materials reported to exhibit this mesophase have been dimers or bimesogens where the two mesogenic units are linked by a flexible methylene spacer, 1,3,28–40 however trimers,41 tetramers 42 and polymers 43 are also known to exhibit the NTB phase. Recently it has been experimentally demonstrated that the thermal stability of the NTB phase displays a strong dependency on the angle between the two mesogenic units. 44 The observation of the NTB phase in ether-linked bimesogens 33,34 runs contrary to previous theories on the nature of the relationship between molecular architecture and the NTB phase, which have stated that the bend angle in ether linked materials is too large, thus the bend elastic constant too high, to support the formation of the NTB phase.14

In this work we present a series of methylene and ether linked materials along with their mesomorphic properties. We use phase diagrams to determine the virtual N-NTB transition temperatures for those materials with no enantiotropic or monotropic NTB phase and discuss the relationship between the physical properties and phase behaviour of the various analogues

**Experimental**

Compounds **1**-**6** were prepared as described previously.31 Compounds **6**-**11** were prepared by the Steglich esterification between 1,7-*bis* (4-hydroxyphenyl)heptane and an appropriate benzoic acid, in a modification of our previously reported synthesis.2 Compounds **14**-**24** were prepared by the Steglich esterification between 4,4'-(pentane-1,5-diylbis(oxy))diphenol 31and an appropriate benzoic acid (Scheme 1).

Eth scheme.tif

Scheme 1: Synthetic pathway used to prepare compounds 12-24.

Geometry optimisations of the molecular structure of the products were performed at the B3LYP/6-31G(d) level of theory in Gaussian G09 revision d01.45 Small angle X-ray Scattering was performed on a Bruker D8 Discover equipped with a custom built temperature controlled furnace. Full experimental details including Gibb’s phase diagrams for binary mixtures with CB9CB are given in the ESI to this article.

**Results and Discussion**

**Methylene linked bimesogens**

A series of materials based on previously published nonamethylene linked liquid crystal bimesogens were prepared. The materials were composed of a heptamethylene spacer unit terminated by two phenyl-benzoate ester mesogenic units. In order to vary the properties of these dimers, the terminal group of the mesogenic units was altered, giving methylene-lined dimers with a heptamethylene spacer and polar end groups. 31 Several additional methylene linked dimers with a heptamethylene spacer and apolar terminal groups (namely alkyl and alkyloxy) were synthesised. The mesogenic behaviour of these compounds is reported in Table 1.



|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Transition Temperatures / °C | | | | | | |
| Compound no. | R | Cr |  | NTB |  | N |  | Iso |
| **1** | CN | • | 149.0  [43.18] | (• | 120.0  [0.62] | • | 139.0)  [1.43] | • |
| **2** | SCN | • | 105.0  [36.51] | (• | 103.3)  [0.4] | • | 120.5  [0.18] | • |
| **3** | NO2 | • | 113.3  [24.22] | - | - | - | - | • |
| **4** | F | • | 91.5  [48.31] | - | - | - | - | • |
| **5** | CF3 | • | 114.9  [39.15] | - | - | - | - | • |
| **6** | C2H5 | • | 71.5  [30.8] | - | - | - | - | • |
| **7** | C3H7 | • | 108.0  [33.0] | (• | 47.6  [#] | • | 49.5)  [1.40] | • |
| **8** | C4H9 | • | 56.3  [32.0] | - | - | - | - | • |
| **9** | OC2H5 | • | 108.3  [58.83] | (• | 95.3)  [0.65] | • | 108.8  [0.54] | • |
| **10** | OC3H7 | • | 89.6  [52.80] | (• | 69.1  [1.0] | • | 75.5)  [0.2] | • |
| **11** | OC4H9 | • | 87.0  [36.60] | (• | 79.2  [1.2] | • | 85.9)  [0.4] | • |

Table 1:Molecular structures and thermal behaviour of compounds 1-11. Monotropic phase transitions are given in parentheses. Transition enthalpies as determined by DSC are in kJ mol-1 and denoted in square brackets.31 # enthalpy unobtainable, transition observed by microscopy whereas during DSC the transition occurred simultaneously with crystallisation

