Liquid Crystals

ISSN: (Print) (Online) Journal homepage: www.tandfonline.com/journals/tlct20

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To cite this article: Calum J. Gibb, John M. D. Storey & Corrie T. Imrie (2024) Molecular curvature and the twist-bend liquid crystal phases: the effect of the spacer, Liquid Crystals, 51:11, 1956-1963, DOI: 10.1080/02678292.2024.2373941

To link to this article: https://doi.org/10.1080/02678292.2024.2373941

LIQUID CRYSTALS
2024, VOL. 51, NO. 11, 1956–1963
https://doi.org/10.1080/02678292.2024.2373941

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Molecular curvature and the twist-bend liquid crystal phases: the effect of the spacer

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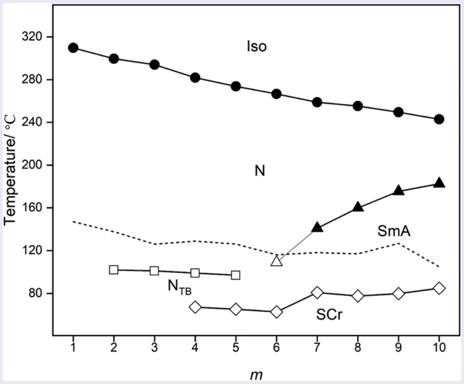
ABSTRACT

The synthesis and characterisation of ten members of the 4[{[4({5[4((4-cyanophenyl)phenyl]oxy)pentoxy}yl)phenyl]methylidene}amino] phenyl 4-alkyloxybenzoates is presented. These dimers are referred to using the acronym CBO5OIBeO*m* in which *m* refers to the number of carbon atoms in the terminal chain and varies from 1 to 10. The CBO5OIBeO*m* series exhibits nematic (N), twist-bend nematic (N_{TB}), and smectic A (SmA) phases depending on the length of the terminal chain. Although the N_{TB} phase is observed, these dimers do not exhibit the twist-bend smectic C (SmC_{TB}) phases. By comparison, the structurally similar CB6OIBeO*m* series does exhibit the SmC_{TB} phases, and this strongly suggests that the formation of the SmC_{TB} phase is more sensitive to molecular curvature than that of the N_{TB} phase.



ARTICLE HISTORY
Received 1 March 2024
Accepted 10 June 2024

KEYWORDS
Dimers; twist-bend nematic phase; twist-bend smectic phases; molecular bend

Introduction

First predicted independently by Meyer [1] and Dozov [2], the experimental discovery of the twist-bend nematic (N_{TB}) phase was made using the odd-membered liquid crystal dimer, CB7CB [3–5]. In his seminal work, Dozov also predicted the existence of the twist-bend smectic C (SmC_{TB}) phases, and they have also been discovered [6–9], again for odd-membered liquid crystal dimers. Molecular bend is now widely recognised as a pre-requisite for the formation of such phases. Although considerable research has been undertaken on the N_{TB} phase, there are relatively few reports of the SmC_{TB} phases (for example [10–19]). Indeed, beyond the requirement for molecular bend, little is known about the structure–property relationships governing the formation of the twist-bend smectic phases. It has been shown using a generalised Maire-Saupe theory [20] that the formation of the N_{TB} phase is very sensitive to molecular bend and will only form over a finite range of bend angles, and this prediction has been borne out by experimental observations.

A liquid crystal dimer consists of molecules containing two mesogenic groups attached by a flexible spacer [21]. The spacer is normally an alkyl chain and the number of atoms, *n*, linking the mesogenic groups determines the shape of the molecules. In essence, an odd-membered dimer (*n* = odd) gives rise to a bent molecule and an even-membered (*n* = even) a linear molecule. When designing

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Supplemental data for this article can be accessed online at https://doi.org/10.1080/02678292.2024.2373941.

bent-dimers with a view to observing twist-bend phases, there are several structural features that can be manipulated in-order to tune molecular curvature. The simplest change is to increase the length of the odd-membered spacer, and this increases the conformational flexibility of the spaces and enhances the linearity of the molecule. This change has been shown to have an effect on the bulk thermal properties of symmetric dimers [22–24], in which the mesogenic units are identical; non-symmetric dimers [25–27], in which they differ; and higher oligomers [28]. In general, increasing the length of an odd-membered spacer in a given homologous series first increases the transition temperatures arising from the changing shape, but on further increasing chain length the transition temperatures begin to fall given the increasing volume fraction of alkyl chains. A change in molecular curvature can also be achieved by changing the linking group between the spacer and mesogenic units. This is evident when comparing the behaviour of CB7CB, CB6OCB and CBO5OCB [3,24,29]. Here, increasing the number of ether-links enhances the linearity of the molecules, and a increase in the N-I transition temperatures results.

