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c5cp07605f

Miscibility studies of two twist-bend nematic liquid crystal dimers with different average molecular curvatures. A comparison between experimental data and predictions of a Landau mean-field theory for the N$_{TB}$–N phase transition

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We have developed a Landau model that predicts a first order twist-bend nematic−nematic phase transition consistent with heat capacity measurements.

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Miscibility studies of two twist-bend nematic liquid crystal dimers with different average molecular curvatures. A comparison between experimental data and predictions of a Landau mean-field theory for the N_{TB}−N phase transition

Q1 Q2

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We report a calorimetric study of a series of mixtures of two twist-bend liquid crystal dimers, the 1″,7″-bis(4-cyanobiphenyl)-4′-yl heptane (CB7CB) and 1″-(2′,4-difluorobiphenyl-4′-yloxy)-9″-(4-cyanobiphenyl-4′-yloxy) nonane (FFO9OCB), the molecules of which have different effective molecular curvatures. High-resolution heat capacity measurements in the vicinity of the N_{TB}−N phase transition for a selected number of binary mixtures clearly indicate a first order N_{TB}−N phase transition for all the investigated mixtures, the strength of which decreases when the nematic range increases. Published theories predict a second order N_{TB}−N phase transition, but we have developed a self-consistent mean field Landau model using two key order parameters: a symmetric and traceless tensor for the orientational order and a short-range vector field which is orthogonal to the helix axis and rotates around of the heliconical structure with an extremely short periodicity. The theory, in its simplified form, depends on two effective elastic constants and explains satisfactorily our heat capacity measurements and also predicts a first-order N_{TB}−N phase transition. In addition, as a complementary source of experimental measurements, the splay (K_1) and bend (K_3) elastic constants in the conventional nematic phase for the pure compounds and some selected mixtures have been determined.

1 Introduction

The mesogenic behavior of liquid crystalline materials is often enriched by the appearance of several mesophases with different symmetries when the sample is cooled from the isotropic phase. The observation of more than one nematic phase in certain materials and the corresponding phase transitions is a matter of great current interest, in particular the twist-bend nematic. One of the early studies of a liquid crystal dimer, with an odd spacer, showing a nematic–nematic transition was reported by Sepelj et al.[1] although the nature of the low-temperature nematic phase was not identified and so was labelled N_x. Similar dimers with odd spacers having a N_x–N transition were reported by Panov et al.[2] and the behaviour of such dimers has also been studied[3–5] but again without the low-temperature nematic being properly identified. Cestari et al.[6] have examined an odd liquid crystal dimer and observed a nematic–nematic transition but, as the result of an extensive investigation based on numerous techniques, were able to identify the low-temperature nematic as we shall see shortly. A slightly different dimer again with an odd spacer but having one chiral mesogenic group has been reported by Zep et al.,[7] surprisingly this system is found to form seven nematic phases over a narrow temperature range.

The theoretical possibility for the existence of different uniaxial nematic phases of achiral molecules, differing in their local director distributions was proposed by Meyer,[8] over 40 years ago; he argued that a local spontaneous polarization may cause distortion of the nematic director distribution, although this was largely ignored. Later the same idea was pursued by Lorman and Mettout,[9] who proposed a theoretical Landau model based on local ferroelectric polarisation for the

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nematic–nematic transition,[10] which was further developed by others.[11,12]

In 2001, Dozov[13] developed a purely elastic Landau theoretical model for achiral bent-core molecules in which elastic distortions induce local spontaneous bend in the nematic director, resulting in structural deviation from the uniformly-aligned nematic phase. A uniform bend deformation in the nematic phase is geometrically impossible giving rise to a symmetry-breaking transition resulting in two possible different nematic ground states, either the modulated splay-bend state which is achiral or the heliconical twist-bend which is chiral. In parallel with Dozov's study, Memmer[14] independently generated similar results through Monte Carlo simulations of rigid and non-polar V-shaped molecules which yielded the heliconical twist-bend nematic phase (N_{TB}).

It is the N_{TB} that is of prime interest in the current study. There had been a number of reports of nematic–nematic phase transitions for bent-core or banana mesogens, but the structural characteristics of the new nematic phases had not been identified.[1,2–5,15–17] However, recently a very detailed investigation of the flexible bent-shaped liquid crystal dimer 1″,7″-bis(4-cyanobiphenyl)-4′-yl heptane (CB7CB)[6] concluded that one of the two nematic phases exhibited by this compound is the twist-bend nematic phase (N_{TB}), in agreement with Dozov's predictions.[13] The mesogen CB7CB now appears to be the model liquid crystal on which research about this new phase is mainly focused.[18–26]

The heliconical twist-bend nematic phase appears as a state in which the spontaneous bend of the director is accompanied by a twist deformation in order to satisfy topological constraints. The induced twist can be left-or right-handed and the sample is expected to form a conglomerate of degenerate domains having opposite chirality even though the constituent molecules are achiral.[23] The directors are arranged into a helix with the director being tilted with respect to the helix axis and with a periodicity (p) predicted and measured from about 7 nm,[13,21,22,24,25] up to 15 nm for rigid bent-core mesogens.[27]

One of the open questions is the nature of the primary physical and molecular mechanism responsible for the twist-bend nematic phase. It is obvious that molecular bend or curvature is necessary, but is not sufficient since most of the bent-core mesogens fail to exhibit the twist-bend nematic phase.[28] At this point, the authors think that any bent molecule should form the N_{TB} phase. However, the transition temperature may be so low that other phases intervene before the N_{TB} phase is formed. Clearly, the formation of the twist-bend phase depends critically on the details of the mesogenic structure, but the core-flexibility of molecules in certain liquid crystal dimers seems to promote effective molecular curvatures favouring heliconical structures; however the ultimate physical mechanism causing the director modulation is controversial. On the one hand, some researchers attribute the existence of the twist-bend nematic phase to a flexoelectric coupling between bend deformation and electric polarization[8–12] although non-polar molecules do yield the N_{TB} phase. Alternative formulations of the theory only consider purely elastic distortions of the director due to molecular curvature.[13,14,21] Both theoretical

approaches can be developed in the framework of a Landau theory on the basis of the Oseen–Frank elastic free energy. Dozov[13] described the twist-bend nematic phase with a negative bend elastic constant (K_3) and the purely elastic free energy needs to be developed to fourth order to provide an upper bound to the energy. One of the most important concerns arises from the fact that the theory needs a drastic simplification of the number of terms and the simplified version predicts a second-order N_{TB}–N phase transition, which is not supported by experimental determinations.[3,6,26] In the case of flexoelectric coupling, Shamid et al.[11] have considered the polar order as an additional order parameter, but again such a Landau theory needs to be simplified and the approximate solution also predicts a second-order N_{TB}–N phase transition. The same authors[11] proposed the definition of an effective bend elastic constant (K_3^{eff}) which could be negative in the N_{TB} phase and positive in the uniform nematic phase. The problem here is that at the phase transition, K_3^{eff} as defined by Shamid et al.,[11] tends to minus infinity and there have been no experimental indications of this possibility.

Regarding the negative bend elastic constant required in Dozov's elastic theory, molecular calculations on certain non-symmetric odd liquid crystal dimers provide negative K_3 values for high enough nematic order parameters but such compounds were not found to exhibit the twist-bend nematic phase.[29] As for the experimental determinations of the bend elastic constant over the uniform nematic phase of twist-bend liquid crystal dimers, it is observed that the bend elastic constant decreases as temperature decreases on approaching the N–N_{TB} phase transition, leading to small values at the phase transition but increasing slightly or being nearly temperature independent before N_{TB} is reached.[25,30–32] In addition, very recently Yun et al.[33] have tried to measure K_3 in the N_{TB} phase of CB7CB showing anomalous and positive values.

