INVITED ARTICLE
The relationship between molecular structure and the incidence of the \( N_{TB} \) phase

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In this work, we present the first part of a study into the relationship between molecular structure and the occurrence of the ‘twist-bend nematic phase’ (\( N_{TB} \)). Given the large amount of chemical space that might reasonably be expected to give rise to the \( N_{TB} \) phase, this paper is only concerned with methylene-linked bimesogens bearing polar terminal groups based on the initial work of George Gray on cyanobiphenyls. As with other studies, we find that the \( N_{TB} \) phase is observed only for materials that contain an odd number of methylene units in the spacer chain. It also appears that, in a given series of materials, there is a weak negative correlation between the dipole moment of the individual mesogenic units and the thermal stability of the \( N_{TB} \) phase. Furthermore, we find that increasing the length–breadth ratio of the individual mesogenic units also provides a significant increase in the thermal stability of the \( N_{TB} \) phase. The electrooptic behaviour of two materials, one with a terminal nitrile unit and one with an isothiocyanate group, was investigated. The \( N_{TB} \) phase of the NCS-terminated material can be switched with a large applied voltage (20 V \( \mu m \)); however, the analogous nitrile-terminated material showed no electrooptic response under these conditions. Either the threshold voltage to switching is simply lower for isothiocyanate materials than nitriles or that there is more than one phase currently identified as the twist-bend nematic.

Keywords: \( N_{TB} \); twist bend; structure–property relationship; DFT; dimers; liquid crystal

Introduction

In 1973, George Gray, Ken Harrison and John Nash reported on the liquid crystal properties of the 4'-alkyl-4-cyanobiphenyls and their potential for applications in display devices.[1] Subsequently, these materials became the subject of many scientific and applications-driven researches. One adaption of the materials was to create dimers of their chemical architectures resulting in the formation of bimesogens.[2,3] When the linking methylene spacer between the aromatic units was set to be of odd parity, unusual phase behaviour was observed, and the discovery of a new twist-bend phase based on the nematic phase was found for the 1,0-di-(1*-cyanobiphenyl-4-y) alkanes, CBNCB.[4]

Since the reclassification of the lower temperature phase exhibited by odd members of the 1,0-di-(1*-cyanobiphenyl-4-y) alkanes, CBNCB, series of materials as the twist-bend nematic phase (\( N_{TB} \)), there has been a flurry of activity culminating in a series of excellent works concerning the structure of this phase, and its characterisation by methods as diverse as \(^2\)H NMR, FFTEM, electric field studies, calorimetry and polarised optical microscopy.[4–16] However, the widely accepted heliconical model for the \( N_{TB} \) phase has been called into question, with a recent \(^2\)H NMR study suggesting the material is not helical,[17] whereas others remain wedded to the presence of a local helical structure.[18] Most studies on ‘\( N_{TB} \)’ materials have focused on the 1,0-di-(1*-cyanobiphenyl-4-y)alkanes, CBNCBs, or the 1,11-bis(2',3'-difluoro-4'-alkyl-[1,1’4’,1”-terphenyl]-4-y)undecane (M2/M3) materials; this reflects the small number of compounds that are known to definitively exhibit this phase. Moreover, too few compounds are known to exhibit the \( N_{TB} \) phase to allow for any semblance of a structure–property relationship to be drawn. The elucidation of such relationships is important because it allows new materials to be obtained through rational design rather than serendipitous discovery.[19]

The discovery of the \( N_{TB} \) phase in ether-linked dimeric materials has dispelled the widely held belief that only methylene-linked dimers can exhibit the twist-bend phase.[20,21] Furthermore, a recent work by Chen et al. has shown that the \( N_{TB} \) can be observed in bent-core materials, and thus is not confined to dimeric mesogenic architectures.[22] An overview of the materials currently known to give the \( N_{TB} \) phase is given in Figure 1.

In this paper, we present the first part of a structure–property relationship for liquid crystal dimers and the \( N_{TB} \) phase. Here, we have limited ourselves to discussing methylene-linked, symmetrical compounds bearing a polar terminal group (i.e. units that would be expected to give positive values of the dielectric anisotropy if used as the basis for a low...
molar mass material) as shown by the general structure given in Figure 2.

From this structure, three property–structure correlations were developed, (i) where we develop correlations associated with introducing a linking group, X, within the aromatic core; (ii) where we broaden the aromatic core by introducing a lateral fluoro-substituent, W; and (iii) where the polarity is varied by introducing various polar groups, Y, at the termini of the aromatic units. In the following sections, these categories are sequentially discussed as a function of varying or constant methylene spacer length, n.

**Experimental**

1,0-di-(1”-Cyanobiphenyl-4-yl)heptane (CB7CB) and 1,0-di-(1”-cyanobiphenyl-4-yl)nonane (CB11CB) were prepared via literature methods and found to be >99.5% purity by reverse-phase HPLC assay.[16]

The intermediate diphenols i1–i5 (see Scheme 1) were prepared in three steps: anisole was first acylated with a diacyl chloride followed by ketone reduction and then demethylation to yield the desired diphenols. The dibenzoic acid i6 was prepared via acylation of bromobenzene with azealoyl chloride, followed by reduction of the ketone functionalities with TFA/Et3SiH. Low-temperature lithiation, carboxylation and finally acidification afforded i6.

The diphenols were esterified with the appropriate carboxylic acids to afford compounds 1–5 and 7–19, as shown in Scheme 2, whereas the dibenzoic acid i6 was esterified with 4-cyanophenol to yield compound 6, as shown in Scheme 3.

