

## **The induction of the N<sub>tb</sub> phase in mixtures**

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## The induction of the $N_{tb}$ phase in mixtures

We report the induction of the  $N_{tb}$  phase over a wide temperature and concentration range in a binary system. This was achieved by addition of a flexible dopant without LC properties to a flexible dimer exhibiting only a nematic LC phase. The  $N_{tb}$  phase was identified by POM, DSC and XRD techniques.

Keywords: Twist-bend nematic; Liquid crystal dimers; liquid crystal - non liquid crystal mixtures; nematic-nematic transition

### 1. Introduction

The  $N_{tb}$  phase, characterized by spontaneous formation of chiral domains with a helical pitch on the 10 nm scale and pseudo-layer structure, formed by chemically non-chiral compounds is one of the recently observed examples of chiral symmetry breaking in liquid crystals [1–7]. Previously this effect has been more associated with higher ordered liquid crystal (LC) phases, such as lamellar, columnar and cubic arrays [8–12].  $N_{tb}$  phase formation is most commonly associated with systems containing two mesogens separated by flexible odd-numbered spacers. However, examples of bent-core mesogens, as well as oligomeric and main-chain polymers have been reported too [13–16]. The  $N_{tb}$  mesophase is relatively robust to the addition of linear mesogens and it can even be stabilised by adding nematogens [17,18]. Moreover, it can be formed by supra-molecular association of mesogenic groups [18,19] and has been observed in multicomponent mixtures [20,21]. Until now, the question of whether  $N_{tb}$  phase behaviour can be induced systematically by adding a dopant to a conventional nematic and hence modulating the assembly behaviour of the nematogen has not been investigated.

Here, we show that it is possible to achieve  $N_{tb}$  phase formation systematically by adding a non-LC dopant to a nematic dimer. The molecules used in this study were selected for their structural simplicity in order to ease future theoretical and experimental studies, to link conceptually to existing systems and to obtain relatively low transition temperatures, making physical investigations more accessible.

## 2. Experimental

The known compound CBOC5OCB (Figure 1(a)) with a nematic phase range of almost 85 °C was selected as the matrix [22]. The material CBC3CB (Figure 1(a)), which is not liquid crystalline was selected as a dopant. The structural similarity to CBOC5OCB was selected to ensure full miscibility over a wide concentration range.

For the first step in the investigation, a phase diagram between these two materials was constructed. Mixtures were investigated by Polarizing Optical Microscopy (POM), Differential Scanning Calorimetry (DSC) and X-ray Diffraction (XRD). **The experimental details and the instrumentation used in this work are presented in the ESI.**

## 3. Results and Discussion

The temperature-composition phase diagram, as a function of CBC3CB mol%, collected on cooling is presented in Figure 1(b). **Composition information and transition temperatures are listed in the ESI (Table 1).** The LC behaviour of the mixtures was found to be monotropic, in other words not thermodynamically stable. However, on cooling the compositions were stable for at least a day, thus allowing for their detailed characterization.

[Insert Figure 1 here]

Progressing from the pure CBOC5OCB, on the left of the phase diagram, the added presence of CBC3CB results in a near linear decrease of the stability of the N phase. This is expected as the ‘non-LC’ dopant is added and indicates that the constituent dimers are fully miscible [23] on cooling in compositions up to roughly 63 mol% of CBC3CB. The introduction of 11.8 mol% of CBC3CB (mixture 6), was sufficient to induce  $N_{tb}$  phase formation, with a phase onset at 86.6 °C. Surprisingly, the  $N_{tb}$  phase is observed up to 63.1 mol% of CBC3CB (mixture 3), where the composition contains predominantly a material which is not liquid crystalline. Additionally, the crystallization temperatures decrease with increasing CBC3CB content. Interestingly, no crystallization of the samples was detected at concentrations higher than 22.3 mol% of CBC3CB (mixture 5) in DSC experiments. Optically detectable crystallization occurred after the samples were left at room temperature for at least 24h.

After induction of the  $N_{tb}$  phase at 11.8 mol% CBC3CB, a slight stabilisation of the phase was observed at 22.3 mol% (mixture 5). Further addition of the non-LC dimer destabilised the phase with the N- $N_{tb}$  temperature transitions exhibiting an almost linear dependence on composition until the phase was no longer detected above 63.1 mol% of CBC3CB.

We note a much steeper decrease of the N phase stability on addition of further CBC3CB to CBOC5OCB than that of the  $N_{tb}$  mesophase. Looking at the phase diagram one could anticipate an intersection of the stability ranges of the N and the  $N_{tb}$  phases, with a direct Iso- $N_{tb}$  phase transition, but this was not detected. On the contrary what was actually observed was large regions with co-existing isotropic, nematic and crystal phases, but no  $N_{tb}$  phase, at 68.1 mol% of CBC3CB (eg mixture 2; see Figure S1 in the ESI for POM micrograph). This is indicative of demixing of the

materials. As this region of the phase diagram is not the focus of this report, it will not be discussed further. With further increase of CBC3CB only the crystal phase was observed in the mixtures.