One of the main difficulties with the Oseen–Frank theory is that in the free energy, the bend elastic constant is only properly defined for the conventional uniform nematic phase. However, it has been suggested that alternative elastic constants are appropriate for the N_{TB}-phase[34,35] in the application of the classic Oseen–Frank theory.[29]

It seems to be evident that one possible way to further the understanding of the physical mechanisms for the nematic twist-bend phase is the experimental study of the nematic to twist-bend nematic phase transition. Additional carefully chosen accurate measurements should allow us to provide data to test or improve existing theoretical models or to propose others. It is particularly interesting to cite the efforts to generalize the Maier–Saupe theory to the twist-bend nematic phase.[35] This is based on just three key order parameters: a single microscopic order parameter (the orientational order) and two macroscopic order parameters (the conical angle and the pitch of the heliconical structure) which characterize the position-dependence of the director. From such an approach it appears that the role of the curvature of the V-shaped molecule is essential for a coherent picture of the N_{TB}–N phase transition, and that the dependence of the transitional properties on this curvature is delicate.

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In this paper, we report high-resolution heat capacity measurements in the vicinity of the N_{TB}–N phase transition in binary mixtures of two twist-bend liquid crystal dimers, the molecules of which have different effective molecular curvatures. In addition a self-consistent mean-field Landau model is developed to describe these measurements. The components of the mixtures, for which experimental results are reported, are the classic compound CB7CB and $1''$-$(2',4$-difluorobiphenyl-$4'$-yloxy)-$9''$-(4-cyanobiphenyl-$4'$-yloxy)nonane (hereafter referred to by the acronym FFO9OCB) which has recently been shown to exhibit a monotropic N_{TB}-phase.[32] Measurements are also reported of the splay (K_1) and bend (K_3) elastic constants in the conventional nematic phase for the pure compounds and some selected mixtures, as a function of both temperature and mole fraction. These experimental results provide further insight into the nature of the N_{TB}–N phase transition, and the validity of our proposed model used to describe the phase transition.

2 Materials and methods

Both pure liquid crystal dimers CB7CB and FFO9OCB were synthesized according to the procedures reported earlier.[32,36,37] Fig. 1 shows the molecular geometry of both liquid crystal dimers with the spacer in the all-*trans* conformation. For CB7CB, molecular calculations[6] show that for higher values of the nematic order parameter (low temperatures) the more extended conformers, with angles (χ) on average of about $120°$ between the long or para axes of the terminal mesogenic groups, are stabilized at the expense of the less extended conformers, with angles on average of about $30°$. Unfortunately, no calculations are available for the conformational distribution of FFO9OCB, but for the shorter-chain homologue FFO5OCB, calculations made by Cestari *et al.*[29] indicate that the most extended conformers have angles χ, on average, of about $120°$ for the order parameters comparable to those found
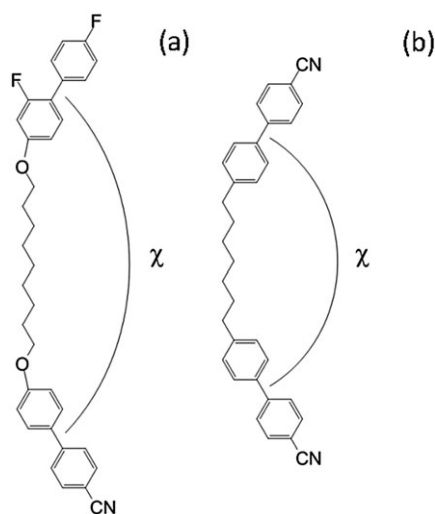

Fig. 1 Chemical structures of (a) the non-symmetric odd ether-linked dimer FFO9OCB and (b) the symmetric odd methylene-linked dimer CB7CB.

from the calculations for CB7CB dimer. For such conformers the angle between the terminal mesogenic groups tends to increase as the length of the flexible chain increases, resulting in a FFO9OCB dimer in which the most probable conformers are likely to be more extended than those of the CB7CB dimer. This also results from the difference in the links between the spacer and the mesogenic groups of ether and methylene.[38]

Binary mixtures with mole fractions of CB7CB of 0.10, 0.21, 0.36, 0.48 and 0.82 were prepared, with great care, in sealed hermetic aluminum pans. These pans with the corresponding amount of pure compounds for every mixture were placed into a glass bottle which was heated up to 400 K (the isotropic phase) in an oil-bath and was ultrasonicated for about four hours to ensure a homogeneous mixture. The samples were then introduced to a cooling room for 12 hours. The quality of mixing was assessed by analysing for possible mass loss, and by means of high resolution calorimetry in the vicinity of the N–I phase transition. If the mixture is not homogeneous, the preparation process is repeated as many times as necessary.

Heat capacity measurements at atmospheric pressure were performed using a DSC-Q2000 from TA-Instruments working in the modulated mode (MDSC) which, like an alternating current (AC) calorimeter, besides providing heat capacity data, simultaneously gives phase shift data (ϕ) that allow the determination of the two-phase coexistence region for weakly first-order phase transitions. In our work, the experimental conditions were adjusted in such a way that the imaginary part of the complex heat capacity data vanished. The system is also calibrated by using precise latent heat data measured for other homologues through adiabatic calorimetry; the MDSC-technique is also suitable for quantitative measurements of latent heats of first order transitions, even if they are weak. A more detailed description of the MDSC technique can be found elsewhere.[39,40]

Capacitance measurements to determine the splay (K_1) and bend (K_3) elastic constants were carried out using 8 μm anti-parallel planar aligned cells. The method consists of inducing the planar to homeotropic Fréedericksz transition in the sample by applying an AC signal at a frequency of 5 kHz from an Agilent Precision LRC meter E4890A. The capacitance of the sample is monitored as a function of the applied voltage which is varied from 0.1 V_{rms} to 16 V_{rms}, with a waiting time of 30 s between the application of the AC signal and the acquisition of the capacitance value. Ultimately, values of the K_1 and K_3 elastic constants are extracted by fitting the entire voltage dependence of the capacitance to the theory.[41] A more detailed description of the technique can be found elsewhere.[42]

3 Experimental results

The binary phase diagram for FFO9OCB + CB7CB mixtures is shown[32] in the inset of Fig. 2. Initial studies of the phase transition properties of binary mixtures were obtained from MDSC measurements of the heat capacity over heating runs at 1 K min^{-1} from about 240 K up to the isotropic phase, for samples previously cooled down slowly (at the rate of 1 K min^{-1}),

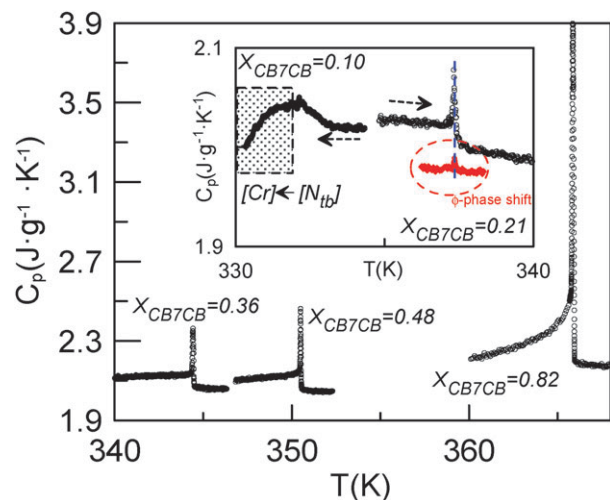This journal is © the Owner Societies 2016

