INVITED ARTICLE

On orientational order in nematic and twist-bend nematic phases: A ^{2}H-NMR study of binary mixtures of the odd dimer,1″,9″-bis(4-cyanobiphenyl-4'-yl) nonane, (CB9CB), and the monomer, 4-pentyl-4'-cyanobiphenyl, (5CB-d$_2$)

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ABSTRACT

Here we explore those factors that influence the orientational order in both nematic and twist-bend nematic phases. The systems used for our NMR experiments are binary mixtures of a dimer and a related monomer thus enabling its behaviour to be controlled continuously, through its composition rather than chemical structure. Earlier studies have revealed that as the temperature is lowered in the nematic phase the orientational order frequently passes through a maximum prior to the formation of the N$_{TB}$ phase. A confirmative indication of this unusual behaviour is that the Haller function cannot fit this dependence over the entire nematic range; such behaviour is intriguing. In the N$_{TB}$ phase the measured order parameter is often insensitive to decreasing temperature for systems with strong N$_{TB}$-N transitions often associated with a narrow nematic range. For those mesogens with longer nematic ranges and hence weaker N$_{TB}$-N transitions the order parameter decreases more markedly with temperature. As expected for the weak transitions the behaviour of the order parameter is observed to be essentially continuous across the transition. Associated with the orientational order in the N$_{TB}$ phase is the conical angle and an off-diagonal element of Saupe ordering matrix.

KEYWORDS Pretransitional behaviour; conical angle; Haller function; Saupe ordering matrix; transitional entropy, nematic range, chiral quadrupolar splitting, Gay-Berne
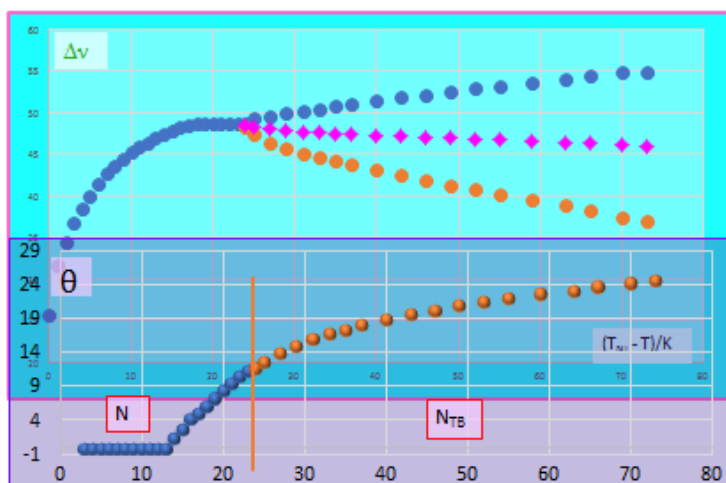
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1.Introduction

The structure of the twist-bend nematic phase, N_{TB}, is analogous to that of the chiral nematic phase, N^*, but with the director tilted with respect to the heliconical axis. In addition the constituent molecules are achiral and the heliconical structure results albeit indirectly, primarily from the molecular curvature. The prediction of the twist-bend phase has its origin in the paper by Meyer [1]. However, this important prediction was largely neglected and only resurrected after a seminal study by Dozov [2]. This was based on a Landau-like theory with the key coefficients being related to the elastic constants, K_i, in which the twist coefficient K_3 plays a central role. The twist-bend nematic phase is predicted to occur when K_3 is, in effect, negative and the other two elastic constants, K_2, twist and K_1, splay, satisfy the inequality $K_2 < K_1/2$. For the opposite inequality namely $K_2 > K_1/2$ another modulated but achiral structure is predicted; we shall refer to this towards the end although Dozov did not find this so interesting, given the fascinating chirality of the N_{TB} phase. The other feature of this nematic phase is that it is composed of degenerate, chiral domains having opposite handedness. The helical structure of the N_{TB} phase was also found at about the same time in a Monte Carlo simulation of Gay-Berne V-shaped molecules by Memmer [3].

Subsequently the existence of the twist-bend nematic phase was demonstrated for the lower odd liquid crystal dimer CB7CB where ^{2}H-NMR spectroscopy was used to demonstrate the chirality of the phase despite the achirality of the constituent molecules and the nematic phase at higher temperatures [4]. There have been significant studies of this phase chirality in which the pitch of the helical structure has been shown to be of the order of several molecular lengths [*e.g.* 5,6]; a truly surprising result. Other defining properties of the phase include the conical tilt angle, θ_0, that we shall return to and the orientational order parameters in both the N and N_{TB} phases. For the moment we shall describe briefly, in the following few paragraphs, four key studies of the second-rank orientational order of such phases. In this way we aim to place our own investigation of a series of mixtures formed from two components, one dimer and the other a related monomer, in their proper context.