We note that recently the N-N<sub>tb</sub> transition was reported on isolated droplets of pure CBOC5OCB under extensive supercooling using POM [24,25]. Unfortunately, we were not able to recreate this experiment under controlled conditions (see Figure S2 in the ESI for a POM micrograph).

The enthalpies associated with the Iso-N and N-N<sub>tb</sub> transitions, obtained from DSC measurements, are plotted as a function of mol% and are presented in Figure 2. The N-N<sub>tb</sub> transition enthalpies increase in value with addition of CBC3CB, reaching those observed for pure dimers, such as CBC7CB [26], CBC9CB [17], and CBC11CB [27]. An example is mixture **3** (63.1 mol%) with an N-N<sub>tb</sub> enthalpy of 0.47 kJ mol<sup>-1</sup>. Additionally, the enthalpy values for the Iso-N transition decrease as the content of the CBC3CB dimer increases in the mixtures intersecting the corresponding curve for the N-N<sub>tb</sub> transition, as can be seen in Figure 2. These observations correlate fully with earlier results found for dimers and mixed systems showing N-N<sub>tb</sub> transitions [24,28–30], where the width of the N phase has been directly related with the values of the transition enthalpies for the Iso-N transition as well as increased enthalpy values for the N-N<sub>tb</sub> transition.

[Insert Figure 2 here]

The N<sub>tb</sub> phase induced in the mixtures was identified by its distinctive defect texture using POM. Typical examples from mixture **4** are shown in Figure 3(b,c). A sample observed on untreated glasses under crossed polarizers exhibiting the Schlieren texture of the nematic phase (Figure 3(a)) transformed into a blocky texture marking the N-N<sub>tb</sub> transition (Figure 3(b)). On further cooling the texture developed into a polygonal defect pattern, (Figure 3(c)). In Figure S3

(ESI), the DSC curves on cooling of all the  $N_{tb}$  forming mixtures are presented. Broad peaks for the Iso-N transition are attributed to biphasic regions typical in mixtures, in contrast to sharp transitions in the pure compounds.

[Insert Figure 3 here]

X-ray investigations on magnetically aligned samples confirm our phase assignment in all studied mixtures. For mixture **4** the integrated intensities (normalized over the maximum values) collected between 120 °C and 40 °C on cooling and plotted against the diffraction angle  $2\theta$  are shown in Figure 3(d). Data for CBOC5OCB at 130 °C are also included. For the composition **4** in the N phase, the diffraction patterns show only short-range orientational order; see for example Figure 3(e) at 100 °C. The equatorial peak at 100 °C corresponds to a side-to-side separation of 4.55 Å, a typical value for calamitic LCs [31]. In the small-angle region, a single peak is obtained for both nematic phases with d-spacing values ranging from 10.8 Å, in the N phase, to 10.6 Å in the  $N_{tb}$  phase, values of about half the molecular length of the mesogens ( $d_2$ , Table 2 in the ESI). This peak is relatively temperature independent. A similar peak is obtained in the N phase of pure CBOC5OCB (eg at 130 °C in Figure 3(d)) yielding a value of 12.2 Å ( $d_2$ ) about half the molecular length of CBOC5OCB, in an all staggered conformation (27.5 Å), implying a locally interdigitated antiparallel organization.

When mixture **4** was cooled into the  $N_{tb}$  phase at 80 °C (Figure 3(f)) no significant change was recorded for the small-angle intensities. The wide-angle diffraction arcs became narrower and spread further to the meridian, expanding on further cooling into a circle-type pattern at 40 °C (Figure 3(g)). This suggests domain formation in the sample [18]. Moreover, it would be in line with a phase structure where mesogens in a helicoidal structure, but with a tilt to the helix, form right and left-handed domains which are oriented in the external field. The wide-angle peaks in

the  $\theta$ -scans shifted slightly to smaller angles, suggesting a closer lateral molecular packing in the  $N_{tb}$  phase. The small-angle peaks yield values of 10.6 Å, consistent with the concept discussed above. Additionally, the slight reduction of the pseudo d-spacings, going from the N to the  $N_{tb}$  phase, could be due to increasing interdigitation of the molecules with either linear [5] or torsionally twisted hydrocarbon groups [32,33]. The correlation lengths ( $\xi$ ) were calculated via the equation  $\xi=c/\Delta q$ , where  $c$  is the function used to describe the intensity profile and  $\Delta q$  is the full width at half maximum (FWHM), a variation of the Scherrer equation [34] (see Table 2 in the ESI for the tabulated  $\xi$  values). For both nematic phases these calculations gave quite small values ranging from 5.42 Å to 8.35 Å for the N phase to 7.35 Å to 9.83 Å for the  $N_{tb}$  phase. For the  $N_{tb}$  phase this value can be explained by the mesogens being at a tilt to the axis of a helix, with the helix axis being oriented overall parallel to the magnetic field [35]. Overall our XRD results are consistent with previous studies concerning the structure of the  $N_{tb}$  mesophase [32,33,35–40]. Recently, duplex formation has been proposed [38,41,42]. We note that for this system at low concentrations of CBC3CB (roughly 12 mol%) only one in five duplexes would contain species promoting helicoidal structure formation, this would indicate that either CBC3CB is very efficient as a dopant or alternatively disfavours the concept of duplexes.