As shown in Table 1 compounds **1** and **2** are the only materials bearing polar terminal groups that were found to be liquid crystalline whereas **3** – **5** were found to be non mesogenic.31 Of the six apolar (i.e. lacking a polar terminal group) materials reported in Table 1, four were found to exhibit a monotropic NTB phase; compounds **7**, **9**, **10** and **11**, whereas compounds **6** and **8** were found to be non mesogenic. These are the first apolar bimesogens to exhibit the NTB phase with a heptamethylene spacer, previous compounds have always incorporated a nonamethylene spacer.2 When investigated by POM, upon cooling from the amorphous liquid compounds **7**, **9**, **10** and **11** were found to exhibit *schlieren* textures with both 2 and 4 brush singularities, which is consistent with the presence of a nematic phase. Upon further cooling a transition to a blocky texture possessing parabolic defects was observed, this texture is characteristic of the NTB phase (Figure 1).13

Phases CA28.tif

Figure 1: Compound 9 in the nematic phase (a) and NTB phase (b) at 107.9 °C and 93.3 °C respectively. Sample was cooled at 0.1 °C min-1.

DSC was used to further investigate the phase behaviour, a first order transition was observed from the isotropic liquid to the nematic phase whereas the transition from the nematic phase to the lower temperature NTB phase was weakly first order. An example DSC trace (compound **11**, obtained at 10 ° min-1) is shown in Figure 2.