(A) We start with the first ^{2}H-NMR study of the orientational order in the nematic phase of the first twist-bend nematic to be identified, namely the odd liquid crystal dimer CB7CB-d_4. In this the protons in the first and last methylene groups of the heptane spacer were replaced by four deuterons. These deuterons are equivalent in the conventional nematic phase and so the ^{2}H-NMR spectrum contains a single quadrupolar doublet with spacing, $\Delta\nu$, [4], which is plotted in Figure 1. This splitting is related to the Saupe order parameter, S_{CD}, for the C-D bonds with respect to the nematic director which for CB7CB is aligned parallel to the magnetic field of the spectrometer. The splitting increases monotonically with increasing shifted temperature, ($T_{NI} - T$), as expected for a conventional nematic. At the first-order transition to the twist-bend nematic phase there is a dramatic spectral change as the single quadrupolar splitting is doubled as shown in Figure 1 where one is seen to increase while the other decreases with decreasing temperature. This is a direct consequence of the chirality of the N_{TB} phase and the resultant loss of the equivalence of the two prochiral deuterons on the two methylene groups at positions 1" and 7" of the spacer. In addition, the mean of the two prochiral splittings only changes very slightly with temperature. This is attributed to the competition between the growth in the orientational order and the increase in the conical angle which reduces the quadrupolar splitting

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along the magnetic field by $P_2(\cos\theta_0)$. This dependence could and indeed has been used to provide a route to the determination of the conical angle [6, 7].

(B) Some years later a similar study was made of a chemically-induced twist-bend nematic phase formed by a mixture of six-liquid crystal dimers having odd spacers but only one of which had methylene links the other five had ether links [8]. The twist-bend nematic phase was induced by the addition of the highly curved methylene-linked dimer and most of the measurements were made with 20wt% of this dimer in the mixture, denoted by KA(0.2). However, measurements were also made for the KA mixture without the methylene-linked dimer which formed a nematic phase over most of its range of about 50°C but with a hint that at the last measurement it was about to freeze. The ^{2}H-NMR measurements were made by adding a trace amount of the dimer CB7CB-d$_4$ as a probe. The quadrupolar splitting for the four equivalent deuterons are shown in Figure 2 as a function of (T_{NI} – T) and the monotropic nature of its increase with decreasing temperature is clearly apparent. The results for the KA(0.2) mixture are seen to be strikingly different; $\Delta\nu$ increases over most of the nematic range but not as steeply as for the KA mixture itself. Then at a shifted temperature of about 30°C the quadrupolar splitting passes through a maximum before the weak N_{TB} – N transition is reached and the two prochiral splittings appear in the N_{TB} phase. In addition the mean of these clearly decreases with decreasing temperature apparently as a continuation of that in the N phase and implying a strong increase in the conical angle. Finally it was noted that the clear, pretransitional decrease in the splitting leading to the N_{TB} phase was consistent with the reduction in $\Delta\nu$ for the mean of the prochiral splittings.

(C) Subsequently Emsley *et al.* [9] undertook a detailed study of a dimer DTC5C9 in which two terphenyl groups are linked by a nonane spacer. In their ^{13}C-{^{1}H}-NMR experiments a wealth of carbon chemical shifts were determined as a function of shifted temperature in the nematic and twist-bend nematic phases. The information content of these experiments was far higher than for the ^{2}H-NMR experiments and it proved possible to determine the Saupe order parameter, S_{zz}, for the para-axis of the terphenyl groups. This is shown as a function of (T_{NI} – T) in Figure 3 and it is immediately clear that the order parameter passes through a maximum in the nematic phase. It then decreases continuously into the N_{TB} phase but, necessarily, does not split in the way that the prochiral deuterons do. The results in the N phase away from the maximum were also fitted to the Haller function for the temperature dependence of the order parameter [10]. The form of the function employed is

$$S_{zz}(\Delta T) = S_{zz}(0K)(1 - T/T^*)^\gamma, \tag{1}$$

where $\Delta T = T_{NI} – T$ and T^* is given the value of $T_{NI} + 0.5$. The data in the range for ΔT from 4°C to 17°C was fitted to Equation (1) which yielded reasonable values for the adjustable parameters of $S_{zz}(0K) = 0.82$ and $\gamma = 0.17$. The values for S_{zz} calculated with these parameters over the entire experimental temperature range are shown as crosses in Figure 3. There is a significant difference between the Haller function and the experimental values in the N_{TB} phase which is attributed to the conical angle. More significantly the difference in the N phase suggests that the director is also tilted with respect to the magnetic field. This is explained in terms of the bent molecules with, presumably, a flexible spacer, giving an entangled and intercalated structure of near neighbours but differing from those in the N_{TB} phase by their lack of chirality.