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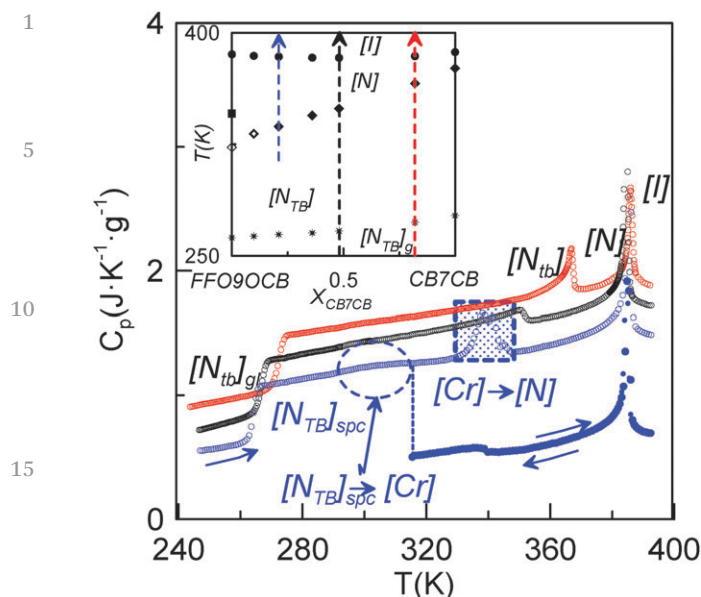
Fig. 2 Heat capacity data as a function of temperature for three selected binary mixtures FFO9OCB + CB7CB (X_{CB7CB} = 0.82-red; X_{CB7CB} = 0.48-black; X_{CB7CB} = 0.21-blue) on heating mode. In the case of the mixture X_{CB7CB} = 0.21, cooling down to 315 K and the subsequent heating are shown. The top-left inset shows the phase diagram for FFO9OCB + CB7CB mixtures. Full symbols (circles, squares, diamonds and stars) correspond to heat capacity measurements recorded on heating at 1 K min^{-1}. The open diamonds are related to the monotropic N_{TB}–N-phase transition on cooling mode.

Fig. 3 High-resolution heat capacity data as a function of temperature in the vicinity of the N_{TB}–N phase transition for some selected binary mixtures FFO9OCB + CB7CB. The inset shows in detail those mixtures closest to pure FFO9OCB.

with the exception of pure FFO9OCB and the mixture with X_{CB7CB} = 0.10. Fig. 2 shows, as an example, the heat capacity measurements for three selected mixtures recorded on heating (marked by the vertical dashed-line arrows in the phase diagram). The total set of mixtures investigated shows the same phase sequence on cooling from the isotropic phase as the pure CB7CB:[6] I–N–N_{TB}–$N_{TB,gl}$ (glassy N_{TB}). However, the heating phase sequence is different depending upon the composition of the mixture. The cooling phase sequence is reversible on heating at least for samples with a mole fraction of CB7CB of 0.36 or higher. The richer the mixture is in FFO9OCB, the more likely there will be for hot crystallization on heating the sample. This is the case with the mixture X_{CB7CB} = 0.21 (blue empty symbols in Fig. 2) for which the supercooled N_{TB} ([N_{TB}]$_{spc}$) phase crystallizes irreversibly on heating at about 300 K ([N_{TB}]$_{spc}$ → [Cr]), and then at 330 K the crystal state passes directly to the N-phase ([Cr] → [N]): consequently, the N_{TB}–N phase transition is not observed. However, the monotropic nature of the N_{TB} phase can be circumvented by cooling down to temperatures no lower than 315 K, which allows us to observe the N_{TB}–N phase transition in a heating experiment, as observed in Fig. 2 for blue solid symbols. It seems that the addition of a methylene-linked dimer (CB7CB) to an ether-linked dimer (FFO9OCB) enhances the stability of the twist-bend nematic phase, as expected and previously observed in other detailed miscibility studies.[31]

An interesting question concerns the character of the N_{TB}–N phase transition for the pure FFO9OCB dimer, for which it has

not been possible to obtain high-resolution calorimetry measurements,[32] and nothing has been concluded about it. However, it is known that pure CB7CB dimer exhibits a first-order N_{TB}–N phase transition.[6] The inset of Fig. 2 shows how the nematic range increases from pure CB7CB dimer when the concentration of CB7CB in the binary mixtures decreases, showing a behaviour analogous to binary mixtures exhibiting the smectic A (SmA) to nematic phase transition.[39] For this phase transition, the SmA–N latent heat (or the entropy change) is reduced as the nematic range is increased and this experimental observation was explained firstly by Kobayashi[43] and McMillan[44] and shortly after by de Gennes,[45] who developed a phenomenological theory for the SmA–N transition based on a Landau mean-field approach. Recently, Mukherjee[46] has developed an improved theoretical analysis within the Landau phenomenological theory about the influence of the chain flexibility on the SmA–N phase transition.

Fig. 3 shows high-resolution heat capacity data for several FFO9OCB + CB7CB mixtures in the vicinity of the N_{TB}–N phase transition. Such measurements were made in quasi-static mode, with heating rates of 0.01 K min^{-1}, a temperature amplitude modulation of ±0.07 K and an oscillation period of 23 s. It is easy to observe how the heat capacity peak representative of the phase transition becomes smaller as the mole fraction passes from pure CB7CB to pure FFO9OCB. The shape of the heat capacity peak of the mixture X_{CB7CB} = 0.82 is analogous to that found for pure CB7CB[6] dimer and represents a first-order N_{TB}–N phase transition. The other mixtures of 0.48 and 0.36 exhibit first-order phase transitions and the heat capacity peaks although weaker still show features of that for pure CB7CB. The inset in Fig. 3 highlights the two mixtures investigated with mole fractions closer to pure FFO9OCB, for which the heat capacity peaks are extremely small. As for X_{CB7CB} = 0.21, the N_{TB}–N phase transition is still first-order as observed for the small peak in the ϕ-phase shift data around the phase transition (red symbols). Regarding the mixture with

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a mole fraction close to pure FFO9OCB (X_{CB7CB} = 0.10), the N_{TB}–N phase transition is only seen on cooling and no conclusions can be reached about the order of the transition because the calorimeter is operating at the limit of its sensitivity. In addition, during the long time of measurement, the sample in the N_{TB} phase tends to crystallize as evidenced by the drift in the heat capacity stabilization. It should be stressed that for the binary phase diagram investigated the heat capacity peak associated with the N_{TB}–N phase transition literally disappears for a sufficiently wide nematic range. This is an important difference with those binary phase diagrams exhibiting the SmA–N phase transition where the transitional entropy decreases as the nematic range increases but the heat capacity peak associated with the SmA–N phase transition is not suppressed even when the transitional entropy is very small or zero.[39,47–49]