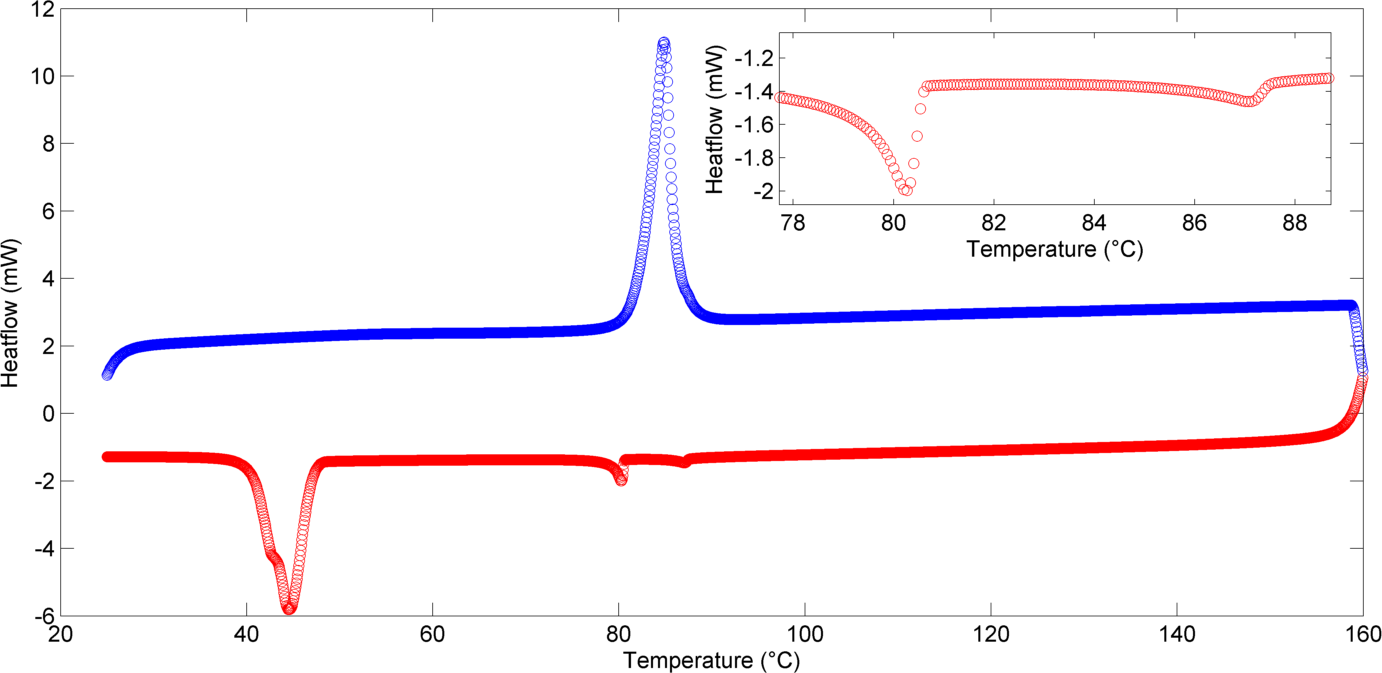


Figure 2: DSC thermogram of compound 11 obtained at a heat/cool rate of 10 °C min-1 with an expansion showing the region between 78 °C and 89 °.

Both the nematic and twist-bend mesophases were also studied *via* variable temperature X-ray diffraction. Upon cooling from the isotropic liquid to the nematic phase a significant increase in scattered intensity in the small-angle region was observed, and upon further cooling into the NTB phase this peak became marginally more defined. Concerning the wide angle region, the broad diffuse scattering peak in the isotropic liquid becomes both less intense and narrower in the nematic phase before broadening again in the NTB phase. The data obtained for compound **2** is shown in Figure 3.

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Figure 3: SAXS data for compound 2, showing scattered intensity (arbitrary units, Z axis), d-spacing (Angstroms, X-axis) and temperature (2 °C steps, °C, Y-axis)

Finally, for all compounds exhibiting a lower temperature phase, the phase was confirmed to be the NTB phase *via* miscibility studies with compound **1**, which itself was shown to unequivocally exhibit this phase through miscibility with CB9CB.31

These results are consistent with previous data that has shown that, for apolar bimesogens, the NTB phase is stabilised more by alkyloxy terminal chains than by alkyl chains.2 Furthermore, the propyl terminated material is the only one of the three alkyl terminated compounds which exhibits the NTB phase. This mirrors our previous results which show that terminal chains of odd parity give more stable NTB phases than those of even parity. 2 We next elected to construct binary phase diagrams between the compounds in Table **1** and CB9CB, allowing extrapolation of virtual N-NTB transitions for materials that do not exhibit the twist-bend phase in their neat state. By assuming a linear relationship between the concentration of the host material and the I-N and N-NTB transitions, something that has been previously demonstrated, 3,31, these phase diagrams were used to calculate the virtual phase transitions for all of the materials, the results obtained are summarised in . Examples of the phase diagrams are shown for compounds **6** and **8** in Figure 4 ,the remainder of the diagrams are presented in the ESI to this article, while statistical analysis of each the linear fits (for both I-N and N-NTB) is also presented in the ESI (table SI-17).

Mixtures_FINAL.tif

Figure 4: Example phase diagrams showing the linear relationship between concentration (wt %) and transition temperatures for compounds 6 and 8 with the standard material CB9CB.

|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Transition Temperatures / °C | | | | | | |
| no. | R | Cr |  | NTB |  | N |  | Iso |
| **1** | CN | • | 149.0 | (• | 120.0 | • | 139.0) | • |
| **2** | SCN | • | 105.0 | (• | 103.3) | • | 120.5 | • |
| **3** | NO2 | • | 113.3 | (\* | *66.1* | \* | *83.1*) | • |
| **4** | F | • | 91.5 | (\* | *34.7* | \* | *56.6*) | • |
| **5** | CF3 | • | 114.9 | (\* | *49.6* | \* | *56.4*) | • |
| **6** | C2H5 | • | 71.5 | (\* | *37.1* | \* | *40.1*) | • |
| **7** | C3H7 | • | 108.0 | (• | 47.6 | • | 49.5) | • |
| **8** | C4H9 | • | 56.3 | (\* | *34.7* | \* | *37.9*) | • |
| **9** | OC2H5 | • | 108.3 | (• | 95.3) | • | 108.8 | • |
| **10** | OC3H7 | • | 89.6 | (• | 69.1 | • | 75.5) | • |
| **11** | OC4H9 | • | 87.0 | (• | 79.2 | • | 85.9) | • |

Table 2: Transition temperatures for compounds 1-11. Virtual transitions determined from phase diagrams are shown in italics and denoted by a "\*". Monotropic phase transitions are quoted in parentheses.