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(D) The final system that we shall consider for the present is the non-symmetric dimer CB6OCB which has also been investigated with ^{13}C-$\{^{1}$H$\}$ NMR [11]. The information content of the experiments is high as it needs to be in view of the inequivalence of the two cyanobiphenyl groups, one with an ether link and the other a methylene link to the spacer. The order parameter, S_{zz}, for the cyanobiphenyl group with the methylene link is shown as a function of $(T_{NI} - T)$ in Figure 4 as closed circles. It is clear that the order parameter again passes through a maximum before reaching the N_{TB} – N phase transition where there is a small discontinuity in the order parameter in keeping with the weak transition. Again the key result is that fitting the temperature dependence of S_{zz} with a Haller function is consistent with the tilt of the director with respect to the magnetic field in both the N and N_{TB} phases although not continuous. The tilt in the nematic phase grows with decreasing temperature but is not continuous with the slightly larger value in the twist-bend nematic phase. Two suggestions were made to explain the behaviour of the order parameter in the nematic phase [11]. One is that a new phase is injected between the N and N_{TB} phases with a tilted director and that this could be the splay-bend nematic phase first predicted by Dozov [1]. As we have also seen, for the N_{SB} phase to be stable requires that $K_2 > K_1/2$ whereas for the twist-bend phase then to become stable needs $K_2 < K_1/2$. As noted, the occurrence of the splay-bend before the twist-bend nematic phase requires more detailed investigation. It is however of interest and possible relevance that in the N_{TB} phase of CB7CB the domains of opposite handedness are separated by a wall of splay-bend nematic [12]. The other possibility is akin to that suggested by Adlem *et al.* [8] namely that the weakness of the N_{TB}-N transition encourages pretransitional behaviour in the nematic phase which will lead to a fluctuational tilt of the director.

It seems clear that the development of an understanding of the variation in the orientational order of the nematic phase in the vicinity of the N_{TB} – N phase transition presents an important and interesting challenge for twist-bend mesogens. Associated with this is the conical angle in the N_{TB} phase and how this changes as the transition to the nematic phase is approached. To achieve this end, rather than study chemically different liquid crystal dimers we have decided to explore the behaviour of a single dimer whose properties can be changed continuously by the addition of a structurally related monomer. The system is the curved odd dimer, 1",9"-bis-4-(4'-cyanobiphenyl) nonane (CB9CB) and its binary mixtures with the rod-like monomer 4-n-pentyl-4'-cyanobiphenyl (5CB) which is specifically deuteriated:

CB9CB

5CB-d$_2$
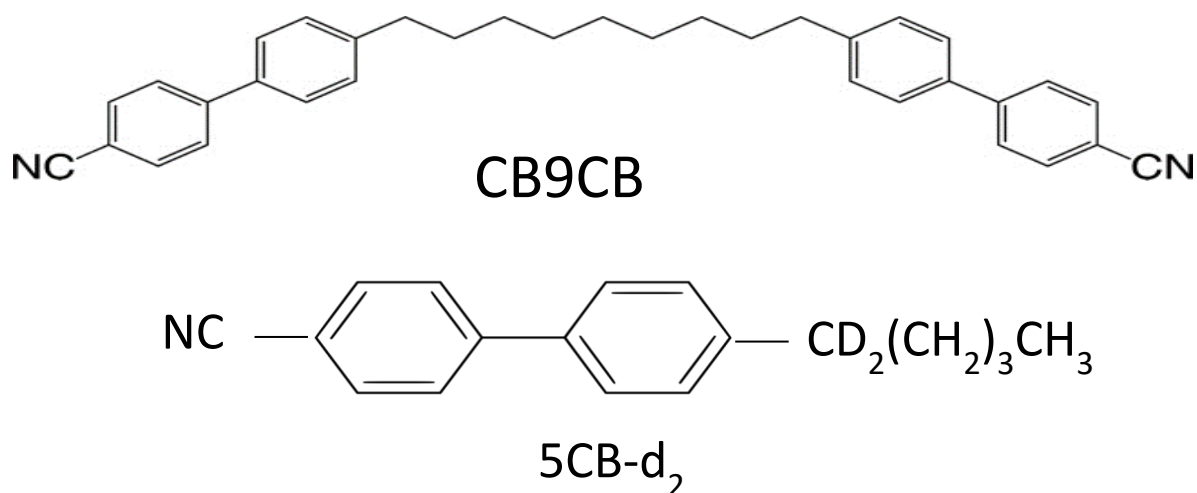
This allowed the orientational order of this simple component to be readily studied with ^{2}H-NMR spectroscopy. This has enabled us to determine various properties as a function of the length of the nematic range and the entropy change of the $N_{TB} - N$ transition. The properties studied were based on the ^{2}H-NMR spectra of 5CB-d$_2$ which, to a good approximation gives the order parameter for the para-axis of the cyanobiphenyl group [13].