Compounds 1–5 were prepared from the diphenols i1–i5 via Steglich esterification with 4-cyanobenzoic acid in good yield. The Steglich esterification was also utilised to prepare analogues of compound 3. Compound 7 was prepared from i3 and 4-cyano-3-fluorobenzoic acid, compound 8 was prepared from i3 and 4-cyano-2-fluorobenzoic acid and compound 9 from i3 and 4-cyanobiphenyl-4’-carboxylic acid. Compounds 10–19 were prepared to investigate how variations in the polar group affect mesophase stability in mesogenic dimers. These were obtained via the Steglich esterification of either i1 or i3 with 4-fluorobenzoic acid (10 and 11), 4-trifluoromethylbenzoic acid (12 and 13), 4-isothiocyanatobenzoic acid (14 and 15), 4-nitrobenzoic acid (16 and 17) and 4-pentafluorosulphanylbenzoic acid (18 and 19).

![Figure 1. Compounds currently known to unequivocally exhibit the N_{TB} phase.[4,6,8,16,20–22]](image)

![Figure 2. General structure of methylene-linked dimers with varying (i) linking groups ‘X’, (ii) mesogenic core units with lateral substituent ‘W’ and multiplicity of rings ‘p’ and (iii) polar terminal groups ‘Y’.](image)
Scheme 1. Synthesis of the key intermediate diphenols ‘i1-i5’ and dicarboxylic acid i6.

Scheme 2. The synthetic route to compounds 1-5 and 7-19 from the intermediate diphenols ii-i5.
Compound 6, with its carboxylate esters ‘reversed’ relative to 1–5, was prepared via the Steglich esterification of \( \text{i6} \) with 4-cyanophenol in moderate yield. Full experimental details are provided in an electronic supplementary information to this article.

Results and discussion

**Linking groups – X – esters**

Perhaps the most well-known examples of materials that exhibit the \( N_{\text{TB}} \) phase are the CBnCB series, which comprise two 4′-cyanobiphenyl groups joined by a methylene spacer. When the spacer parity is even, the materials are nematogenic, whereas when the parity is odd the \( N_{\text{TB}} \) phase is also observed in addition to the conventional nematic phase. Modification of the structures of these materials to include an ester group linking the two aromatic rings gives the PCBnPCB series of materials, i.e. methylene-linked phenyl cyanobenzoate mesogenic units. The transition temperatures of both PCBnPCB and CBnCB families are given in Table 1.

It can be seen from Table 1 that the phase behaviour of the PCBnPCB series of materials broadly mirrors the CBnCB series in that the even members are nematogenic and the odd members exhibit the conventional nematic and the \( N_{\text{TB}} \) phases. The assignment of the lower temperature phase in the PCBnPCB series of materials was made via analysis of the corresponding defects textures and was confirmed unequivocally by miscibility studies with CB11CB (see Figure 7). All members of the PCBnPCB series exhibit a typical \textit{schlieren} texture for the nematic phase when viewed between untreated glass substrates using polarised light microscopy. For compounds with odd spacer parity, a definitive transition from the nematic phase to the \( N_{\text{TB}} \) phase was observed. For each material, a well-defined transition front was observed, and a typical \( N_{\text{TB}} \) texture exhibiting blocky domains, focal-conic and parabolic defects was found (see Figure 3). In the majority of cases, the \( N_{\text{TB}} \) phase, although monotropic in all of the PCBnPCB materials, showed a degree of supercooling.

The various transitional properties of compounds 1–5, as measured by DSC, are presented in Table 2, and plots of enthalpy and entropy as a function of chain length are presented in Figure 4. The N–\( N_{\text{TB}} \) phase transition was observed simultaneously with

![Diagram of the synthetic route to compound 6 from the intermediate dibenzoic acid i6.](image)

**Scheme 3.** The synthetic route to compound 6 from the intermediate dibenzoic acid i6.

Table 1. Transition temperatures (°C) and extrapolated \( N_{\text{TB}} \)-N transition from binary mixtures with \( CB11CB \) for the CBnCB and 1,n-bisphenyl cyanobenzoate (PCBnPCB) materials.

| No. | X       | N | Cr | \( N_{\text{TB}} \) | N  | Iso |
|-----|---------|---|----|---------------------|----|-----|
|     |         | 7 | ●  | 102                 | ●  | 103 |
| 1   | –COO–   | 7 | ●  | 149.0               | (●)| 120.0 |
| 2   | –COO–   | 8 | ●  | 175.0               | –  | –  |
|     |         | 8 | ●  | 195.3               | –  | –  |
| 3   | –COO–   | 9 | ●  | 83.0                | ●  | 105 |
|     |         | 9 | ●  | 157.6               | (●)| 114.5 |
| 4   | –COO–   | 10| ● * | 193.4               | –  | –  |
|     |         | 10| ●  | 174.1               | (●)| 187.2 |
| 5   | –COO–   | 11| ●  | 99.9                | ●  | 108.6 |
|     |         | 11| ●  | 157.6               | (●)| 113.9 |
|     |         |   |    |                     | (●)| 143.8 |

Notes: Transition temperatures for CB7CB, CB9CB and CB11CB were in agreement with literature values, whereas the transition temperatures for CB8CB and CB10CB were taken from the literature.[2,7,12,16,23] *The melting point of CB10CB was not reported.
crystallisation for compound 5, and hence this transition was not observed by DSC; therefore, the values associated with the N–NTB phase transition are not available for this material.

An odd-even effect is apparent for both entropy and enthalpy for the nematic to isotropic liquid transition. Conversely, no such behaviour is apparent for the melting point. The NTB phase is only exhibited by

Table 2. Scaled N/NTB transition values, associated enthalpies (kJ mol\(^{-1}\)) and associated entropies of transition for compounds 1–5.

| No. | N  | \(T_{N\text{N}}-T_{N\text{I}}\) | \(\Delta H_{Cr-N}\) | \(\Delta H_{N-I}\) | \((\Delta S_{Cr-N})/R\) | \((\Delta S_{N-I})/R\) |
|-----|-----|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1   | 7   | 0.86            | 46.34           | 0.12            | 0.63            | 13.20           | 0.06            | 0.19            |
| 2   | 8   |                 | 39.14           | --              | 0.61            | 10.05           | --              | 0.15            |
| 3   | 9   | 0.78            | 45.41           | 0.65            | 1.50            | 12.68           | --              | 0.43            |
| 4   | 10  | --              | 56.77           | --              | 0.70            | 14.64           | --              | 0.18            |
| 5   | 11  | 0.79*           | 33.86           | --              | 2.00            | 9.45            | --              | 0.58            |

Note: *For compound 5, the NTB–N transition temperature was extrapolated from binary mixtures with CB11CB and determined to be 113.9° C; thus, enthalpy and entropy values could not be obtained.