**Ether linked bimesogens**

Replacement of the first and last methylene units of compounds **1** – **12** with ether linking groups gives compounds **14** – **24**. In order to limit the number of variables altered the overall length of the spacer unit was kept the same (seven atoms), thus the spacer in these materials contained five methylene units rather than seven and therefore the overall length is comparable. The mesomorphic behaviour of these materials is summarised in .



|  |  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- | --- |
|  |  | Transition Temperatures / °C | | | | | | |
| no. | R | Cr |  | NTB |  | N |  | Iso |
| **14** | CN | • | 166.6  [53.52] | (\* | *96.8*) | • | 189.2  [3.67] | • |
| **15** | SCN | • | 142.8  [35.59] | (\* | *87.8*) | • | 178.8  [2.27] | • |
| **16** | NO2 | • | 150.5  [77.26] | (\* | *88.3* | (• | 141.2)  [0.13] | • |
| **17** | F | • | 125.1  [50.51] | (\* | *48.7* | (\* | *85.4* | • |
| **18** | CF3 | • | 151.4  [51.83] | (\* | *25.7* | (\* | *49.2* | • |
| **19** | C2H5 | • | 116.1  [39.38] | (\* | *49.6* | (\* | *101.8* | • |
| **20** | C3H7 | • | 127.0  [44.63] | (\* | *58.6* | (\* | *109.3* | • |
| **21** | C4H9 | • | 125.4  [63.92] | (\* | *43.2* | (\* | *89.2* | • |
| **22** | OC2H5 | • | 139.9  [57.14] | (\* | *89.6*) | • | 171.4  [2.9] | • |
| **23** | OC3H7 | • | 108.3  [24.82] | (\* | *72.9*) | • | 143.1  [1.83] | • |
| **24** | OC4H9 | • | 109.0  [27.17] | (\* | *78.7*) | • | 142.2  [1.79] | • |

Table 3: General structure and mesomorphic behaviour of compounds 14-24. Monotropic phase transitions are quoted in parentheses. Transition enthalpies are in kJ mol-1 and denoted in square brackets. Virtual transitions are shown in italics and denoted by a “\*”.

As shown in Table 3, the introduction of an ether moiety into the spacer chain serves to drastically increase both the melting and clearing points of all of the materials presented. Additionally the NTB phase is suppressed in the neat materials as none of the ether linked materials were found to exhibit this mesophase in their neat state. Similarly to the methylene linked materials a series of phase diagrams were constructed for compounds **14** – **24** with CB9CB, allowing virtual transition temperatures to be determined. The results determined from the linear fits to the experimental data are presented in Table 3 and denoted by an asterisk, with example phase diagrams presented in Figure 5.

MIXTURES_2_FINAL.tif

Figure 5: Examples of phase diagrams showing the linear relationship between concentration (wt %) and transition temperatures for compounds 22 and 23 and the standard material CB9CB.

For the polar materials, all but compounds **16** and **17** showed a decrease in the virtual N-NTB transition temperature when an ether moiety was included in the spacer unit. Interestingly however, compounds **11** and **12** as well as all of the apolar bimesogens show an increase in the virtual N-NTB transition temperature in comparison to the methylene linked materials. Indeed the apolar materials show a significantly higher transition temperatures in general when an ether linking group is introduced into the spacer unit. The trends observed for the apolar materials fit well with both those observed for the methylene linked materials reported in the previous section, and for nonamethylene spaced materials in previous studies.2,31 A plot of the difference between I-N and N-NTB for methylene and ether-linked dimers is given in Figure **6**.