Fig. 4 shows the K_3 and K_1 elastic constants for pure FFO9OCB and CB7CB and three selected binary mixtures as a function of the shifted temperature, $T − T_{N_{TB}-N}$, in the N-phase. As regards K_1, and irrespective of the sample, the elastic constant increases as the temperature decreases on approaching the N–N_{TB} phase transition. It is interesting to observe that the value of K_1 at $T_{N_{TB}-N}$ depends on the sample and in this case on the nematic range, the highest value being that of FFO9OCB (that is the widest nematic range) and the lowest being that of CB7CB (that is the narrowest nematic range): binary mixtures necessarily exhibit intermediate values. As regards K_3, there is an initial increase in the elastic constant at temperatures close to the isotropic phase, but the general behavior is to decrease as the temperature decreases on approaching the N–N_{TB} phase transition. It is important to note that pure compounds and binary mixtures follow the same trend towards a similar value for K_3 at $T_{N-N_{TB}}$ close to zero but with a pretransitional increase as in other twist-bend liquid crystal dimers.[32,42] The near

Fig. 4 Temperature dependence of the splay (K_1)-empty symbols- and bend (K_3)-full symbols- elastic constants as a function of the shifted temperature ($T − T_{NTB}$) in the nematic phase for pure FFO9OCB, CB7CB and some selected mixtures: X_{CB7CB} = 0.21, X_{CB7CB} = 0.48 and X_{CB7CB} = 0.82.

universality of this behaviour is consistent with previous theoretical calculations.[5,29]

4 Theoretical Landau model and discussion

The uniform uniaxial nematic phase can be described by a symmetric and traceless tensor order parameter $Q_{\alpha\beta}^{N} = Q_0(T)[n_\alpha n_\beta - (\frac{1}{3})\delta_{\alpha\beta}]$, where α, β = x, y, z are the coordinate axes that define the phase symmetry. De Gennes[50] suggested that the tensor order parameter can be defined in terms of any second rank tensor property. The normalization constant $Q_0(T)$ varies between 0 and 1, and for any particular property can be determined by setting Q_{zz}^{N} = 1 for a fully-oriented system. In practice, $Q_0(T)$ is often identified with the value of the Saupe major order parameter for the primary molecular axis, expressed as the second-rank Legendre polynomial ($\langle P_2(\cos\psi_i)\rangle$; ψ_i is the angle made by the ith molecular axis with respect to the nematic director), n_α is the nematic director and $\delta_{\alpha\beta}$ is the Kronecker delta.

The Landau theory employed to describe the N_{TB}–N phase transition requires, as a first step, the identification of the physical mechanism responsible for the generation of the twist-bend nematic phase from the uniform nematic phase and proceeds by making some simplifying assumptions. In our case, we follow Dozov's procedure,[13,21] according to which the elastic distortion causing the director curvature would be the main cause. As an approximation, we suppose that the nematic order parameter related to the director jumps at the N–N_{TB} phase transition by δQ as evidenced experimentally for some systems.[26] In fact, we assume that the elastic distortion produces an increase in the value of the scalar order parameter which does not coincide with $Q_0(T)$ in the absence of such distortion. In such a way, we consider the following modification of the symmetric and traceless tensor order parameter for the nematic phase:

$$Q_{\alpha\beta} = Q(T)\left[n_\alpha n_\beta - \frac{1}{3}\delta_{\alpha\beta}\right] \qquad (1)$$

where $Q(T) = Q_0(T) + \delta Q$. Of course, in the uniform nematic phase δQ vanishes, thus being a natural choice of a scalar order parameter for the N_{TB} phase. However, other physical properties could be considered as order parameters. For example, Kats and Lebedev[51] introduce as a natural choice for another N_{TB} order parameter, a characteristic short-range vector field φ_α which is orthogonal to the helix axis and rotates around the heliconical structure with an extremely short periodicity (of the order of several molecular lengths). The absolute value of the vector φ_α is related to the tilt angle (θ_0) as $\sin\theta_0$ (denoted hereafter as φ) and has also been chosen as an order parameter by other authors.[11,13,21,26,35] Dozov and collaborators[13,21,26,35] and Shamid et al.[11] also proposed the absolute value of the wave vector, q_0, related with the pitch or periodicity of the helix ($q_0 = 2\pi/p$) as a further order parameter. However, Kats and Lebedev[51] consider that the N–N_{TB} phase transition takes place at a finite q_0 in a similar way as weak crystallization phase transitions or the SmA–N phase transition. In contrast the
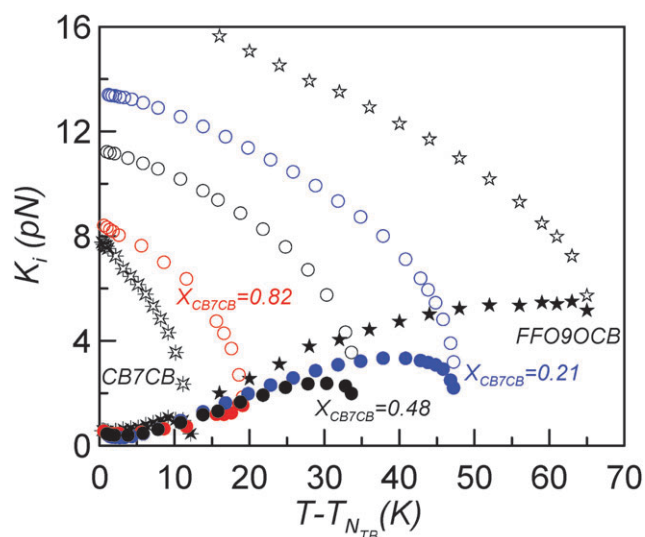
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predictions of the extended Maier–Saupe theory[35] show that the pitch can change with temperature depending on the magnitude of the molecular curvature.

The Landau free energy density of the twist-bend nematic phase can be written in four parts:

$$f_{TB}(Q_{\alpha\beta},\varphi_{\alpha}) = f(Q_{\alpha\beta}) + f(\partial_{\gamma}Q_{\alpha\beta}) + f(\varphi_{\alpha}) + f(\partial_{\gamma}\varphi_{\alpha}) \qquad (2)$$

The term $f(Q_{\alpha\beta})$ is developed in powers of the scalars formed by contraction of the tensor indices:

$$f(Q_{\alpha\beta}) = \frac{1}{2}A_1 Q_{\alpha\beta}Q_{\alpha\beta} + \cdots = f_N(Q_0) + \frac{1}{2}\alpha(\delta Q)^2 + \cdots \qquad (3)$$

Eqn (3) is the homogeneous part of the nematic free energy density with the Landau coefficients (A_1, A_2,...) chosen in a convenient way to obtain a minimum for $\delta Q = 0$, being $f_N(Q_0)$ the free energy density of the uniform nematic state. For simplicity, we only consider the first term in powers of δQ that represents the free energy density cost of increasing the orientational order parameter with respect to the director over $f_N(Q_0)$. The α-parameter ($\alpha > 0$) is a response function ($\alpha(T)$) which depends on the temperature range of the uniform nematic phase (hereafter denoted as NR) and its value is assumed to be dependent on the average bend angle χ ($\chi = 180°$ for rod molecules and decreases as they are bent) and probably the flexibility of the molecules. For binary mixtures formed by molecules with different effective average curvature and flexibility, the mole fraction $X(T)$, along the N_{TB}–N transition depends on NR and acts as an external perturbation changing the response function in such a way that α is a function of the mole fraction ($\alpha(X)$). For temperatures close to T_{NI}, Q_0 is relatively far from saturation and the α-parameter is small but finite because it is easy to increase the orientational order parameter. On the contrary, when $T \ll T_{NI}$ the α-parameter is large because Q_0 is nearly saturated and so it is very hard to increase it.