Figure 3. (colour online) A representative photomicrograph of the optical texture of the NTB phase of diester compound 1 at 118.2°C (×100). The expanded region shows several focal-conic defects, with the ellipse and hyperbola clearly visible.

Figure 4. (colour online) Plot of enthalpy (left, \(\Delta H\), kJ mol\(^{-1}\)) and entropy (right, \(\Delta S/R\)) as a function of methylene spacer length for compounds 1–5.
compounds 1 and 3, with the entropy and enthalpy of the N–N$_{TB}$ transition being significantly larger for compound 3 than for 1. It should also be noted that the entropy of the N–N$_{TB}$ transition for both compounds 1 and 3 is significantly larger than that of the parent N$_{TB}$ materials (e.g. for CB11CB $\Delta S_{N_{TB}-N}/R = 0.011$).[16]

When examined by differential scanning calorimetry (DSC), the peak shape of the N–N$_{TB}$ transition (i.e. heat flow vs temperature) for CB11CB has been observed to vary as a function of the heating/cooling rate of the thermogram.[13] Similar observations were made for compound 1 (PCB7PCB) as shown in Figure 5. The Iso–N and N–N$_{TB}$ transitions appear to be first order at slower scan rates (0.2, 0.5 and 1°C min$^{-1}$), but for faster scan rates (5 and 10°C min$^{-1}$) there is a contribution from kinetic processes associated with the phase transition. The effects observed for both clearing point and transition into the N$_{TB}$ phase indicate that there is substantial reorientation occurring over a temperature range of 2–4° for fast scan rates, for the slower scans the reorientation keeps up with the scan rate and the excess heat produced/adsorbed is incorporated into the base line. However, there is a difference between the two transitions as demonstrated when the enthalpies and entropies are plotted as a function of scan rate for the two transitions for the family of materials (see Figure 6). The liquid-to-nematic phase transition shows a continuous change as a function of scan rate, whereas the N to N$_{TB}$ transition shows a jump in value as the scan rate is increased. The continuous change for the N–I transition indicates that the two phases have similar fluid-like structures and properties, whereas for the N to N$_{TB}$ transition the discontinuity indicates a

![Figure 5](image1.png)

**Figure 5.** (colour online) Variable scan rate DSC thermograms of compound 1 (from top to bottom, 0.2, 0.5, 1, 5 and 10°C min$^{-1}$), demonstrating the thermally reproducible nature of both Iso–N (right) and N–N$_{TB}$ (left) transitions.

![Figure 6](image2.png)

**Figure 6.** (colour online) Plot of the associated enthalpies ($\Delta H$, kJ mol$^{-1}$) and entropies ($\Delta S/R$) for compound 1 as a function of DSC scan rate.
difference in the relative viscosities and ordering of the two phases.

Although the $N_{TB}$ phase was shown to be exhibited by compounds 1 and 3 via its distinctive associated defect textures, miscibility studies with CB11CB were used to give an unequivocal phase assignment. The resulting Gibbs’ phase diagrams are presented in Figure 7 for compounds 1 (PCB7PCB) and 3 (PCB9PCB) in binary mixtures with CB11CB.

It can be seen from Figure 7 that in both cases the nematic and $N_{TB}$ phases of the two materials were found to be miscible with those of CB11CB across the entire phase diagram, with both showing a near-linear relationship with respect to temperature. Thus, it can be concluded that the lower temperature phase exhibited by compounds 1 and 3 is indeed the $N_{TB}$ phase, a fact that is reflected by their associated defect textures. By using the measured enthalpies of fusion and melting points for 1, 3 and CB11CB, it is possible to predict the composition and thermal behaviour of the eutectic mixture through the Schröder-van Laar equation.[24, 25] This formula is generally quite successful at predicting the eutectic behaviour of mixtures of calamitic nematic liquid crystals. The Schröder-van Laar equation predicts that for binary mixtures with CB11CB the eutectic mixture occurs at 13.9 wt% of 1 and 11.6 wt% of 3. However, in the phase diagram of binary mixtures of compound 1 (PCB7PCB) and CB11CB, the eutectic mixture is at approximately 23 wt% of 1, whereas for compound 3 (PCB9PCB) and CB11CB binary mixtures it occurs at 35% of compound 3. Although the predicted results are only within 20% of the experimental values, they still indicate that the eutectic points for mixtures of the crystal phases are not unreasonable and the phase behaviours in the phase diagrams are classical. Thus, on this basis, the $N_{TB}$ phase is not a soft crystal phase.

It is interesting to note the more general differences in the thermal behaviours of the PCBlPCB series and the CBnCB series of materials. For example, although the analogous members of each series exhibit identical phase sequences, their transition temperatures differ significantly and in all cases members of the PCBlPCB series exhibit higher $N$-$N_{TB}$ transition temperatures and higher isotropisation points, which is probably due to the longer aromatic core units of the PCBlPCBs. These increases are mirrored in the melting points of members of the PCBlPCB series, which are also higher than analogous members of the CBnCB series. Consequently, the $N_{TB}$ phase remains monotropic in all of the odd members of the PCBlPCB series, whereas CB7CB, CB9CB and CB11CB all exhibit enantiotropic $N$-$N_{TB}$ phase transitions. The increase in melting point as a consequence of the incorporation of an ester functionality into the molecular architecture likely stems from increased electrostatic interactions between molecules, which serve to stabilise a crystalline packing arrangement. A similar effect may be responsible for the increase in the thermal stabilities of the nematic and $N_{TB}$ phases, although it should be noted that the ester group also increases the aspect ratio of the two arms of the dimer (via increasing length), which may also increase mesophase stability. The incorporation of a carboxylate ester will also increase or reduce the dipole moment, depending on the relative orientation to the terminal polar group. In the PCBlPCB materials, the ester effectively opposes the dipole caused by the cyano group, and thus tempers the dipole moment of each mesogenic unit. In order to investigate this, a number of analogues of compound 3 but with structures designed to give variation in dipole moment were prepared; the thermal behaviour of these materials is presented in Table 3.