The layout of this paper is as follows. The mesogenic systems and their source that we have selected to study together with their key properties are described in Section 2. The nature of the central ^{2}H-NMR experiments and their interpretation, including the order parameters for 5CB-d$_2$ and the director tilt for the nematic phase of the four mixtures are given in Section 3. Here we explain the delineation of the nematic phase employing the Haller function. We turn to the twist-bend nematic phase of the same four mixtures in Section 4 to determine and discuss their orientational order, conical angle and chirality. The final Section contains our conclusions.

2. Experimental

Early in the history of the twist-bend nematic phase the liquid crystal dimer CB9CB was shown to exhibit a nematic-nematic transition based on X-ray scattering [14]. Further details of this behaviour were published in a paper by Tripathi et al. [15] which was primarily concerned with the phase behaviour of the binary mixture of CB9CB and the monomer 5CB. The transition temperatures and enthalpies were measured with high resolution adiabatic scanning calorimetry. These showed that T_{NI} and $T_{N_{TB}N}$ [15] both decrease with increasing concentration of 5CB although the net effect is that the nematic range grows slightly with the concentration of the monomer. In addition the transitional entropy, $\Delta S_{N_{TB}N}/R$, also decreases with the reduced transition temperature $T_{N_{TB}N}/T_{NI}$ as the results in Figure 5 clearly show.

For our studies the sample of CB9CB was obtained from Merck and its transition temperatures, $T_{NI} = 121°C$ and $T_{N_{TB}N} = 106°C$ are in good accord with those reported earlier [15, 16]. The specifically deuteriated monomer, 5CB-d$_2$ was prepared in the following way. 4-bromobiphenyl was acylated with pentanoylchloride and AlCl$_3$ to the 4-bromo-4'-pentanoylbiphenyl. The reduction to the 4-bromo-4´-α-d$_2$-pentylbiphenyl was accomplished with LiAlD$_4$/AlCl$_3$ in CDCl$_3$ [17] followed by cyanation with CuCN in N-methylpyrrolidone. The final product was purified by column chromatography and then distilled under reduced pressure. The specific deuteriation was checked by NMR and mass spectrometry and found to be better than 98%. The nematic-isotropic transition temperature for 5CB-d$_2$ was determined to be 35°C, as expected.

Four mixtures of the dimer containing 5.70wt%, 14.70wt%, 25.65wt%, and 36.65wt% of the deuteriated monomer were prepared by weight directly into standard 5mm NMR tubes and were homogenised by heating into the isotropic phase and shaking repeatedly. These mixtures are denoted by DM(5.70), DM(14.70), DM(25.65) and DM(36.65), respectively. Our original measurements [18] were made on a 400 MHz Bruker AVII spectrometer using a single pulse sequence and a magnetic field of 9.40T; this high field made it possible to align the heliconical axis from a previously aligned nematic phase. None the less, we found it more expedient to use a Varian Chemagnetics CMX Infinity 400MHz spectrometer to record the ^{2}H-NMR spectra

because it gave greater temperature stability and enabled us to obtain a higher density of data. We used a single pulse sequence of 5μs width and a delay of 0.05s between successive pulses. The number of FID transients used was 4000-6000 depending on the strength of the deuterium NMR signal. The spectra were saved in 8192 words of computer memory. In these experiments the original sample tubes were shortened and sealed so that they could be placed horizontally in the probe of the Varian spectrometer. It is these results that are presented in our paper here. Before doing so we shall provide some general comments concerning NMR spectroscopy and the spectral analysis.