The structure of the nematic phases obtained in the studied mixtures is rationalized in the context of the shape and flexibility of the statistically achiral constituents. On mixing the two dimers, in the high-temperature N phase, the nematic environment of CBOC5OCB induces orientational order to CBC3CB molecules, absent in the pure CBC3CB fluid at the same temperatures. However, the CBC3CB present perturbs the ordering of CBOC5OCB and the temperature stability of the N phase decreases dramatically.

For the  $N_{tb}$  phase the arrangement is more complex. The introduction of moderate amounts of CBC3CB (11.8 mol%) are needed for  $N_{tb}$  formation and we observed a small increase of the mesophase stability at 22.3 mol% of the non-LC dopant. For higher concentrations a reduction of the  $N_{tb}$  stability occurs, before demixing starts after addition of more than 65 mol% CBC3CB. These results indicate that phase formation is not due to specific attractive molecule-to-molecule [19] or in our case host-dopant interactions. Moreover, our results suggest that interdigitation of the two types of molecules occurs. A schematic representation of the assembly is shown in Figure 3(h) and a schematic representation of the molecules can be seen in Fig 3(i).

Given the smaller number of accessible conformational states of CBC3CB when compared to CBOC5OCB, due to its shorter spacer, we propose that CBC3CB acts as a template and that CBOC5OCB adjusts its conformational statistics so that CBOC5OCB is closer in shape to CBC3CB, becoming thus on average more bent and twisted; this can be achieved for example by a number of eclipsed conformations of the central hydrocarbon chain in order to optimize their interactions, or in other words to minimize excluded volume [43]. This view is supported too by the increasing enthalpy values at the N- $N_{tb}$  transition (See Fig. 2) with increasing CBC3CB content.

The observed induction of a new liquid crystal phase is distinctly different from that where hydrogen bonding of species is employed for liquid crystal phase formation [44,45] or through halogen bonding [46] and different from liquid crystal phase formation due to excluded volume effects as reported recently [47] or by the balance between the charge-transfer interactions, dipolar interactions and excluded volume effects [48].

## 4. Conclusion

To summarise, based on POM, DSC and XRD techniques, we report for the first time the induction of the  $N_{tb}$  phase in binary systems on adding a non-LC dopant, CBC3CB, to a nematic dimer, CBOC5OCB. The  $N_{tb}$  phase is formed in a wide concentration range going from roughly 12-63 mol% of the dopant. We propose that  $N_{tb}$  phase induction is due to energy minimization by adjustment of molecular conformations of the non-chiral and flexible molecules, mainly of CBOC5OCB towards more bent and twisted conformations, thus favouring overall the formation of a chiral domain nematic phase.

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## List of figure captions

Figure 1. a) Molecular structures and phase sequences of the compounds used in this study, b) Temperature-concentration phase diagram for the CBC3CB-CBOC5OCB binary mixtures as a function of CBC3CB mol%. The squares represent the Iso-N transition. The diamonds indicate the N-N<sub>tb</sub> transition. The circles mark the Crystallization. The triangles denote the Iso-Cr transition. The star symbol marks the demixing composition (mixture **2**). The lines are a guide to the eye.

Figure 2. Enthalpy values associated with the Iso-N and N-N<sub>tb</sub> transitions as a function of CBC3CB mol%.

Figure 3. (a-c) Optical textures on untreated glasses under crossed polarizers on cooling of mixture **4**; a) N phase at 95 °C; b) N<sub>tb</sub> phase at 80 °C; c) N<sub>tb</sub> phase 77 °C. The scale bar represents 100 μm, d) θ-scans for mixture **4** between 40-120°C (CBOC5OCB at 130 °C included) and two-dimensional diffraction patterns; e) N at 100 °C; f) N<sub>tb</sub> at 80 °C, g) N<sub>tb</sub> at 40 °C; h) Possible helicoidal arrangement of interdigitated CBC3CB and CBOC5OCB molecules in the N<sub>tb</sub> phase, i) schematic depiction of the molecular shapes of CBC3CB, twisted and ben conformation of CBOC5OCB and fully extended CBOC5OCB.