**Orientation of linking groups and lateral substituents**

Having established that ester as well as biphenyl derivatives exhibits $N_{TB}$ phases, we decided to examine...
classical substitution patterns associated with the aromatic cores of the mesogens and their effects on property–structure correlations for a constant number of methylene units. Firstly, we chose to examine the directionality of the linking group X (in this case COO, compounds 3 and 6); secondly, lateral fluorination in the outer ring (compounds 6–8); and thirdly, extension of the aromatic core (compound 9) in a bid to radically change the aspect ratios of the mesogenic cores. In this study, we also investigated the dipolar properties of the materials through semi-empirical, DFT and MP2 methods in order to relate mesophase formation to dipole strength. The results obtained for the various phase transitions are given in Table 3.

Firstly, the reversal of the ester unit (compare structure 3 with 6) results in a larger dipole moment for the mesogenic cores and a drop in the N–N_{TB} transition temperature of almost 20°C. Furthermore, a similar comparison can be made for compounds 7 and 8 where a fluorine atom is incorporated into the terminal ring of compound 3. For compound 7, the dipole associated with the fluorine substituent augments the dipole of the nitrile group and acts as a disrupter to pairwise interactions of the molecules, whereas for compound 8, the dipole of the fluorosubstituent opposes the nitrile dipole. When rapidly cooled compound 7 exhibits a transient N_{TB} phase just prior to crystallisation at 90°C, however, accurate measurement of the N–N_{TB} transition is difficult and cooling at slower rates leads to crystallisation directly from the nematic phase. For compound 8, the N–N_{TB} transition was measured to be 108.6°C, which is somewhat higher than for 7. Both melting and clearing points of compound 7 are significantly suppressed compared with compound 8, owing to disruption of the molecular pairing caused by fluorine atom in the 3-position. This is an indicator that lateral interactions are potentially important to stabilisation of the N_{TB} phase.

Replacement of the 4-phenyl 4′-cyanobenzoate mesogenic unit used in compound 3 with 4-phenyl 4′-(4″-cyanophenyl)benzoate in compound 9 gives a significantly increased length-to-breadth ratio for each mesogenic unit. As a consequence, compound 9 has a slightly higher melting point than 3, a significant increase in the N–N_{TB} transition, which is enantiotropic, and a dramatic increase in the clearing point. As compound 9 has virtually the same computed dipole moment as compound 3 (as shown in Figure 5), we ascribe the increase in the N_{TB} thermal stability in this compound to steric factors associated with the aspect ratio.

Examination of the phase transitions by DSC confirms the phase transition temperatures determined by thermal polarised light microscopy and provides information on the enthalpies and entropies associated with the phase transitions as shown in Table 4. Although thermodynamic data for the N to N_{TB} transitions for compounds 7 and 8 were not determined due to the onset of recrystallisation, there is still sufficient data to make some comparisons as follows. For compounds 3 and 6, the magnitudes

| No. | R | Cr | N_{TB} | N | Iso |
|-----|---|----|--------|---|----|
| CB9CB | NC–O | ● | 83 | ● | 105 | ● | 119.8 | ● |
| 3 | NC–O | ● | 157.6 | ● | 114.5 | ● | 146.6 | ● |
| 6 | NC–O | ● | 125.2 | ● | 95.0 | ● | 138.4 | ● |
| 7 | NC–O | ● | 108.4 | ● | – | ● | 97.8 | ● |
| 8 | NC–O | ● | 150.0 | ● | 108.6 | ● | 128.5 | ● |
| 9 | NC–O | ● | 165.5 | ● | 179.6 | ● | 324.0 | ● |

Note: †The N_{TB} phase could be observed using uncontrolled, rapid cooling; however, this method precludes obtaining an accurate temperature value for the N–N_{TB} transition.
of the enthalpies and entropies of the N\textsubscript{T\textsubscript{TB}}−N and N−I\textsubscript{so} transitions are reversed with respect to one another. Compound 3 has lower values than 6 for the clearing point, but higher relative values for the N to N\textsubscript{T\textsubscript{TB}} transition. This indicates that for compound 3 the nematic phase is more liquid-like and disordered than for compound 6, whereas the N\textsubscript{T\textsubscript{TB}} phase for 6 is more similar in ordering within the nematic phase than is the case for compound 3. This may reflect the opposing dipole of the carbonyl moiety relative to the nitrile for compound 3 in comparison to compound 6. For compounds 7 and 8, although we cannot comment on the N to N\textsubscript{T\textsubscript{TB}} transition, the clearing point enthalpies show that compound 7 has a much lower enthalpy and entropy than 8. This indicates that there is a much larger change in molecular organisation at the phase transition for 8 than 7, and thus the inner fluoro-substituent is more disruptive than the 3-fluoro-substituent. Remarkably compound 9 has very low values of the entropy and entropy for the two phase transitions, indicating that the local organisation does not change appreciably on passing from the liquid to the N\textsubscript{T\textsubscript{TB}} phase, which is probably due to a relatively higher organisation of the molecules in the isotropic liquid due to the higher aspect ratio.