In the isotropic phase the rapid tumbling of the monomer, 5CB-d_2, means that the anisotropy in the quadrupolar tensor, **q**, of each deuteron is averaged to zero since its trace is also zero. In consequence the spectrum contains a single line. On passing from the isotropic to the nematic phase the single line is replaced by two spectral lines of equal intensity. The spacing, $\Delta\nu$, between the peaks in this doublet is determined by the orientational order of the monomer and the anisotropy of **q**. Examples of such ^{2}H-NMR spectra are given in Figure 6 for the mixture DM(25.65); two of the four spectra are for the N phase. The spectral lines are sharp and it can be seen that the quadrupolar splitting changes slightly as the transition to the N_{TB} is approached; the significance of this will be apparent shortly. The two deuterons are equivalent and so the two quadrupolar splittings are degenerate. The quantities measured are given by

$$\Delta\nu_1 = (3/2)q_{CD}S_{CD1} \text{ and } \Delta\nu_2 = (3/2)q_{CD}S_{CD2,} \qquad (2)$$

where q_{CD} is the component of **q** along a C-D bond, equal to 168kHz, and S_{CD} is the component of the Saupe ordering matrix along the same bond. The experiments in the nematic phase give the order parameters for the C – D bond; however, it is more informative to understand the order of the cyanobiphenyl group, in particular the order parameter, S_{zz}, for the para or long axis of the monomer, denoted by z. This seems to be possible because a previous ^{1}H-{^{2}H} NMR investigation of 5CB-d_{15} provides the proton-proton dipolar couplings in the protonated phenyl ring to which the nitrile group is attached [13]. This shows that the ordering matrix is only weakly biaxial about z. So to facilitate the analysis of order parameters in our studies, given the limited data available, we have assumed that the ordering matrix for the protonated phenyl ring is uniaxial about the para-axis. With this reasonable approximation, the order parameter for this axis, is related to that of the C – D bond by

$$S_{zz} = S_{CD1}P_2(\cos\gamma_1), \qquad (3)$$

where γ_1 is the angle between the C – D_1 bond and the para-axis. A similar expression is valid for the C – D_2 bond. Before leaving this result for the nematic phase we should note that it depends essentially on the order parameters for both the C – D bond and the para-axis approximating to uniaxiality.

The situation is more complex in the N_{TB} phase as the two prochiral deuterons in the α-position of the pentyl chain of 5CB-d_2 are no longer equivalent because of the phase chirality [19, 20]. The two quadrupolar splittings separated by their chiral splitting are immediately and clearly apparent in the N_{TB} phase as maybe seen from the two spectra in Figure 6. About a degree into the N_{TB} phase a small splitting develops on the original pair of quadrupolar peaks; the slight difference in heights of the peaks suggests some variation in linewidths. However this difference

reduces as the temperature is lowered and the chiral splitting also grows. There are then two quadrupolar splittings, $\Delta\nu_{CD1}$ and $\Delta\nu_{CD2}$, whose magnitudes depend on the geometry of the methylene group and how it is ordered. The paper by Beguin *et al.* [21] and that by Robles-Hernández *et al.* [16] give the details of how the two splittings depend on the ordering and molecular geometry; the details are complex and so here we shall give just the outline of the derivation. As we have seen from Equation (2) the quadrupolar splittings depend on the two order parameters for the C – D bonds and these are related to the order parameters for the axis system set in the methylene group shown in Figure 7. In this figure the two deuterons are denoted by D_1 and D_2, R denotes the butyl chain attached to the carbon atom and X indicates the cyanobiphenyl group. The axis system is denoted by *abc* where *a* divides the two C - D bonds, axis *b* is in to the XCR plane and perpendicular to *a*; finally *c* is perpendicular to both *a* and *b*. The C – D_1 and C – D_2 bonds both make an angle β with axis *a*. In the N phase the *ab* plane is a mirror plane and so the Saupe ordering matrix will be that in (1) and in the chiral N_{TB} phase the mirror plane is removed and the Saupe matrix is that in (2):

$$(1) \begin{pmatrix} Saa & Sab & 0 \\ Sab & Sbb & 0 \\ 0 & 0 & Scc \end{pmatrix} \qquad (2) \begin{pmatrix} Saa & Sab & Sac \\ Sab & Sbb & Sbc \\ Sac & Sbc & Scc \end{pmatrix} . \qquad (4)$$

In the nematic phase the components of **S** along the two C –D bonds are

$$S_{CD1} = S_{aa}\cos^2\beta + S_{cc}\sin^2\beta \qquad (5)$$

and

$$S_{CD2} = S_{aa}\cos^2\beta + S_{cc}\sin^2\beta. \qquad (6)$$

The associated quadrupolar splittings are equal,

$$\Delta\nu_{CD1} = (3/2)q_{CD}\{S_{aa}\cos^2\beta + S_{cc}\sin^2\beta\} = \Delta\nu_{CD2} , \qquad (7)$$

as expected. In the N_{TB} phase the order parameters for the two C – D bonds expressed in terms of this coordinate system are

$$S_{CD1} = S_{aa}\cos^2\beta + S_{cc}\sin^2\beta + S_{ac}\sin2\beta \qquad (8)$$

and

$$S_{CD2} = S_{aa}\cos^2\beta + S_{cc}\sin^2\beta - S_{ac}\sin2\beta. \qquad (9)$$