It is assumed, although yet to be established experimentally, that the formation of the $\mathrm{SmC_{TB}}$ phases will be similarly sensitive to the molecular bend angle. The first example of an $\mathrm{SmC_{TB}}$ phase for a non-symmetric dimer, assigned as the $\mathrm{SmC_{TB\text{-}\alpha}}$ phase, was observed in the CB6OIBeO*m* series (Figure 1(a)) [30]. In the $\mathrm{SmC_{TB\text{-}\alpha}}$ phase, the molecules are tilted with respect to the layer normal and the tilt direction in consecutive smectic layers forms a helical structure driven by steric interactions between neighbouring molecules due to their bent molecular shape. The structure may be described as an ideal clock arrangement in which the azimuthal angle between the layers is equal to 90° and periodic over 3–4 smectic layers giving rise to the phase's optical uniaxiality observed experimentally [9]. The pitch-length of the helix decreases on cooling. The CB6OIBeO*m* series [30] consist of cyanobiphenyl and benzylideneaniline benzoate mesogenic units connected by a hexyloxy (6O) spacer, that ensures the molecular bend required for the observation of the twist-bend phases. The CB6OIBeO*m* series displays fascinating liquid crystal polymorphism which appears to be dependent on the relative lengths of the spacer (*n*) and the terminal chain (*m*). When the length of the spacer is greater than that of the terminal chain ($n > m$), the N and $\mathrm{N_{TB}}$ phases are observed. As *m* increases, the $\mathrm{N_{TB}}$ phase is extinguished at around $n = m$, and instead smectic phases are observed including the $\mathrm{SmC_{TB\text{-}\alpha}}$ phase but extinguished for $n < m$. This relationship has now also been shown in corresponding materials containing longer spacers [31].

Here we investigate the effect of molecular curvature on the formation of the $\mathrm{SmC_{TB\text{-}\alpha}}$ phase and report the synthesis and characterisation of the 4[{[4({5[4((4cyanophenyl) phenoxy]yl)pentyl}oxy)phenyl]methylidene}amino] pheny 4-alkyloxybenzoates (CBO5OIBeO*m*) (Figure 1(b)). We have replaced the hexyloxy spacer in the CB6OIBeO*m* with the diether-linked (O5O) spacer and as we will see, this increases the linearity of the dimers.

Experimental

The synthetic route used to obtain the CBO5OIBeO*m* series was performed using a five-step process which is outlined in Figure 2. The synthesis of CBO5Br and the 4aminophenyl-4'-(alkyloxy)benzoate esters (I2) have been described elsewhere [30–33]. 4'-((5-(4-formylphenoxy)pentyl)oxy)-[1,1'–biphenyl]-4-carbonitrile (I1) was prepared by a standard Williamson ether synthesis [34] between 4-hydroxybenzaldehyde and CBO5Br. The CBO5OIBeO*m* series was obtained by a condensation reaction between I1 and the appropriate 4aminophenyl-4'-(alkyloxy)benzoate ester (I2). Complete synthetic details, structural and purity analysis for the final products and their intermediates are provided in the accompanying ESI.