In order to elucidate the results obtained from DSC, the dipole moments for the aromatic fragments of compounds 3, 6, 7 and 8 as well as 4-methyl-4-cyanobiphenyl moiety were computed at the PM6, B3LYP/6–31 G\textsuperscript{*} and MP2/6–31 G\textsuperscript{*} levels of theory. It can be seen from the results obtained (Figure 8) for the three levels of theory that the aromatic moieties that have the lower dipole moment are those where

| No. | \(T_{N\textsubscript{BB}}/T_{N\textsubscript{T\textsubscript{BB}}}\) | \(\Delta H_{C\textsubscript{N}}\) | \(\Delta H_{N\textsubscript{BB}}/C\textsubscript{0}\) | \(\Delta H_{N\textsubscript{BB}}/C\textsubscript{0}\) | \(\Delta H_{C\textsubscript{N}}/R\) | \(\Delta H_{N\textsubscript{BB}}/C\textsubscript{0}/R\) | \(\Delta H_{N\textsubscript{T\textsubscript{BB}}}/C\textsubscript{0}/R\) | \(\Delta H_{N\textsubscript{T\textsubscript{BB}}}/C\textsubscript{0}/R\) |
|-----|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 3   | 0.78            | 45.406          | 0.650           | 1.499           | 12.679          | 0.202           | 0.430           |
| 6   | 0.69            | 63.019          | 0.359           | 1.801           | 19.028          | 0.117           | 0.526           |
| 7   | 0.85            | 56.900          | *               | 0.430           | 17.937          | *               | 0.140           |
| 8   | 0.55            | 79.600          | *               | 2.200           | 22.626          | *               | 0.659           |
| 9   | 0.30            | 42.309          | 0.006           | 4.455           | 11.601          | 0.001           | 0.897           |

Notes: *Recrystallisation occurred prior to the onset of the N\textsubscript{T\textsubscript{TB}} phase during DSC studies irrespective of cooling rate, therefore the enthalpy and entropy could not be determined. †The N\textsubscript{T\textsubscript{TB}} phase could be observed using uncontrolled, rapid cooling; however, this method precludes obtaining an accurate temperature value for the N−N\textsubscript{T\textsubscript{TB}} transition.

Figure 8. Plot of computed dipole moments at the PM6 (blue), B3LYP/6–31 G\textsuperscript{*} (red) and MP2/6–31 G\textsuperscript{*} (green) levels of theory for the displayed mesogenic ‘fragments’.
either the ester-linking groups have an opposed dipole moment of the carbonyl unit to that of the nitrile or where the fluoro-substituent is located in an opposing position again to the nitrile. Interestingly, the moieties for compounds 3 and 6 were used in previous studies on the development of nematogens for display device applications.[26,27] In these studies, it was shown that compounds with the terminal moiety of material 3 were more likely to exhibit smectic C rather than nematic phases, which was attributed to a much lower dipole moment than for the relative moiety of compound 6, and hence this was a test for compound 3 to examine whether it would support smectic C formation rather than that of an N\textsubscript{TB} phase. Nevertheless, no correlation could be found between the melting and clearing points with computed dipole moments at any level of theory. However, it appears there is a correlation between dipole moment and the thermal stability of the twist-bend nematic phase (as there was for the smectic C phase reported previously), as measured by the N to N\textsubscript{TB} transition temperature. Increases in the dipole moment lead to a reduction in the phase stability, as shown in Figure 9.

In terms of molecular pairing, it is well known that simple cyano-terminated materials form dynamic intermolecular dimer pairs through quadrupolar interactions of the nitriles. However, with fluorine in the 3-position the phase behaviour is significantly different, possibly as a result of the fact that this substitution pattern breaks up the formation of quadrupolar interactions between the terminal cyano functionalities of neighbouring molecules.[19,28,29] Although the thermal stability of the N\textsubscript{TB} phase is clearly dependent to some extent on the molecular dipole moment, this is not the only factor as illustrated by compound 9, the N\textsubscript{TB} to N transition temperature for which is 65°C higher than the related ‘2-ring’ compound 3. The implication is that steric factors, and specifically the aspect ratio and stronger π–π interactions, have some role to play in dictating the relative thermal stability of the N\textsubscript{TB} phase.

Changing the terminal group

Having examined the variations in linking groups and lateral substitution, in this section we examine changes to the terminal polar groups of the aromatic moieties while maintaining the same structure for the rest of the molecule with seven or nine methylene units, i.e. the change in end group is the variable. However, at an ensemble level, there will be differences in structure, e.g. other polar groups, notably NCS, do not give rise to intermolecular pairing in the same manner as the nitrile unit.[30] Thus, in order to further probe the relationship between dipole moment and the N\textsubscript{TB} phase, a family of materials based on compounds 1 and 3 (PCB7PCB and PCB9PCB, respectively) were prepared via esterification of i1 and i3 with commercially available benzoic acids bearing various polar groups in the 4-position. The end groups fall into two groups, conjugative (CN, NCS, NO\textsubscript{2}) and non-conjugative (F, CF\textsubscript{3}, SF\textsubscript{5}). The phase transitions for these materials are given in Table 5 and the thermodynamic behaviour in Table 6.

The first point to note is that the terminal groups that are not conjugative do not exhibit the N\textsubscript{TB} phase. This indicates that polarisability in the mesogenic units is important for the formation of bend-twist phases. Conversely, the conjugative isothiocyanate unit supports the formation of the N\textsubscript{TB} phase,

![Figure 9](image-url) (colour online) A plot of the N to N\textsubscript{TB} transition temperature of compounds 3, 6, 8 and 9 as a function of computed dipole moment at three different levels of theory.
whereas the nitro compound 16 is non-mesogenic and nonamethylene analogue 17 is monotropic nematic.