The quadrupolar splittings are then

$$\Delta\nu_{CD1} = (3/2)q_{CD}\{S_{aa}\cos^2\beta + S_{cc}\sin^2\beta + S_{ac}\sin2\beta\} \qquad (10)$$

and

$$\Delta\nu_{CD2} = (3/2)q_{CD}\{S_{aa}\cos^2\beta + S_{cc}\sin^2\beta - S_{ac}\sin2\beta\}. \qquad (11)$$

The mean of the two quadrupolar splittings in the N_{TB} phase is given by

$$(\Delta\nu_{CD1} + \Delta\nu_{CD2})/2 = (3/2)q_{CD}\{S_{aa}\cos^2\beta + S_{cc}\sin^2\beta\}, \qquad (12)$$

which, as can be seen from Equation (7), is analogous to the behaviour of the N phase. By taking the difference $(\Delta\nu_{CD1} - \Delta\nu_{CD2})$ we find

$$\Delta(\Delta\nu) = (\Delta\nu_{CD1} - \Delta\nu_{CD2})/2 = |(3/2)q_{CD}P_2(\cos\theta_0)\, S_{ac}\sin2\beta|; \qquad (13)$$

since the angle between the two C-D bonds is to a good approximation equal to the tetrahedral angle Equation (13) can be written as

$$\Delta(\Delta\nu) = 2\sqrt{2}\, q_{CD}P_2(\cos\theta_0)\, S_{ac}. \qquad (14)$$

So that the off-diagonal element of the Saupe ordering matrix, S_{ac}, which depends solely on the phase chirality can be obtained from the chiral quadrupolar splitting

$$S_{ac} = \Delta(\Delta\nu)/\{2\sqrt{2}\, q_{CD}P_2(\cos\theta_0)\}. \qquad (15)$$

3. Results and Discussion

3.1. Nematic

The length of the nematic phase prior to the formation of the twist-bend nematic phase is known to weaken the strength of the $N_{TB}-N$ transition [22]; this might well be expected to influence the pretransitional behaviour in the nematic phase [23]. We begin with the orientational order parameter, S_{zz}, for the monomer 5CB-d_2 dissolved in the dimer to the extent of 36.65wt%; this mixture, DM(36.65), has a nematic region of 29ºC. This is, however, comparable to those observed for the dimers DTC5C9 where it is 36.6ºC (see Figure 3) and CB6OCB where it is 44ºC (see Figure 4). This result for DM(36.65) is shown as a function of the reduced temperature, T/T_{NI}, in Figure 8(a). It can be seen that in the nematic region close to the N_{TB} phase there is a small but significant maximum in the order parameter plot at a reduced temperature of 0.93. In view of this unusual nematic behaviour we decided to quantify the order parameter in terms of the Haller function [10] which is known to provide a good fit to nematic properties. The function takes the form:

$$S_{zz}(T) = S_{zz}(0)\{1 - y(T/T_{NI})\}^{\gamma}, \qquad (16)$$

where $S_{zz}(0)$ denotes the order parameter at absolute zero, y corrects for the fact that the order parameter at T_{NI} is not zero and the exponent γ allows for the temperature dependence of $S_{zz}(T)$. The values of these parameters were quantified with the following methodology. In this we take the log of Equation (16) for the Haller function giving

$$\log[S_{zz}(T)] = \log[S_{zz}(0)] + \gamma\log[\{1 - y(T/T_{NI})\}]; \qquad (17)$$

here experience suggests that the coefficient y can be set equal to 0.999. Thus the plot of $\log[S_{zz}(T)]$ versus $\log[\{1 - 0.999(T/T_{NI})\}]$ should be linear, but this is not quite the case for the 21 data points measured for DM(14.70). The error reflecting the quality of the fit of the Haller function to the experimental data corresponds to the Correlation-Coefficient, R^2, of 0.9868; the mismatch occurs for temperatures close to the transition to the N_{TB} phase. The next step is to remove four of these points and to repeat the fitting procedure which gives a value for R^2 of 0.9968 showing the improvement. The fit can be further improved by reducing the number of data points to 13 although the reduction in the error is small, to only 0.9989. At this point in the

procedure we use the non-linear version of Equation (16) making minor changes to the coefficients and arrive at

$$S_{zz}(T) = 0.993\{1 - 0.999(T/T_{NI})\}^{0.176} . \tag{18}$$

It is the numerical results in this equation which gave the Haller function shown as open circles in Figure 8(c), it is apparent that for a reduced temperature of about 0.97 the Haller function starts to deviate from the experimental results. The Haller coefficients giving the best fits for the four mixtures are listed in Table 1 and were used to evaluate the Haller functions in Figures 8(a-d).We return now to the best fit of the Haller function to the experimental results shown in Figure 8(a) for DM(36.65).The Haller-predicted values of the order parameters are shown in Figure 8(a) and it is apparent that they provide a good but not perfect fit whose significance we shall return to.