Results and discussion

As described earlier for the CB6OIBeO*m* series, the phase behaviour of the CBO5OIBeO*m* series depends

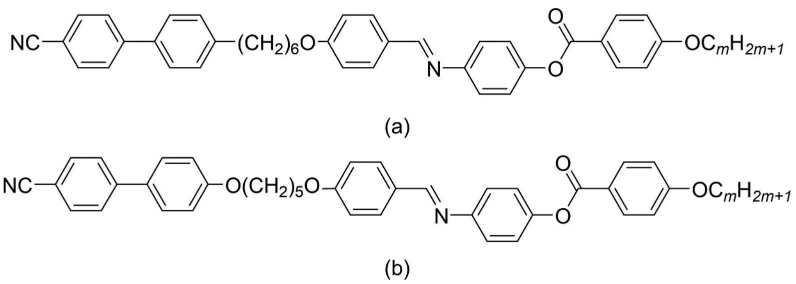

Figure 1. The molecular structure of the (a) CB6OIBeO*m* and (b) CBO5OIBeO*m* series, where $m = 1–10$.

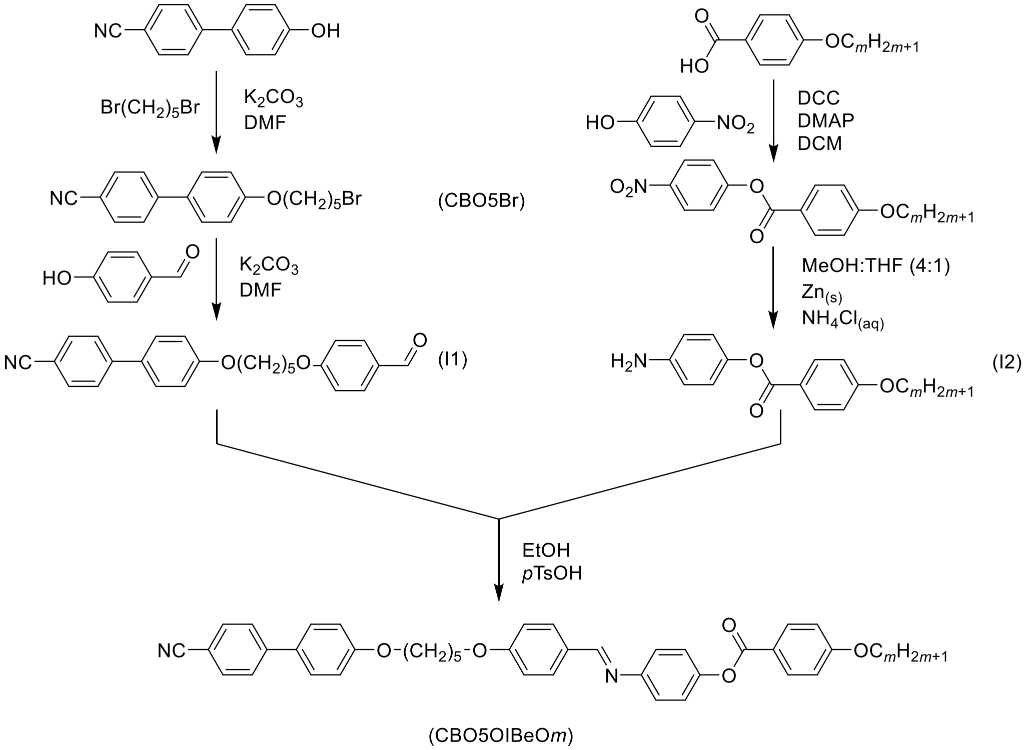

Figure 2. Synthetic scheme for the synthesis of the CBO5OIBeO*m* series, where *m* = 1–10.

on the relative lengths of the spacer and terminal chain. A summary of the transitional properties of the CBO5OIBeO*m* series is shown in Table 1 and the dependence of the transition temperatures on terminal chain length is shown in Figure 3. All members of the CBO5OIBeO*m* series exhibit an N phase. The N phases were assigned by the observation of a schlieren texture containing 2 and 4-point brush defects when viewed between untreated glass slides (Figure 4(a)) which flashed when mechanical stress was applied. Within cells treated for planar alignment, the N phase presents as a uniform texture (Figure 4(b)). The N-I transitions are detected using DSC (for example, see Figure 5). Increasing *m* sees an essentially linear decrease in the values of $T_{N\text{-}I}$ (see Figure 3). This reflects the dilution of interactions between the mesogenic groups due to the increased volume fraction of alkyl chains [35]. The values of the scaled entropy changes (ΔS/R) associated with the N-I transition, are consistent with this assignment.