The second term $f(\partial_{\gamma}Q_{\alpha\beta})$ corresponds to the spatial derivatives of the $Q_{\alpha\beta}$ given by eqn (1). The lowest order terms for $f(\partial_{\gamma}Q_{\alpha\beta})$ can be written as:

$$f(\partial_{\gamma}Q_{\alpha\beta}) = \frac{1}{2}L_1(\partial_{\alpha}Q_{\beta\gamma})\partial_{\alpha}Q_{\beta\gamma} + \frac{1}{2}L_2(\partial_{\alpha}Q_{\alpha\gamma})\partial_{\beta}Q_{\beta\gamma} + \cdots \qquad (4)$$

where L_1 and L_2 are the lowest order elastic coefficients. If we assume that for $Q_{\alpha\beta}$ only the director (n_{α}) changes spatially, eqn (4) can be written as:

$$f(\partial_{\gamma}Q_{\alpha\beta}) = L_1 Q^2[S^2 + T^2 + B^2] + \frac{1}{2}L_2 Q^2[S^2 + B^2] + \cdots \qquad (5)$$

in terms of the splay vector $S_{\alpha} = n_{\alpha}(\partial_{\gamma}n_{\gamma})$, the twist pseudo-scalar $T = n_{\alpha}\varepsilon_{\alpha\beta\gamma}\partial_{\beta}n_{\gamma}$ and the bend vector $B_{\alpha} = \varepsilon_{\alpha\nu\mu}n_{\nu}\varepsilon_{\mu\beta\gamma}\partial_{\beta}n_{\gamma}$. Eqn (5) can be developed according to eqn (1) as:

$$f(\partial_{\gamma}Q_{\alpha\beta}) = \left(L_1 + \frac{L_2}{2} + \cdots\right)Q_0^2 S^2 + (L_1 Q_0^2 + \cdots)T^2$$
$$+ \left(L_1 + \frac{L_2}{2} + \cdots\right)Q_0^2 B^2 + 2\left(L_1 + \frac{L_2}{2} + \cdots\right)Q_0\delta Q B^2 + \cdots$$
$$(6)$$

Let us consider the following relationships according to the Oseen–Frank theory:

$$(2L_1 + L_2 + \cdots)Q_0^2 = K_1 \qquad (7a)$$

$$2L_1 Q_0^2 + \cdots = K_2 \qquad (7b)$$

$$(2L_1 + L_2 + \cdots)Q_0^2 = K_3 \qquad (7c)$$

where K_1, K_2 and K_3 in eqn (7) are the so-called elastic constants for splay, twist and bend respectively. If in eqn (4) only terms to second order in $Q_{\alpha\beta}$ are considered a degeneracy in the splay and bend elastic constants through eqn (7a) and (7c) would be obtained, a fact which is contrary to experimental measurements. A third order extra term in $Q_{\alpha\beta}$ must be taken into account. With these definitions, eqn (6) is the classical Oseen–Frank free energy for the N phase with additional terms representing the coupling between δQ and the bend distortion as well as other couplings. If we consider the first term in δQ to be of prime importance for generating the twist-bend nematic phase, then we must introduce a parameter λ defined by:

$$(2L_1 + L_2 + \cdots)Q_0 = \lambda \qquad (8)$$

The significance of λ will be discussed later. Eqn (6) can be written as follows:

$$f(\partial_{\gamma}Q_{\alpha\beta}) = \frac{1}{2}K_1 S^2 + \frac{1}{2}K_2 T^2 + \frac{1}{2}K_3 B^2 + \lambda\delta Q B^2 + \cdots \qquad (9)$$

The third term in eqn (2) can be written in powers of the scalars corresponding to the short-range vector field φ_{α}. In fact, a vector order parameter only has a scalar invariant, the length squared of the vector $\varphi_{\alpha}\varphi_{\alpha} = \varphi^2$ and the successive even powers in such a way that the third term of eqn (2) can be developed as:

$$f(\varphi_{\alpha}) = \frac{1}{2}a_0(T - T_0)\varphi^2 + \cdots \qquad (10)$$

where a_0 is definite positive and $a_0(T - T_0)$ is positive in the uniform nematic phase but negative in the N_{TB} phase giving rise to a negative free energy that favours the tilt of the director with respect to the helix axis.

The last term in eqn (2) corresponds to the spatial derivatives of the short-range vector field φ_{α} and it is needed in order to guarantee a finite and stable value of the helical pitch for the twist-bend nematic phase. This idea was earlier developed by Mukherjee[52] in the Landau model for the SmC–I phase transition in order to guarantee a finite wave-length for the smectic density wave. The lowest order terms can be written as:

$$f(\partial_{\gamma}\varphi_{\alpha}) = -\frac{1}{2}b_0(\partial_{\alpha}\varphi_{\alpha})^2 - \frac{1}{2}b_1(\partial_{\gamma}\partial_{\gamma}\varphi_{\alpha})\partial_{\beta}\partial_{\beta}\varphi_{\alpha} + \cdots \qquad (11)$$

where b_0 and b_1 are defined positive and the term given by eqn (11) gives rise to a negative free energy that favours a finite pitch for a tilted director.

The Landau free energy density of the twist-bend nematic phase (see eqn (2)) obtained by adding eqn (3), (9), (10) and (11) can be written as a function of two variational parameters ($\delta Q,\varphi$) assuming that Q_0 is the scalar order parameter of the uniform nematic phase and characterized only, as an

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approximation, by the term $f_N(Q_0)$:

$$f_{TB}(\delta Q, \varphi) = f_N(Q_0) + \frac{1}{2}\alpha(\delta Q)^2 + \frac{1}{2}K_1 S^2 + \frac{1}{2}K_2 T^2$$

$$+ \frac{1}{2}K_3 B^2 + \lambda \delta Q B^2 + \frac{1}{2}a_0(T - T_0)\varphi^2 \qquad (12)$$

$$- \frac{1}{2}b_0(\partial_\alpha \varphi_\alpha)^2 - \frac{1}{2}b_1(\partial_\gamma \partial_\gamma \varphi_\alpha)\partial_\beta \partial_\beta \varphi_\alpha + \cdots$$

The overall free energy $f_{TB}(\delta Q, \varphi)$ of eqn (12) must then be minimized with respect to δQ, giving

$$\delta Q = -\frac{\lambda}{\alpha}B^2 \qquad (13)$$

The value of δQ given by eqn (13) must be positive in the twist-bend nematic phase. Thus λ should be negative to ensure that δQ increases the nematic orientational order parameter with respect to the director in the N_{TB} phase. This is also supported by the fact that λ represents the coupling parameter between δQ and the director bend, so the contribution to the free energy density in eqn (12) must be negative because the local spontaneous bend of the director must be favoured in the N_{TB} phase. By substituting eqn (13) into eqn (12) the overall free energy density of the N_{TB} phase can be written as:

$$f_{TB}(\varphi) = f_N(Q_0) + \frac{1}{2}K_1 S^2 + \frac{1}{2}K_2 T^2 + \frac{1}{2}K_3 B^2 - \frac{\lambda^2}{2\alpha}B^4$$

$$+ \frac{1}{2}a_0(T - T_0)\varphi^2 - \frac{1}{2}b_0(\partial_\alpha \varphi_\alpha)^2 \qquad (14)$$

$$- \frac{1}{2}b_1(\partial_\gamma \partial_\gamma \varphi_\alpha)\partial_\beta \partial_\beta \varphi_\alpha + \cdots$$