In order to elucidate the melting behaviour, the dipole moment for each aromatic fragment was computed at the various levels of theory (PM6, B3LYP/6–31 G* and MP2/6–31 G*). It can be seen from Figure 10 that the CF₃ group has a dipole moment intermediate between the SCN and CN groups, yet the trifluoromethyl compounds (12 and 13) are non-mesogenic, which is probably due to the lack of conjugation between the polar end group and the aromatic unit. It should be noted that the analogous calamitic materials of these polar, non-mesogenic dimers would not be necessarily expected to be liquid crystalline. Similarly, the F and SF₅ end groups are generally considered to be inferior to the nitrile group in their ability to support the mesomorphic state, which is illustrated for the series of polar 4-phenyl (4-alkylcyclohexyl) materials.[31] Again the end groups are not in conjugation with the aromatic rings. For the conjugative systems, the nitro materials have the highest dipole moments, and therefore the interactions are too strong in order to support mesophase formation. The relatively low enthalpies for the melting points suggest that repulsive interactions may be more dominant.

From this we conclude that the occurrence, and indeed absence, of the Nₜₐₜ phase in this family of materials is supported by conjugative polarisable interactions, but where the dipoles are large repulsive effects may dominate, whereas low values for the dipole result in weak interactions which cannot support the structure of the phase.

**Electrooptic studies**

In order to assess the behaviour of both nematic and Nₜₐₜ phases under applied electric fields, compounds 3

| No. | X     | n | Cr | Nₜₐₜ | N | I     |
|-----|-------|---|----|------|---|-------|
| 1   | CN    | 5 | ●  | 149  | (●) | 120.0 | 139.0 |
| 3   | CN    | 7 | ●  | 157.6| (●) | 114.5 | 146.6 |
| 10  | F     | 5 | ●  | 91.5 | –   | –     | –     |
| 11  | F     | 7 | ●  | 97.6 | –   | –     | –     |
| 12  | CF₃   | 5 | ●  | 114.9| –   | –     | –     |
| 13  | CF₃   | 7 | ●  | 102.4| –   | –     | –     |
| 14  | SCN   | 5 | ●  | 105.1| (●) | 103.3 | 120.5 |
| 15  | SCN   | 7 | ●  | 97.7 | ●   | 103.7 | 127.4 |
| 16  | NO₂   | 5 | ●  | 113.3| –   | –     | –     |
| 17  | NO₂   | 7 | ●  | 105.4| –   | –     | (●) 97.8|
| 18  | SF₅   | 5 | ●  | 126.5| –   | –     | –     |
| 19  | SF₅   | 7 | ●  | 123.0| –   | –     | –     |

**Table 5. Transition temperatures (°C) of some polar methylene-linked dimers.**

| No. | X     | n | Cr | Nₜₐₜ | N | I     |
|-----|-------|---|----|------|---|-------|
| 1   | CN    | 7 | 0.86| 46.336| 0.260| 0.542| 13.202| 0.083| 0.158|
| 3   | CN    | 9 | 0.78| 43.176| 0.764| 1.426| 12.679| 0.202| 0.430|
| 10  | F     | 7 | –   | 48.312| –   | –     | 15.936| –   | –     |
| 11  | F     | 9 | –   | 47.310| –   | –     | 15.348| –   | –     |
| 12  | CF₃   | 7 | –   | 39.152| –   | –     | 12.136| –   | –     |
| 13  | CF₃   | 9 | –   | 55.691| –   | –     | 17.836| –   | –     |
| 14  | SCN   | 7 | 0.86| 36.505| 0.242| 0.176| 11.608| 0.077| 0.054|
| 15  | SCN   | 9 | 0.81| 34.165| 0.089| 0.274| 11.081| 0.029| 0.082|
| 16  | NO₂   | 7 | –   | 24.217| –   | –     | 7.537| –   | –     |
| 17  | NO₂   | 9 | –   | 29.534| –   | 0.168| 9.327| –   | 0.055|
| 18  | SF₅   | 7 | –   | 37.192| –   | –     | 11.193| –   | –     |
| 19  | SF₅   | 9 | –   | 36.904| –   | –     | 11.205| –   | –     |

**Table 6. Scaled N/Nₜₐₜ transition values, associated enthalpies (kJ mol⁻¹) and associated entropies of transition for dimers 1, 3 and 10–19.**
and 15 were flow-filled into 5 μm cells (Linkam) treated to give homogeneous alignment (antiparallel buffed polyimide) via capillary action. Both compounds gave well-aligned nematic phases, but cooling into the N_{TB} phase gave the ‘rope-like’ texture as shown in Figure 11, with the stripe direction being parallel to the rubbing direction.

The nematic phases of both compounds 3 and 15 responded to an applied electric field in a manner typical for low-molecular-weight materials of positive dielectric anisotropy. A Fréedericksz transition was observed at low frequency (<0.1 Hz) and voltage (<2 V μm⁻¹) for both materials. Increasing the frequency (>0.1 Hz) leads to the appearance of Williams’s domains, the type of domains being dependent on the frequency, amplitude and waveform utilised. Photomicrographs of the patterns obtained in the nematic phase for compound 15 at a low applied frequency (~1 Hz) are given in Figure 12.

At low frequency (sub 1 Hz, Figure 12(a–d)), there was a significant amount of dynamic motion associated with the Williams’s domains. The cell containing compound 15 was also subjected to investigation at higher frequencies, with the patterns obtained presented in Figure 10. At a frequency of 200 Hz and amplitude of 14 V μm⁻¹ (Figure 13(a)), a square-grid-type pattern was observed, consistent with the multi-directional domains previously reported for ether-linked bimesogens.[20] By increasing the frequency

Figure 10. Structure of a ‘mesogenic fragment’ (top), and a plot of dipole moments computed at PM6 (blue), B3LYP/6–31 G* (red) and MP2/6–31 G* (green) levels of geometry optimised at the same level of theory, as a function of ‘X’ group.
into the megahertz regime, the dynamic motion observed at low frequency was almost entirely suppressed. A rich variety of patterns could be observed at high frequency, including chevron-like structures (Figure 13(c) and (g)) and tubular structures (Figure 13(d–f)).