When the length of the terminal chain is shorter than that of the spacer (*n* > *m*), the N_{TB} phase is observed at temperatures below the N phase, excluding the shortest homologue which exhibits only an N phase. This presumably reflects the rather limited temperature range to which CBO5OIBeO1 cools below its melting point prior to crystallising, rather than any more fundamental reason for it not to show the N_{TB} phase. The N_{TB} phase was assigned by either the observation of rope-like or blocky textures when viewed between untreated glass slides (Figure 4(c)) and a striped texture when viewed within thin cells treated for planar anchoring (Figure 4(d)). On

Table 1. Transition temperatures (°C) and associated-scaled entropy changes, in brackets, for the CBO5OIBeOm series.

m	m.p./°C	SCr-/°C	N_{TB}-N/°C	SmA-N/°C	N-I/°C
1	147.0 (10.1)	-	-	-	309.7 (0.65)
2	137.7 (12.4)	-	[102.0]† (≈0)	-	299.7 (1.02)
3	126.0 (14.1)	-	[101.0]† (≈0)	-	294.1 (0.61)
4	128.9 (14.2)	[67.1] (1.96)	[99.0]† (≈0)	-	281.9 (0.69)
5	126.2 (15.0)	[65.2] (1.38)	[97.0]† (≈0)	-	273.7 (0.59)
6	116.1 (14.1)	[62.6] (0.79)	-	[109.0] (0.01)	266.6 (0.59)
7	118.2 (13.9)	[80.7] 1.15)	-	141.0 (0.01)	258.8 (0.50)
8	117.0 (15.6)	[77.6] (0.74)	-	160.0 (0.01)	255.3 (0.48)
9	126.8 (17.1)	[79.8] (0.64)	-	175.4 (0.01)	249.6 (0.45)
10	104.9 (14.4)	[84.9] (0.82)	-	182.5 (0.01)	243.0 (0.39)

†microscope observation, [] monotropic transition.

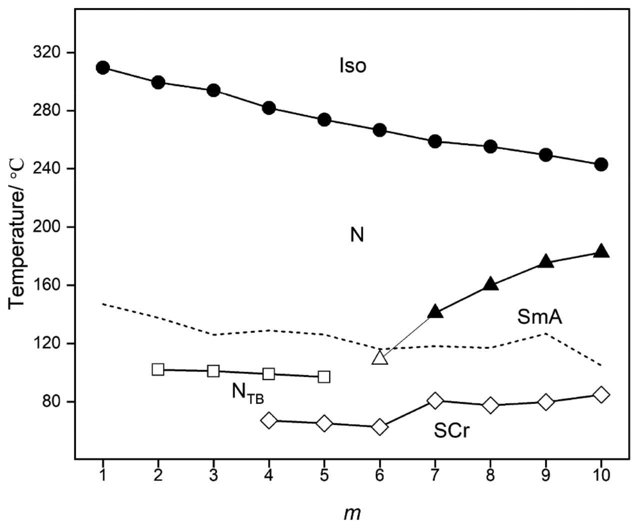

Figure 3. Temperature dependence of the transition temperatures on increasing terminal chain length (*m*) for the CBO5OIBeO*m* series. Melting points are denoted by the dotted line, solid symbols indicate enantiotropic phase transitions, and open symbols indicate monotropic phase transitions.

increasing *m*, from 2–5, a small decrease in the value of $T_{NTB\text{-}N}$ of just 5°C is observed (Figure 3) suggesting that the shape of the molecules remains essentially constant for these terminal chain lengths. The small reduction of $T_{N\text{-}NTB}$ over these chain lengths is consistent with the view that the N-N_{TB} transition is predominantly shape driven [3,24,29]. The entropy changes associated with the N-N_{TB} transition are essentially zero and this reflects the extensive nematic range exhibited by these dimers [26].