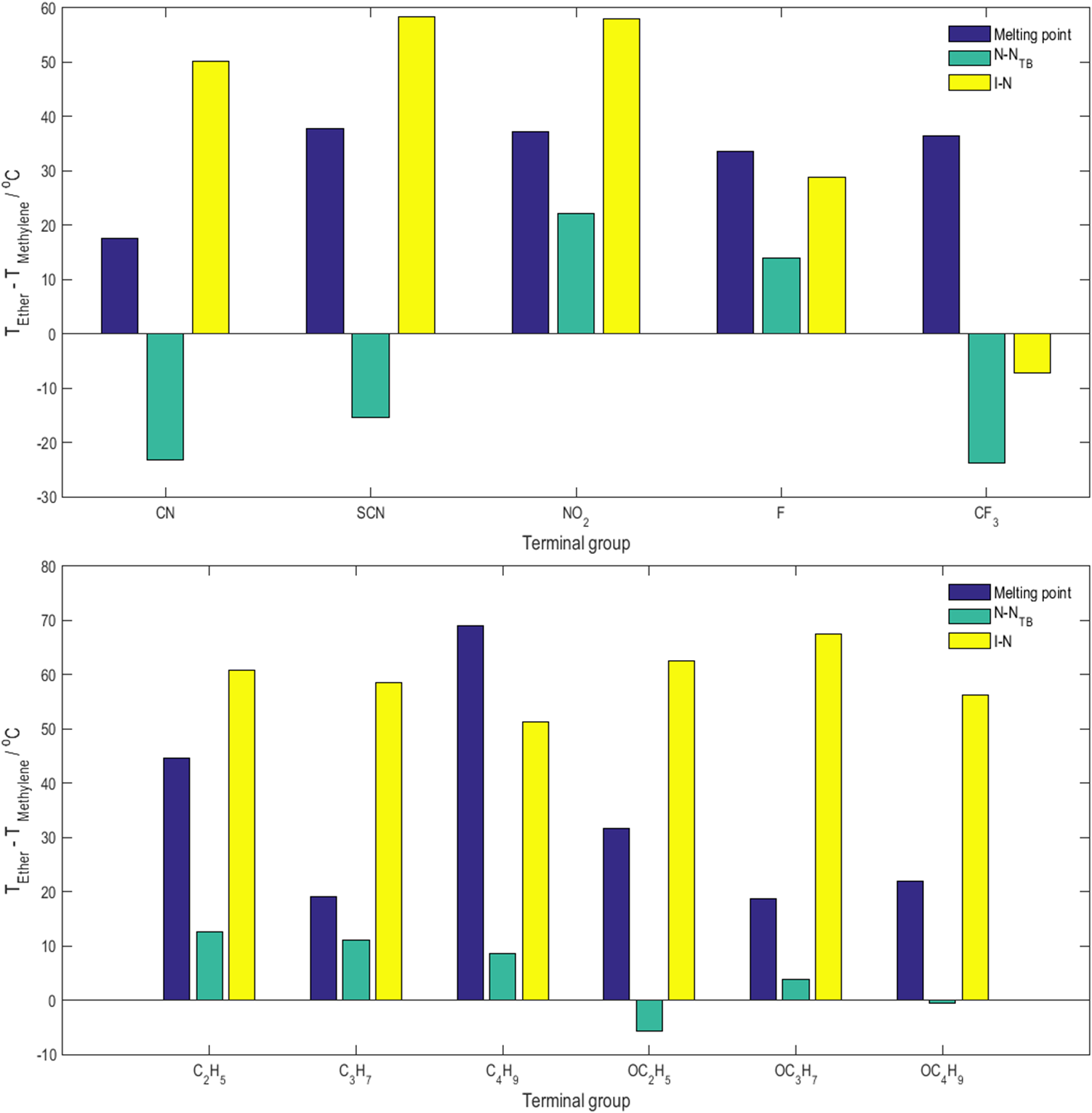


Figure 6: Plots of the difference in transition temperatures between ether and methylene linked materials (Tether  - Tmethylene / °C) for polar (top) and apolar (bottom) terminal groups.

For materials with a polar terminal group the clearing point is significantly higher when the linking group is an ether rather than a methylene group. With respect to the NTB phase, it appears that the trend is a small destabilisation when the methylene unit is replaced by an ether linkage, however increases in transition temperature were observed with nitro (compound **16**) and fluoro (compound **17**) terminated analogues. For apolar materials, the same increase in clearing point is apparent when the methylene unit is replaced with an ether linking group. For alkyl terminated materials, the virtual N-NTB transition is marginally higher for ether linked systems than for methylene, however in alkoxy terminated materials this trend does not occur. It would appear that although the NTB phase can, for certain compounds, be stabilised by the incorporation of ether linkages in lieu of methylene groups, the observation of the nematic to twist-bend nematic transition in the neat materials is precluded by short ranges of supercooling and high melting points. This runs counter to both established thinking, namely that the introduction of ether linkages should destabilise the NTB phase. For polar materials, however, the etherific compounds showed a generally less stable NTB phase than those with methylene spacers.