When cooling compounds 3 and 15 into the N_{TB} phase, the well-documented ‘rope-like’ texture was formed; see Figure 11 for examples of this texture. No response to the applied field could be elicited for compound 3, even at an amplitude of 20 V µm⁻¹ and cell thickness of 5 µm, instead the material irreversibly adopts a homeotropic alignment and the rope texture can only be restored by reheating into the nematic phase and cooling into the N_{TB}. A significant ionic response could, however, be detected. Compound 15
was subjected to the same method of inquiry; however, the behaviour of this material in the N\textsubscript{TB} phase is markedly different from that of 3. Application of a high-frequency (1 kHz), low-amplitude (1 V \textmu m\textsuperscript{-1}) sine waveform transformed the rope texture into a fairly well-aligned, homogenous texture similar to (a) in Figure 13. This ‘light state’ could be extinguished by rotation of the sample, indicating that the alignment of the material was uniform. By increasing the amplitude to 20 V \textmu m\textsuperscript{-1} and lowering the frequency (<20 Hz), it was possible to observe a switching process in the N\textsubscript{TB} phase, from the uniform bright state to a dark state that remained optically extinct upon rotation of the sample, thereby suggesting that the material is homeotropically aligned in the switched state. However, unlike compound 3, switching from this homeotropically aligned state to the original bright state occurred. Hence, it appears that compound 15 shows a field-induced reorientation of the constituent molecules similar to that of a Fréedericksz transition that is typical for a nematic phase formed by materials of positive dielectric anisotropy. However, the angle of switching is small, in the order of 5°. Photomicrographs captured during low-frequency switching (1 Hz) are presented in Figure 11. It should, however, be noted that the switching is not bistable, and if the field is removed at any point during the cycle the sample eventually reverted to the rope texture. Furthermore, if a sufficiently low frequency is used (<0.1 Hz), then the rope texture can be observed to grow in and recede as the strength of the AC field decreases and increases, respectively. Thus, a threshold voltage exists at which the rope texture is transformed to this uniform light state; in compound 3, this threshold was measured to be around 12 V \textmu m\textsuperscript{-1} when the sample was at 100°C (Figure 14).

Now an important question is raised: Why should the N\textsubscript{TB} phase of compound 15 (and indeed, other materials reported in the literature) [9] be reversibly switchable, yet compound 3 and also other literature examples [16,20] are not? Two distinct possibilities arise, the first of which concerns the strength of intermolecular interactions. It is well established that nitrile groups tend to lead to dynamic intermolecular pairing through a quadrupolar interaction, whereas isothiocyanate groups do not tend to do this to the same extent. Thus, the weaker intermolecular forces are more easily overcome in NCS-terminated materials than for the analogous CN-terminated material, meaning that once the CN-terminated analogue adopts a field-induced homeotropic alignment,
relaxation back to a planar aligned state is extremely slow to occur, whereas for the NCS-terminated material relaxation occurs rapidly. Furthermore, at the voltages needed to switch nitrile-terminated materials, there is dielectric breakdown, leading to space-charge and ionic switching; however, due to the lower threshold, this does not occur to the same extent for the isothiocyanate analogues.

A second possibility is that there is more than one phase presently identified as the N\textsubscript{TB}. It has recently been suggested that a ‘splay bend nematic phase’,\cite{32} perhaps to be denoted N\textsubscript{SB}, may also exist in addition to the ‘twist-bend’ nematic. Further, there is experimental evidence to suggest such a phase exists in a family of unsymmetrical, chiral bimesogens.\cite{33,34} It is entirely possible that some of the materials identified as exhibiting the N\textsubscript{TB} phase to date may in fact exhibit this proposed modification. A study of these materials by either freeze-fracture transmission electron microscopy (FFTEM) or \textsuperscript{2}H solid-state NMR are perhaps the only methods, aside from optical microscopy and electrooptic studies, that would be useful in investigating such a possibility.

Conclusions

In this article, we have prepared a number of new dimeric materials that exhibit the twist-bend nematic phase. These materials are prepared from the synthetically versatile ‘diphenols’, aka bis(4-hydroxyphenyl) alkanes; in this work, we have restricted ourselves to discussing polar materials with one carboxylate ester per aromatic mesogenic unit. We find that within a given series of materials there is a negative correlation between the dipole moment of the individual mesogenic units and the thermal stability of the N\textsubscript{TB} phase. Furthermore, we find that increasing the aspect ratio of the individual units also provides an increase in the thermal stability of the N\textsubscript{TB} phase.

The electrooptic behaviour of two compounds, one bearing nitrile groups and one bearing isothiocyanate groups, was investigated. We found that the N\textsubscript{TB} phase of the NCS material could be switched with a large applied voltage (20 V \textmu m\textsuperscript{-1}); however, the analogous nitrile material was unresponsive. This discrepancy leads to two possible conclusions: either the threshold voltage to switching is simply lower for isothiocyanate materials than nitriles because the interactions are weaker or that there is more than one phase currently identified as the twist-bend nematic.

In essence the N\textsubscript{TB} phase appears to be a ‘Goldilocks phase’. Too strong a terminal dipole unit and the phase is suppressed, too low a polarisability associate with a terminal dipole unit and again the phase is suppressed, in-between these extremes the phase is stable, thereby providing us an interesting property–structure to build upon in the rational design of N\textsubscript{TB} materials.

Supplemental data

Supplemental data for this article can be accessed here.