For $m > 5$, the N_{TB} phase is extinguished and the SmA phase emerges on cooling the N phase. The SmA phase has been characterised by the observation of a homeotropic texture between untreated glass slides which does not flash under mechanical stress. The homeotropic texture can be sheared to form focal conic fans (Figure 6(a)). The SmA phase presents as a planar texture within a 1.6 µm cell with a planar anchoring condition (Figure 6(b)). The SmA-N transition is seen as a very weak first-order transition in the DSC thermograms (Figure 5 [left]). The small values of $\Delta S_{SmA\text{-}N}/R$ reflect the wide temperature range of the preceding N phase [26]. The observation of the SmA phase for dimers with $m > 6$ reinforces the emerging observation that, irrespective of the nature of the spacer, the N_{TB} phase is extinguished in dimers based on cyanobiphenyl-benzylideneaniline benzoate mesogenic units when $n = m$ [30,31]. It is noteworthy that the CBO5O IBeO*m* series does not show the $SmC_{TB\text{-}\alpha}$ phase unlike the structurally similar CB6OIBeO*m* series.

For dimers with $m > 3$, a so-called soft-crystalline (SCr) phase is observed (Figure 3) The identification of this phase by POM is non-trivial as the textures observed are paramorphotic and hence vary depending on the phase sequence observed (for examples, see Figure 4(e+f) and Fig. 6(e+f)). The transitions involving the SCr phase are observed as first-order transitions using DSC but with associated entropy changes too small to be associated with conventional crystallisation (see Figure 3). The structure of this phase is unclear and requires further study. The structurally similar CB6OIBeO*m* series exhibits similar soft-crystalline phases, and these have been identified as the HexI phase [36].

Figure 7 compares the transition temperatures of the CBO5OIBeO*m* and CB6OIBeO*m* series [30]. The additional ether link in the spacer of the CBO5OIBeO*m* series increases the value of $T_{N\text{-}I}$ by approximately 20°C compared to that of the corresponding CB6OIBeO*m* dimer

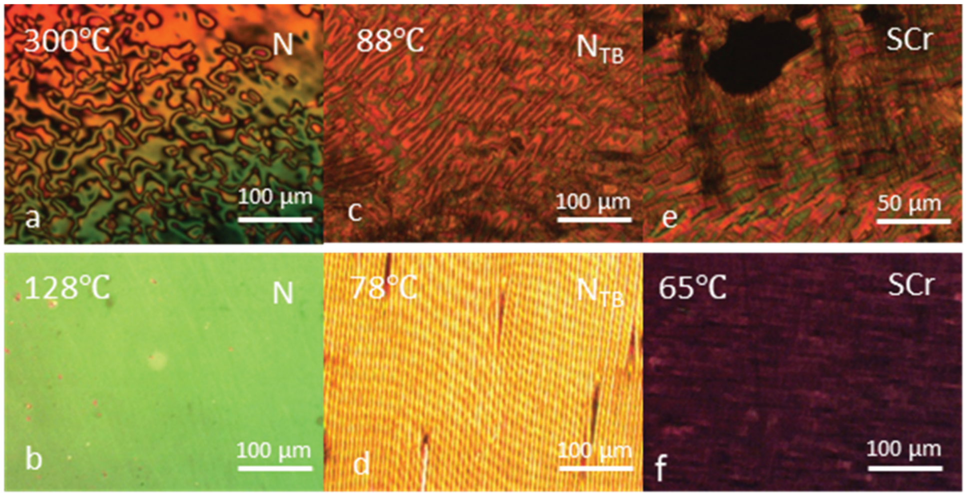

Figure 4. (Colour online) POM textures viewed between untreated glass slides (top) and within a 1.6 µm cell treated for planar anchoring (bottom) of the (a+b) N, (c+d) N_{TB} and (e+f) SCr phases observed for CBO5OIBeO4.