The increase in melting and clearing points for the ether linked materials can be attributed to a change in molecular topology upon introducing the ether moiety. As the bond angle of a C-O-C bond is generally larger (≈115-120°) than a C-C-C bond (≈109.5°), the molecules containing an ether linkage will tend towards being more linear in shape compared to their methylene linked analogues.

As a bent molecular architecture is one of the known prerequisites for the formation of the NTB phase a decrease in molecular bend would lead to a destabilising effect on the NTB phase. This increased linearity is also a probable cause for the increase in melting and clearing points of the materials, as the more linear molecules will be able to more effectively pack into a crystal phase and into the nematic phase as opposed to the more bent materials thereby increasing the thermal stability of these phases. This hypothesis is supported through molecular modelling used to calculate the intermesogen angle of both methylene and ether linked dimers (Figure 7), and correlating this with the transition temperatures.

Anglesrendered.tif

Figure 7: Energy minimised geometries of compounds 1 and 14 showing the differences in intermesogen angle (θ). Geometry optimised at the B3LYP/6-31G(d) level of DFT.

The intermesogen angle of all *trans* conformer of the ether linked compound **14** is significantly larger, *i.e.* less bent, than that of the all *trans* methylene-linked compound **1** (140.8 ° and 106.8 ° respectively). 1D NOESY NMR has been used to show that for both methylene ether-linked dimers the all *trans* conformers is dominant, 44 so while calculating an angle for a single geometry is not as desirable as knowing the full conformational distribution it is still valid in this instance.

Compound **14** has a significantly higher melting point than compound **1**, 166.6 °C versus 149.0. The nematic phase of compound **14** is enantiotropic, with a clearing point of 189.2 °C. This is far more stable than the monotropic nematic phase of compound **1**, with the isotropic to nematic phase transition occurring at 139.0 °C. This shows that the increased linearity of the ether spaced materials stabilises the nematic phase when compared to the more bent methylene linked dimer. With respect to the NTB phase, compound **14** does not exhibit this phase in it's neat state, however, when the N-NTB phase transition of this material is extrapolated from mixtures with CB9CB it is found to occur at 96.8 °C, almost 25 °C lower than the methylene linked analogue, where the N-NTB transition occurs at 120 °C, demonstrating that the linearity of the molecule does indeed have an effect on the NTB phase stability.

**Conclusions**

In this study we have shown that the primary barrier to ether linked materials forming the NTB phase appears to be the substantial increase in melting point caused by the increased linearity imparted by etherific linking group as opposed to its more bent, methylene linked counterpart. Although in some cases the introduction of the ether moiety into the spacer chain served to lower the N-NTB transition, in the majority of the materials presented herein the virtual N-NTB transition of the etherific materials actually occurs at slightly higher temperatures than for their methylene linked analogues. This suggests that the molecular bend is an important factor in the formation of the NTB phase, as dimers with spacers of an even parity do not exhibit this phase as these materials are significantly more linear than those with spacers of odd parity. These results complement the recently reported experimental link between the bend-angle of a dimer and the thermal stability of the NTB phase. 44

In the same vein the change in transitional properties between the methylene linked and ether linked materials can be inferred to be caused by the change in intermesogen angle, as this is the most significant change when comparing these two groups of compounds. The increased N-NTB transitions in the dimers with more flexible terminal chains (alkyl and alkyloxy) as opposed to the drop observed for most of the materials with inflexible, polar terminal groups suggests that the mobility of these chains serves to disrupt the packing between the molecules, offsetting the higher ordering made possible by the more linear molecular architecture. Although this disruption allows the NTB phase to form more easily, it is still not sufficient to see it in the neat material.

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