References

[1] Gray GW, Harrison KJ, Nash JA. New family of nematic liquid crystals for displays. Electronics Lett. 1973;9:130. doi:10.1049/el:19730096.
[2] Emsley JW, Luckhurst GR, Shilstone GN, Sage I. The preparation and properties of the \textalpha\textsubscript{o}-bis(4,4’-Cyanobiphenyloxy)alkanes: nematogenic molecules with a flexible core. Mol Cryst Liq Cryst. 1984;102:223–233. doi:10.1080/14065848070532.
[3] Imrie CT, Henderson PA. Liquid crystal dimers and oligomers. Curr Opin Colloid Interface Sci. 2002;7:298–311. doi:10.1016/S1359-0294(02)00092-4.
[4] Panov VP, Nagaraj M, Vij JK, Panarin YP, Kohlmeier A, Tamba MG, Lewis RA, Mehl GH. Spontaneous periodic deformations in nonchiral planar-aligned bimesogens with a nematic-nematic transition and a negative elastic constant. PRL. 2010;105:167701. doi:10.1103/PhysRevLett.105.167801.
[5] Meyer RB. Structural problems in liquid crystal physics. In: Balian R, Weil G, editors. Les Houches summer school in theoretical physics, 1973. Molecular fluids. New York (NY): Gordon and Breach; 1976. p. 273–373.
[6] Dozov I. On the spontaneous symmetry breaking in the mesophases of achiral banana-shaped molecules. Europhys Lett. 2001;56:247–253. doi:10.1209/epl/i2001-00513-x.
[7] Cestari M, Diez-Berart S, Dunnur DA, Ferrari A, De La Fuente MR, Jackson DdB, Lopez DO, Luckhurst GR, Perez-Jubindo MA, Richardson RM, Salud J, Timimi BA, Zimmermann H. Phase behaviour and properties of the liquid-crystal dimer 1’-7’-bis(4-cyanobiphenyl-4’-yl) heptane: A twist-bend nematic liquid crystal. Phys Rev. 2011;84E:031704.
[8] Tripathi CSP, Losada-Pérez P, Glorieux C, Kohlmeier A, Tamba MG, Mehl GH, Leys J. Nematic-nematic phase transition in the liquid crystal dimer CBC9CB and its mixtures with 5CB: a high-resolution adiabatic scanning calorimetric study. J Phys Rev. 2011;84:041707. doi:10.1103/PhysRevE.84.041707.
[9] Panov VP, Balachandran R, Nagaraj M, Vij JK, Tamba MG, Kohlmeier A, Mehl GH. Microsecond linear optical response in the unusual nematic phase of achiral bimesogens. Appl Phys Lett. 2011;99:261903. doi:10.1063/1.3671996.
[10] Henderson PA, Imrie CT. Methylene-linked liquid crystal dimers and the twist-bend nematic phase. Liq Cryst. 2011;38:1407–1414. doi:10.1080/02678292.2011.624368.
[11] Beguin L, Emsley JW, Lelli M, Lesage A, Luckhurst GR, Timimi BA, Zimmermann H. The chirality of a twist-bend nematic phase identified by NMR.
chiral nematic liquid crystal phase of an achiral rigid bent-core mesogen. Rev E. 2014;89:022506.

[23] Emsley JW, Luckhurst GR, Shilstone GN. The orientational order of nematogenic molecules with a flexible core. Mol Phys. 1984;53:1023–1028. doi:10.1080/00268978400102811.

[24] Hulme DS, Raynes EP, Harrison KJ. Eutectic mixtures of nematic 4′-substituted 4-cyanobiphenyls. J C S Chem Comm. 1974;3:98–99. doi:10.1039/c39740000098.

[25] Raynes EP. Mixed systems: phase diagrams and eutectic mixtures. In: Goodby JW, Collings PJ, Kato T, Tschierske C, Gleeson H, Raynes EP, editors. The handbook of liquid crystals. 2nd ed. Vol. 1. New York (NY): Wiley; 2014. p. 351–363.

[26] Goodby JW, Leslie TM, Cladis PE, Finn PL. Characterization of two isomeric cyanoo-ester homologous series (I). In: Johnson J, Griffin AC, editors. Liquid crystals and ordered fluids. Vol. 4, New York (NY): Plenum; 1984. p. 89–110.

[27] Cladis PE, Finn PL, Goodby JW. Characterization of two isomeric cyanoo-ester homologous series (II). In: Johnson J, Griffin AC, editors. Liquid crystals and ordered fluids. Vol. 4, New York (NY): Plenum; 1984. p. 203–231.

[28] McDonnel DG, Raynes EP, Smith RA. Dipole moments and dielectric properties of fluorine substituted nematic liquid crystals. Liq Cryst. 1989;6:515–523. doi:10.1080/02678298908034171.

[29] Cladis PE, Mandle RJ, Goodby JW. Re-entrant phase transitions in liquid crystals. In: Goodby JW, Collings PJ, Kato T, Tschierske C, Gleeson H, Raynes EP, editors. The handbook of liquid crystals. 2nd ed. Vol. 2, New York (NY): Wiley; 2014. p. 1–30.

[30] Jadzyn J, Hellemans L, Czechowski G, Legrand C, Douali R. Dielectric and viscous properties of 6CBBT in the isotropic and nematic phases. Liq Cryst. 2000;27:613–619. doi:10.1080/026782900202453.

[31] Kirsch P, Bremer M, Heckmeier M, Tarumi K. Liquid crystals based on hypervalent sulfur fluorides: pentafuorosulfonyl as polar terminal group. Angew Chem Int Ed. 1999;38:1989–1992. doi:10.1002/(SICI)1521-3773(19990712)13:14<1989::AID-AnIE1989>3.0.CO;2-K.

[32] Dosov I. To bend, or not to bend: that is the question. Paper presented at the 25th International liquid crystal conference; 2014 Jun 29–Jul 4; Dublin.

[33] Zep A, Aya S, Aihara K, Ema K, Poecieha D, Madrak K, Bernatowicz P, Takezoe H, Gorecka E. Multiple nematic phases observed in chiral mesogenic dimers. J Mater Chem C. 2013;46–49. doi:10.1039/c2tc00163b.

[34] Davis EJ, Mandle RJ, Archbold CT, Goodby JW. Manuscript in Preparation.