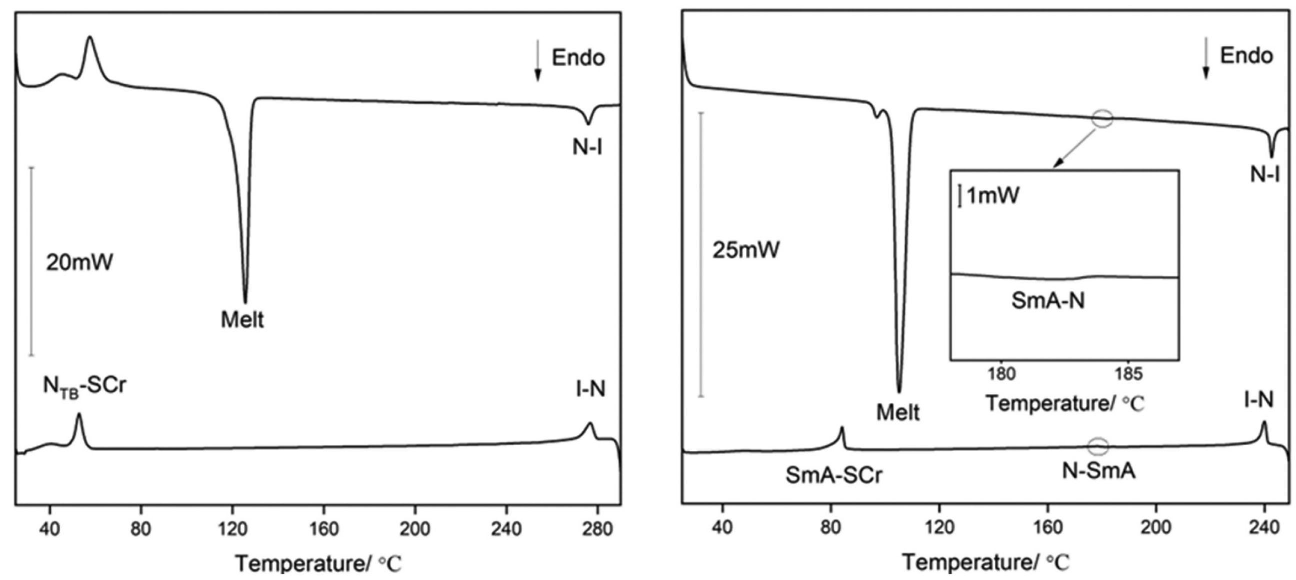

Figure 5. DSC thermograms for CBO5OIBeO4 [left] and CBO5OIBeO10 [right].

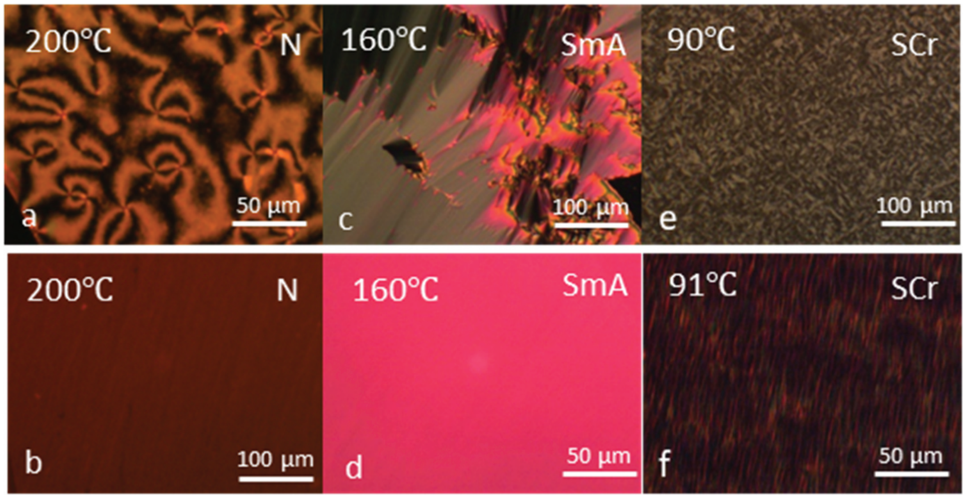

Figure 6. (Colour online) POM textures viewed between untreated glass slides (top) and within a 1.6 µm cell treated for planar anchoring (bottom) of the (a+b) N, (c+d) SmA and (e+f) SCr phases observed for CBO5OIBeO10.