For simplicity in eqn (14), we can consider a 1D distortion of the director $n_\alpha = (\varphi \cos(q_0 z), \varphi \sin(q_0 z), (1 - \varphi^2)^{1/2})$ and the short-range vector field $\varphi_\alpha = (\varphi \cos(q_0 z), \varphi \sin(q_0 z), 0)$ in such a way that it is verified: $S^2 = 0$; $T^2 = q_0^2 \varphi^2$; $B^2 = q_0^2 \varphi^2(1 - \varphi^2)$; $(\partial_\alpha \varphi_\alpha)^2 = 0$; $(\partial_\gamma \partial_\gamma \varphi_\alpha)\partial_\beta \partial_\beta \varphi_\alpha = q_0^4 \varphi^2$. Eqn (14) takes the following form depending now on two variational scalar parameters, φ and q_0:

$$f_{TB}(\varphi, q_0) = f_N(Q_0) + \frac{1}{2}K_3 q_0^2 \varphi^2 + \frac{1}{2}a_0(T - T_0)\varphi^2$$

$$+ \frac{1}{2}(K_2 - K_3)q_0^2 \varphi^4 - \frac{\lambda^2}{2\alpha}q_0^4 \varphi^4 \qquad (15)$$

$$+ \frac{\lambda^2}{\alpha}q_0^4 \varphi^6 - \frac{1}{2}b_1 q_0^4 \varphi^2 + \cdots$$

Minimization of eqn (15) with respect to the absolute value of the wave vector q_0 gives:

$$q_0^2 = \frac{K_3 + (K_2 - K_3)\varphi^2}{-\frac{4\lambda^2}{\alpha}\varphi^4 + \frac{2\lambda^2}{\alpha}\varphi^2 + 2b_1}$$

$$\qquad (16)$$

$$\approx \frac{K_3}{2b_1} + \frac{(K_2 - K_3)b_1 - \frac{K_3 \lambda^2}{\alpha}}{2b_1^2}\varphi^2 + \cdots$$

At this point it is important to interpret carefully the physical meaning provided by eqn (16). At first glance, q_0 should take a

finite value even if φ at the phase transition is null. This result agrees with the consideration of Kats and Lebedev[51] and also with one of the conclusions of Barbero et al.[53] Eqn (15) takes the following form by substituting eqn (16) and reordering in powers of φ:

$$f_{TB}(\varphi) = f_N(Q_0) + \frac{1}{2}K_3^{eff}\varphi^2 + \frac{1}{4}K_2^{eff}\varphi^4 + \frac{1}{6}E\varphi^6 + \cdots \qquad (17)$$

where

$$K_3^{eff} = \frac{K_3^2}{4b_1} + a_0(T - T_0) \qquad (18a)$$

$$K_2^{eff} = \frac{K_3}{b_1}\left[K_2 - K_3 - \frac{\lambda^2 K_3}{2\alpha b_1}\right] \approx \frac{K_3}{b_1}\left[K_2 - \frac{\lambda^2 K_3}{2\alpha b_1}\right] \qquad (18b)$$

$$E = \frac{3\lambda^2 K_3^2}{2\alpha b_1} + \frac{3(K_2 - K_3)}{b_1} + \cdots \qquad (18c)$$

Eqn (18a) defines an effective bend elastic constant (K_3^{eff}) which is a function of temperature because K_3 varies with temperature for liquid crystal dimers,[29] but is definite positive in the uniform nematic phase according to experimental determinations,[25,31–34,54] as shown in Fig. 4. Thus, K_3^{eff} is positive in the uniform nematic phase and negative in the twist-bend nematic phase as discussed previously by Dozov.[13] In the following, the combination of both effects can be written as $K_3^{eff} = K_{3,0}(T - T_C)$ where $K_{3,0}$ defined as positive and T_C is a virtual critical temperature renormalized from T_0, the meaning of which will be discussed later.

Eqn (18b) is denoted by K_2^{eff} because it is expressed as a correction to the twist elastic constant (K_2 defined as positive) by both K_3 and $(\lambda^2 K_3)/(2\alpha b_1)$. Calculations[29] for odd liquid crystal dimers as well as experimental data[31] give $K_2 > K_3$ and at temperatures close to the N–N_{TB} phase transition the effect of K_3 over K_2 may be neglected in such a way that the important correction to K_2 comes from $(\lambda^2 K_3)/(2\alpha b_1)$. It is just the value of this last term, defined as positive, that drives K_2^{eff} from positive to negative. As we have mentioned, for binary mixtures, the response function α may be thought of as depending upon the composition of the mixture or the nematic range (NR). As regards K_2, there are no experimental determinations in a binary system but calculations of K_2 made by Cestari et al.[29] suggest a comparable behaviour with temperature as K_1, with $K_2 < K_1$. Fig. 4 shows how K_1 at the N_{TB}–N phase transition is a function of the composition and a similar behaviour could be assumed for K_2 in such a way that K_2^{eff} may be considered as a function of the mole fraction in a binary system ($K_2^{eff}(X)$).

Eqn (18c) defines a parameter E that may be thought of as composition dependent in a binary system but is always positive.

The equilibrium value of the φ-order parameter is obtained by minimizing eqn (17) with respect to $\varphi([\partial f_{TB}/\partial \varphi] = 0)$. This means that for the N_{TB} phase:

$$\varphi_{TB}^2 = \frac{1}{2E}\left[-K_2^{eff} + \left((K_2^{eff})^2 - 4EK_{3,0}(T - T_C)\right)^{\frac{1}{2}}\right] \qquad (19)$$

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and $\varphi_{\mathrm{N}} = 0$ in the uniform nematic phase. The transition temperature ($T_{\mathrm{N_{TB}-N}}$) can be determined using the condition $f_{\mathrm{TB}} = f_{\mathrm{N}}$ in eqn (17) and also the minimization condition ($[\partial f_{\mathrm{TB}}/\partial\varphi] = 0$). Two mathematical solutions are obtained at the phase transition:

$$\varphi_{\mathrm{N_{TB}-N}} = 0 \tag{20a}$$

$$\varphi_{\mathrm{N_{TB}-N}}^{2} = -\frac{3K_2^{\mathrm{eff}}}{4E} \tag{20b}$$

The solution given by eqn (20a) implies no discontinuity in the φ-order parameter and so, the $\mathrm{N_{TB}-N}$ phase transition is second order and takes place when $T_{\mathrm{N_{TB}-N}} = T_{\mathrm{C}}$. However, would it be possible for a second order $\mathrm{N_{TB}-N}$ phase transition compatible with a zero heliconical angle (θ_0) but with a finite non-zero q_0? We believe that both facts are irreconcilable and so, either the $\mathrm{N_{TB}-N}$ phase transition takes place when K_3 is zero or is always first order. Strangely, Barbero et al.[53] consider a finite wave vector to be compatible with a second order $\mathrm{N_{TB}-N}$ phase transition. The solution given by eqn (20b) is only possible if K_2^{eff} is negative, a consequence of the term $(\lambda^2 K_3)/(2\alpha b_1)$ being larger than K_2. In fact, as discussed previously, the term $(\lambda^2 K_3)/(2\alpha b_1)$ decreases as the nematic range of the binary mixtures increases. Thus, K_2^{eff} becomes less negative as the nematic range increases and the nematic range limit would occur when K_2^{eff} vanishes. Therefore, the model described by eqn (17) supports the possibility of a first order $\mathrm{N_{TB}-N}$ phase transition, the strength of which decreases as the nematic range increases. The $\mathrm{N_{TB}-N}$ phase transition is first order at a temperature $T_{\mathrm{N_{TB}-N}} = T_1$ given by

$$T_1 = T_{\mathrm{C}} + \frac{3\left(K_2^{\mathrm{eff}}\right)^2}{16EK_{3,0}} \tag{21}$$