The order parameter results for the mixture DM(25.65) are shown in Figure 8(b) and the nematic range, as expected, is shorter at ~23°C although only 6°C shorter than for the previous mixture. Just prior to the formation of the N_{TB} phase the order parameter hardly changes at all with decreasing reduced temperature showing a plateau-like behaviour. This is not such a dramatic change as found for DM(36.65) but it is not really what is expected for a nematic phase. To help quantify this behaviour we have again tried to fit the order parameters to the Haller function in Equation (14). The best fit is shown in Figure 8(b) and the parameters employed to obtain this are given in Table 1. It is clear from the plot that the fit is good until a reduced temperature of about 0.955 whose significance will be discussed shortly.

For the mixture DM(14.70), with the smaller concentration of 5CB-d$_2$, the nematic behaviour is apparently even more normal. That is the behaviour of the order parameter continues to increase with decreasing temperature, albeit slightly, until the N_{TB} phase is reached, as can be seen in Figure 8(c). Again we have fitted the overall behaviour to the Haller function and the quality of the fit is apparent in this Figure; strangely the difference between Haller and experiment is still significant over a range before the N_{TB} phase is reached. The values of the fitting parameters are given in Table 1.

Table 1. The transitional properties of CB9CB and its mixtures with 5CB-d$_2$.

Composition/wt%	5.70	14.70	25.65	36.65	0
$(T_{NI} - T_{N_{TB}N})$/°C	17	20	24	30	15.7*
$\Delta S_{N_{TB}N}$ /R	0.0214	0.0125	0.0056	0.0012	0.0369*
$S_{zz}(0)$	0.988	0.980	0.984	0.999	
y	0.999	0.998	0.999	0.999	
z	0.168	0.171	0.171	0.176	
$^{!!}\Delta S_{zz}$	0.025	0.032	0.036	0.036	
ΔT_{Haller} / °C	10	11	15	22	

$\Delta\Delta T_{Pretrans}$ / °C	6	8	8	7
$\Delta\Delta T_{Pretrans}$ / °C (From θ in N)	7	10	10	10

NB. $(T_{NI} - T_{N_{TB}N}) = \Delta T_{Haller} + \Delta\Delta T_{Pretrans}$

NB. T_{NI} = 119.77 °C and $T_{N_{TB}N}$ = 104.07 °C*

* From ASC measurements [15].

!! Here $\Delta S_{zz} = S_{zz}(Haller) - S_{zz}(Experiment)$ evaluated at the N- N_{TB} transition

The order parameters determined for the final mixture to be studied, with its small concentration of 5CB-d$_2$, namely DM(5.70), are shown in Figure 8(d). As expected the temperature variation in S_{zz} is still more usual and grows as the N_{TB} phase is reached. However, we still wish to see if the experimental dependence can be fitted over the entire range with the Haller function. A glance at the plots in Figure 8(d) reveals, surprisingly, that the answer is no. However, the temperature range over which the disagreement appears is somewhat less than for the other mixtures.

An alternative route of exploring the difference between the Haller function and the experimental order parameter, S_{zz}, and that expected for a conventional nematic is to plot the difference, $\Delta(S_{zz})$, between the order parameters, $S_{zz}(Hall)$ and $S_{zz}(exp)$. This difference is shown as a function of the shifted temperature in Figure 9 for the two extreme mixtures, namely DM(5.70) and DM(36.65). As expected, at the nematic-isotropic transition the results for both mixtures the $\Delta(S_{zz})$ scatter initially about zero. Then for the dilute solution DM(5.70) $\Delta(S_{zz})$ grows to about 0.028 over a temperature range of about 6K. For DM(36.65) with its higher concentration of 5CB-d$_2$ $\Delta(S_{zz})$ scatters about zero for a temperature range of about 21K. After this the difference grows to a value of about 0.036 which takes place in a range of about 8K. The ability of the nematic phase to deviate from more conventional behaviour is seen to result from the presence of the N_{TB} phase after the nematic phase. This behaviour is related to the addition of the monomer 5CB which also causes the nematic range to increase and the transition to the N_{TB} to weaken as is apparent from the phase diagram in Figure 5. Although the weakening of the transition to the N_{TB} phase could cause the extent of the difference $\Delta(S_{zz})$ to grow there may well be other causes.