(Figure 7 [left]). A similar difference between the two series is also observed in the values of $T_{SmA\text{-}N}$ (Figure 7 [right]). This reflects the more linear shape arising from the diether-linked spacer as discussed earlier as well as an increase in the interactions between the mesogenic units due to the increased polarisability of the cyanobiphenyl moiety. Geometry optimised and electrostatic isosurface potential structures of members of the two series obtained using DFT are shown in Figure 8. The more linear shape of the CBO5OIBeO*m* series is clearly evident as well as the enhanced polarisability of the cyanobiphenyl mesogenic unit owing to the conjugation of the linking oxygen atom. By contrast, the values of $T_{N\text{-}N_{TB}}$ are lower for the CBO5OIBeO*m* series than for the corresponding member of the CB6OIBeO*m* series by approximately 40°C (Figure 7 [right]). This is again a reflection that the N-N_{TB} transition is predominantly shape driven [2,20,25] and that the -O5O - spacer increases the linearity of the dimer.

Let us now consider the similarities in phase behaviour between these two series. In both, for $n > m$, N_{TB} phases are observed on cooling the N phase. As the terminal chain is increased in length and exceeds that of the spacer ($n < m$), the N_{TB} phase is extinguished, and the SmA phase is observed. In the case of the CB6OIBeO*m* series, this occurs for $m = 6$ and for the CBO5OIBeO*m* series for $m = 5$. We turn our attention to the tendency to exhibit the $SmC_{TB\text{-}\alpha}$ phase. We have seen that the CB6OIBeO*m* series exhibits the $SmC_{TB\text{-}\alpha}$ phase for $m = 7$ and 8, whereas the

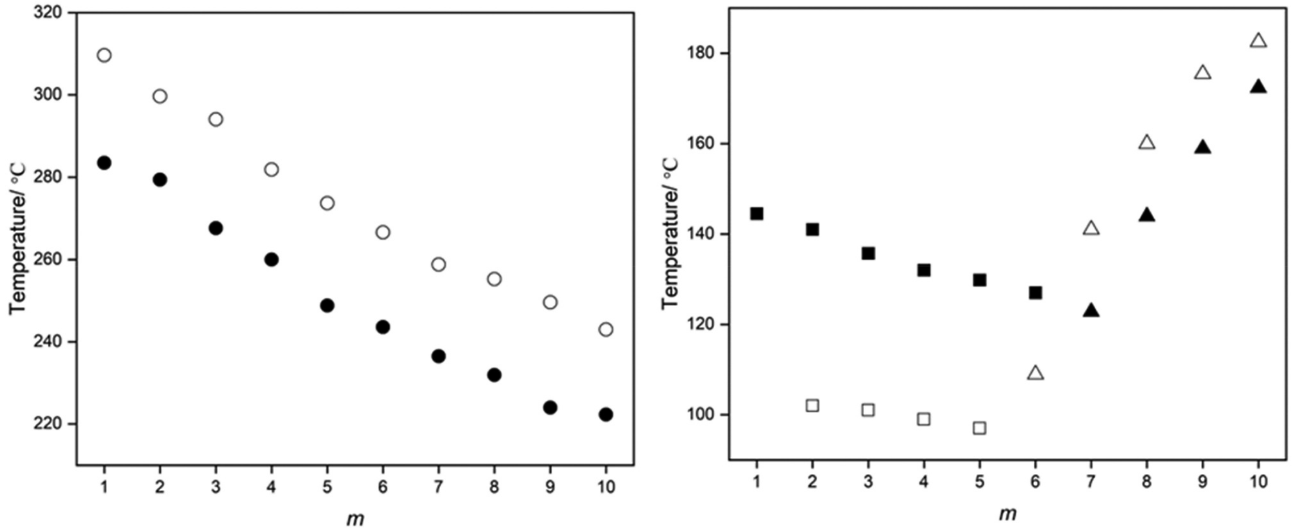

Figure 7. Comparison of $T_{N\text{-}I}$ [circle] (left), and $T_{NTB\text{-}N}$ [square] and $T_{SmA\text{-}N}$ [triangle] (right) on increasing m for the CB6OIBeOm [solid] and CBO5OIBeOm [open] series.