Eqn (19) can be written as

$$\varphi_{\mathrm{TB}}^2 = \left(\frac{K_{3,0}}{E}\right)^{\frac{1}{2}}\left[\frac{-K_2^{\mathrm{eff}}}{2\left(EK_{3,0}\right)^{\frac{1}{2}}} + (T_{\mathrm{K}} - T)^{\frac{1}{2}}\right] \tag{22}$$

where T_{K} represents the metastability limit of the twist-bend nematic phase, defined as

$$T_{\mathrm{K}} = T_{\mathrm{C}} + \frac{\left(K_2^{\mathrm{eff}}\right)^2}{4EK_{3,0}} \tag{23}$$

The excess heat capacity ($\Delta C_{\mathrm{p}} = C_{\mathrm{p,TB}} - C_{\mathrm{p,N}}$) can be obtained from the excess free energy density ($\Delta f = f_{\mathrm{TB}} - f_{\mathrm{N}}$) given by eqn (17) as

$$\Delta C_{\mathrm{p}} \approx -T\left[\frac{\partial^2(\Delta f)}{\partial T^2}\right]_{V,\phi} = T_{\mathrm{C}}A^*\left[\frac{T_{\mathrm{K}} - T_1}{T_{\mathrm{K}} - T}\right]^{\frac{1}{2}} \tag{24}$$

where the new parameter A^* is defined as

$$A^* = -\frac{3K_{3,0}^2}{K_2^{\mathrm{eff}}} \tag{25}$$

In order to test the theory, we have fitted it to measurements of the heat capacity for the mixtures reported earlier in this paper. For example, Fig. 5 shows the excess heat capacity for $X_{\mathrm{CB7CB}} = 0.36$ taken from the heat capacity measurements of Fig. 3.
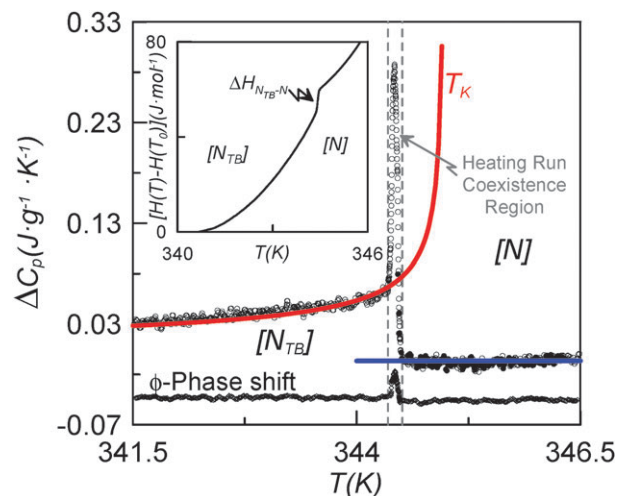

Fig. 5 Detailed view of the $\mathrm{N_{TB}-N}$ phase transition excess heat capacity peak for $X_{\mathrm{CB7CB}} = 0.36$ taken from Fig. 3. Data of the ϕ-phase shift is superimposed to the excess heat capacity peak to delimit the coexistence region. Red line shows the fitting according to eqn (24). The inset shows the integrated enthalpy.

Table 1 Characteristic parameters of the $\mathrm{N_{TB}-N}$ phase transition according to eqn (24) and the entropy change

X_{CB7CB}	A^* (J g K^2) $\times 10^3$	T_{K} (K)	T_1 (K)	T_{C} (K)	$\Delta S_{\mathrm{N_{TB}-N}}/R$
1	1.7^a	376.72^a	376.57^a	376.17^a	0.066(5)
0.82	2.2	365.97	365.92	365.77	0.035(6)
0.48	0.6	350.93	350.84	350.58	0.009(7)
0.36	0.6	344.86	344.81	344.65	0.004(8)
0.21	—	—	—	—	0.002(8)

^{a} Data taken from ref. 6.

The latter is the closest binary mixture to pure FFO9OCB that can be analysed using eqn (24) with acceptable fitting results. More dilute mixtures (see the inset of Fig. 3) give rise to very small heat capacity peaks, the analysis of which via eqn (24), is difficult to achieve with the required accuracy. The ϕ-phase shift data allow us to delimit the phase coexistence region characteristics of a first order phase transition. The red line shows the fitting according to eqn (24) with A^*, T_1, T_{C} and T_{K} as fitting parameters listed in Table 1 together with those corresponding to the other binary mixtures analysed. The blue line corresponds to the excess heat capacity of the nematic which must be zero according to the assumptions of the model. It should be stressed that the temperature discontinuity metric ($T_1 - T_{\mathrm{C}}$) given by eqn (21) is consistent with the results listed in Table 1, but the dependence of ($T_1 - T_{\mathrm{C}}$) with the mole fraction of CB7CB, as suggested by eqn (21), is not straightforward because the fitting procedure provides a certain uncertainty in giving both temperatures T_1, T_{C}.

The inset of Fig. 5 shows the integrated enthalpy for $X_{\mathrm{CB7CB}} = 0.36$ calculated, as an example, according to:

$$H(T)H(T_0) = \Delta H_{\mathrm{N_{TB}-N}} + \int_{T_0}^{T} \Delta C_{\mathrm{p}}\mathrm{d}T \tag{26}$$

where $\Delta H_{\mathrm{N_{TB}-N}}$ is the latent heat associated with the $\mathrm{N_{TB}-N}$ phase transition. The value of $\Delta H_{\mathrm{N_{TB}-N}}$ is easily identified in the
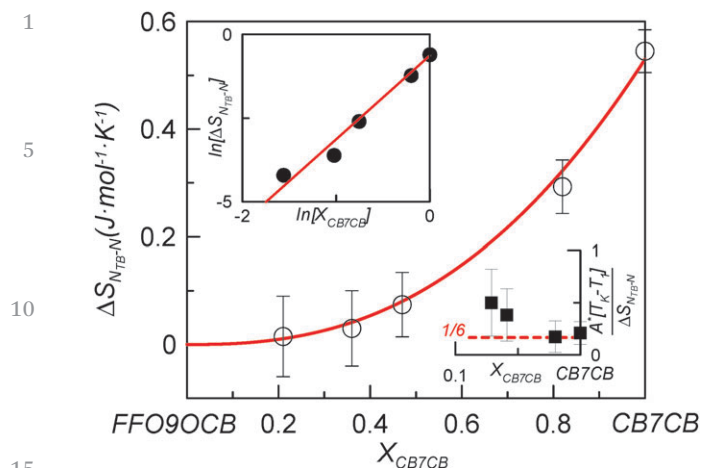
Fig. 6 The entropy change associated to the N_{TB}–N phase transition as a function of the composition of CB7CB for some selected binary mixtures FFO9OCB + CB7CB. The top-left inset shows the entropy data in a logarithmic scale. The bottom-right inset shows $(A^*[T_K - T_1])/\Delta S_{N_{TB}-N}$ as a function of the composition of CB7CB.

inset of Fig. 5. The experimental entropy change calculated from the latent heat data is shown in Fig. 6 as a function of the mole fraction of CB7CB and also listed in Table 1. This calculation is extended to pure CB7CB and all of the prepared mixtures with the exception of $X_{CB7CB} = 0.10$. The top-left inset of Fig. 6 shows the entropy data on a logarithmic scale in such a way that the linear trend (the best fitting function namely $\Delta S_{N_{TB}-N} \sim 0.5(X_{CB7CB})^{5/2}$) implies that there is no composition for which the entropy change could vanish. Thus, as a main conclusion, it seems that for the mixtures of the binary system investigated together with both pure compounds the N_{TB}–N phase transition is first order and their strength diminishes as the composition moves from pure CB7CB to FFO9OCB or in other words, as the nematic range increases.