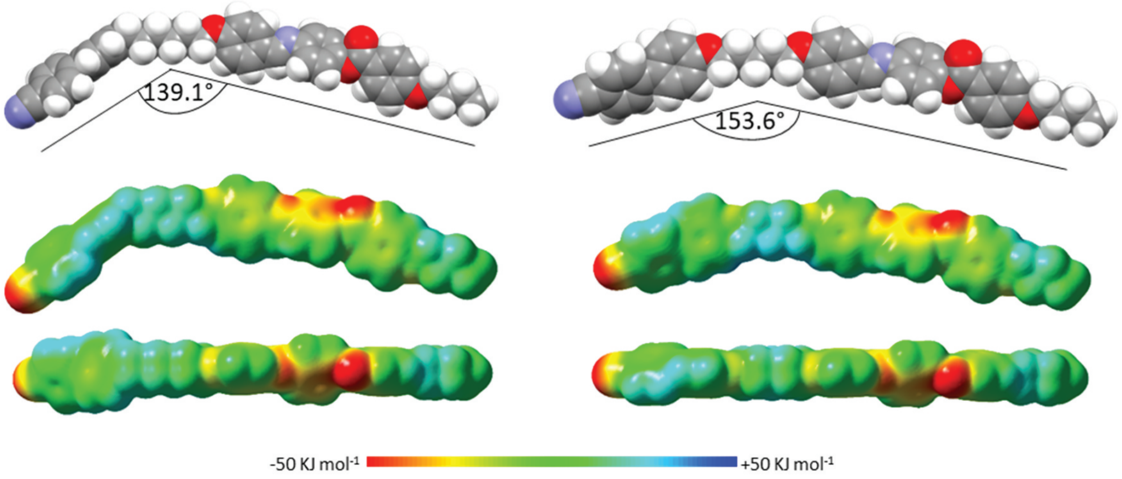

Figure 8. (Colour online) Energy minimised space filling models (top) showing the more bent structure of the CB6OIBeO*m* series (left) and the electrostatic isosurface potentials (bottom) showing the more electron rich CBO5OIBeO*m* series (right). The homologues with *m* = 4 have been shown as representative examples and both are calculated at the B3LYP 6–31 G(d) level of theory [37–40].

CBO5OIBeO*m* series does not show twist-bend smectic behaviour. To date, the $SmC_{TB\text{-}\alpha}$ phase has only been observed for the CBO6IBeO*m* series and its analogues with longer spacers [30,31]. The molecular bend angle is largely determined by the flexible spacer, whereas increasing the terminal chain will tend to promote smectic behaviour. We have seen in Figure 7 that the hexyloxy spacer gives rise to a significantly more bent molecule that will not pack as effectively into the SmA phase, and hence the lower values of $T_{SmA\text{-}N}$ seen for the CB6OIBeO*m* series (see Figure 7 [right]). By comparison the more linear CBO5OIBeO*m* series packs more efficiently in the SmA phase and at the same time exhibits lower $T_{N\text{-}N_{TB}}$ transition temperatures. These factors combine such that the CBO5OIBeO*m* series shows SmA behaviour for shorter terminal chain lengths than the more bent CB6OIBeO*m* series. The absence of SmC_{TB} behaviour for the CBO5OIBeO*m* series indicates that although these more linear dimers satisfy the bend requirement for the formation of the N_{TB} phase, they are not sufficiently bent to form the $SmC_{TB\text{-}\alpha}$ phase. From a molecular design point of view, this suggests that the $SmC_{TB\text{-}\alpha}$ phase is even more sensitive to molecular curvature than the N_{TB} phase.

Conclusions

We have reported the synthesis and characterisation of the CBO5OIBeO*m* series and this exhibits the N, N_{TB} and SmA phases. When compared to the behaviour of the CB6OIBeO*m* series [30], changing the nature of the spacer to include a second ether-link increases $T_{N\text{-}I}$ and $T_{SmA\text{-}N}$ but decreases $T_{N\text{-}N_{TB}}$. This is accounted for in terms of the second ether-link increasing the linearity of the molecule and reflects the predominantly shape driven nature of the N-N_{TB} transition. Changing the spacer to -O5O- extinguishes the $SmC_{TB\text{-}\alpha}$ phase and this suggests that the formation of the twist-bend smectic phases is even more sensitive to molecular curvature than for the N_{TB} phase.

Disclosure statement

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

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