The relationship corresponding to the entropy change at the N_{TB}–N phase transition ($\Delta S_{N_{TB}-N}$) given by the Landau model can be written from eqn (17) and (20b) as:

$$\Delta S_{N_{TB}-N} = -\left[\frac{\partial(\Delta f)}{\partial T}\right]_{T=T_1} = -\frac{3K_{3,0}K_2^{eff}}{4E} \quad (27)$$

Eqn (27) is consistent with a dependence of the transitional entropy ($\Delta S_{N_{TB}-N}$) on the mole fraction of CB7CB because K_2^{eff} and E are themselves composition dependent. There is an excellent correspondence between our experimental data and the proposed Landau model via the following relationship for a negative K_2^{eff}:

$$\frac{A^*[T_K - T_1]}{\Delta S_{N_{TB}-N}} = \frac{1}{6} \quad (28)$$

obtained by combining eqn (21), (23), (25) and (27). The bottom-right inset of Fig. 6 shows our data for the binary mixtures investigated with a satisfactory compatibility with eqn (27).

On the other hand, from eqn (27), our simplified Landau model shows how the entropy change at the N_{TB}–N phase transition ($\Delta S_{N_{TB}-N}$) is directly proportional to the size of the

heat capacity peak ($A^*[T_K - T_1]^{1/2}$). Thus, in the framework of our Landau model when $\Delta S_{N_{TB}-N}$ decreases the size of the heat capacity peak decreases as well. Therefore, it could be said that when the N_{TB}–N phase transition is first order but extremely weak, the characteristic heat capacity peak is nearly undetectable.

The proposed model could be refined by the inclusion of fluctuations of the nematic director as in other theoretical approaches.[51] However, as we can observe from Fig. 3 or 5, the highly asymmetric heat-capacity peak with no excess heat capacity above the N_{TB}–N transition is exactly what is expected for a phase transition with negligible director fluctuations of the nematic director.

5. Concluding remarks

Before summarising the conclusions of this study of the nematic to twist-bend nematic phase transition in a particular binary system, it is worth considering the general predictions of theory concerning the nature of phase transitions in liquid crystal systems. These have been much studied in the past for model systems for a wide variety of different liquid crystal phases, including many phases that have yet to be identified experimentally.[55] However, the nematic to twist-bend nematic phase that is the object of the present study was not specifically considered.[55] Two predictions can be drawn from symmetry considerations. Firstly if the transition is between two phases of the same symmetry, then the transition must be first-order. The classic example of this is the gas-isotropic liquid transition, for which, in the pressure-temperature phase diagram, the line of first order transitions terminates in a critical end-point. Comparable transitions occur in liquid crystal phases such as the modulated smectic A phases, denoted as SmA, SmA$_2$, and SmA$_d$, for which transitions between the phases must be first order. Further interesting examples[46,56] are the predicted transitions between different SmA phases comprised of flexible molecules. These phases are characterised as conformationally-ordered or conformationally-disordered, and the transitions between them are necessarily first order. While such transitions have not been positively identified in low molecular weight systems, the theoretical basis may be applicable to certain types of nematic–nematic transitions in flexible mesogens, of the type studied in this paper.

The second prediction about phase transitions that can be derived from considerations of symmetry is the impossibility, in the absence of external symmetry breaking, of a transition between a chiral and an achiral phase. However, this point introduces the complication of scale, which is ignored by simple symmetry considerations. The traditional chiral nematic phase (also known as cholesteric) on a scale much smaller than the pitch is identical to an achiral nematic, so simple considerations of symmetry can only be applied at a macroscopic scale. At this scale, we may assert that the symmetries of the conventional nematic phase and the twist-bend nematic phase are the same ($D_{\infty h}$), and that the phases are both achiral, since macroscopically the domains of opposite chirality in the twist-bend nematic phase must compensate. These considerations suggest that the

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phase transition between the nematic and the twist-bend nematic should be first order, though of course other factors such as inclusion of fluctuations and issues of different scales could intervene.

The Landau mean-field approach for the N_{TB}–N phase transition proposed in this paper, embodied by eqn (17) in its simplified form, seems to provide a satisfactory explanation of our high-resolution heat capacity measurements in the vicinity of the N_{TB}–N phase transition in binary mixtures of CB7CB and FFO9OCB. Both odd dimers have molecular conformations with different average curvatures, and, in their mixtures, the addition of the methylene-linked dimer (CB7CB) to the ether-linked dimer enhances the stability of the N_{TB} phase promoting narrow nematic ranges.

The model gives rise to a finite value of q_0 at the N_{TB}–N phase transition. Such a phase transition could be considered always first order with a strength which depends on an effective elastic constant K_2^{eff} that must be negative. Its absolute value decreases as the nematic range increases.

Experimental measurements of the heat capacity for the investigated mixtures indicate that there is no tricritical point related to the N_{TB}–N phase transition, in contrast to that proposed for the SmA–N phase transition. It is observed that the heat capacity peaks become smaller as the nematic range increases, and ultimately seem to be suppressed. This fact is perfectly explained by the proposed Landau model, and it shows a quantitative difference with what we obtain for binary mixtures showing the SmA–N phase transition. For the systems we have studied,[39,47–49] the SmA–N transition may be second-order, but the associated heat capacity peaks are well defined as observed in the experimental measurements.

The experimental conclusion of this work is that for the mixed system of CB7CB and FFO9OCB mesogenic dimers, the nematic to twist-bend nematic transition is always first-order, and we have proposed a Landau theory which fits our experimental measurements. We do not claim that this is a universal result, and other systems may behave differently. While it is tempting to rely on the predictions of symmetry as absolutes, it is clear that the transitions between different liquid crystal phases are very delicate. Additionally, given the complex molecular structures of the mesogens, there are short-range factors that can influence the nature of the phase transitions. We have noted two of such influences, dipole–dipole interactions as in the modulated smectic A phases, and the possibility of conformational ordering which may indeed be important for the flexible mesogenic dimers studied in this paper. In particular we should note that the formation of chiral domains in the twist-bend nematic phase is driven in our flexible mesogens by the selective stabilization of conformers of different chiral configurations in the left and right helical domains.[20] This mechanism might not apply in other twist-bend phases, such as those formed from rigid bent-core mesogens. Finally, the fact that the twist-bend nematic phase is characterized by a spatially modulated director distribution suggests that, on some scale at least, there may be very weak (undetectable) density modulations in the phase. This would require

additional order parameters in the theoretical description of the nematic to twist-bend nematic phase transitions.

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