Before this is discussed we first wish to determine the temperature dependence of the tilt angle in the nematic phase of the mixtures and how this relates to the pretransitional range. As noted in the Introduction, the deviation of the orientational order parameter from normal nematic behaviour might be caused by the tilt of the director from being parallel to the magnetic field of the NMR spectrometer [9]. As a result of the director tilt the orientational order in the magnetic field direction will decrease and combined with the growth of the order may create the maximum in the order-parameter plot. In addition to this extreme behaviour the order parameter might exhibit a plateau and also a decrease in the rate at which the order parameter will reduce with

decreasing temperature. To determine the tilt angle, θ, we need simply take the ratio of the experimental order parameter to that predicted by the Haller function [9, 12]

$$P_2(\cos\theta(T)) = S_{zz}(T)_{exp}/ S_{zz}(T)_{Hall}. \tag{15}$$

This approach has been adopted for the mixtures of CB9CB and 5CB-d_2 with the results shown in Figure 10(a) – (d). The behaviour found for DM(36.65) is shown in Figure 10(a) in both the N and N_{TB} phases but we shall reserve our comments on those for the N_{TB} phase until later. In the nematic phase the tilt angle, θ, starts at zero which corresponds to the points where the order parameter is accurately predicted by the Haller function. However, when the Haller function predicts S_{zz} to be larger than experiment then θ deviates from zero and increases more or less linearly until the transition to the N_{TB} phase is reached. The temperature range over which θ is essentially non-zero we call the pretransitional region where the tilt angle grows, in keeping with the conical angle in the N_{TB} phase. For DM(36.65) the pretransitional range is approximately 10°C and is listed in Table 1. The results for the order parameters in the N phase of the two mixtures DM(25.65) and DM(14.70) are shown in Figures 10(b) and 10(c), respectively. Their qualitative appearance is similar to that for DM(36.65). In addition the range of their pretransitional behaviour is approximately equal to 11°C as found for DM(36.65). This similarity seems to be rather strange but we shall need to compare them with other properties such as the nematic range and transitional entropy, $\Delta S_{N_{TB}N} /R$ to be certain. The last mixture we have studied here is DM(5.70) with the smallest amount of 5CB-d_2 and the relevant results are shown in Figure 10(d) where the behaviour of the tilt angle appears to be different to that of the other mixtures. The highest value of the tilt angle is about 11° achieved with a jump from zero of about 4°. However, the reason for this discontinuity in θ is not clear although the extent of the pretransitional region of about 7°C is apparent.

The extent of the pretransitional region as reflected by the temperature dependence of the tilt angle in the nematic phase is clearly apparent. Our task now is to understand the molecular factors that contribute to the determination of the observed pretransitional behaviour. Clearly, the entropy change at the N_{TB} - N transition, listed in Table 1 is of significance; another relevant variable is the extent of the nematic phase prior to the formation of the N_{TB} phase. It will also be of interest to explore this further for the mixtures although for single mesogens it has already been observed [24].

3.2. Twist-bend nematic: orientational order and conical angle

In this sub-section we shall deal with the orientational order defined with respect to the director, **n**, S_{zz}^n, and the conical angle, θ_0, that is between the heliconical angle and **n**, which are two of the order parameters for the twist-bend nematic phase. Another quantity is the particularly significant chiral, order parameter which will be addressed in the following sub-section. The parameters, S_{zz}^n and θ_0, are related to the orientational order parameter defined with respect to the heliconical axis which is aligned parallel to the magnetic field of the NMR spectrometer [21]. The orientational order parameters, S_{zz}, for the four mixtures determined as a function of temperature are shown in Figure 11(a-b); the experimental results are shown as solid squares. A striking feature of these results is that for all of the results the order parameter decreases and then only slightly with reduction in temperature. The unusual weak reduction in S_{zz} with

decreasing temperature is attributed to the competition between two factors, one the increase in the orientational order and the other in an increase in the conical angle. It is a difficult task to separate the two contributions but a reasonable approximation is given by Jokisaari *et al.*[7] as

$$|S_{zz}(T)| = |S_{zz}^{n}(T)P_2(\cos\theta_0(T))|. \tag{17}$$

The model then assumes that the order parameter, $S_{zz}^{n}(T)$, is given by the Haller-like function

$$S_{zz}^{n}(T) = (1 - yT/T_{N_{TB}N})^z \tag{18}$$

and

$$\theta_0(T) = \theta_0(0)(1 - y_0T/ T_{N_{TB}N})^{\beta}. \tag{19}$$

There are then five parameters that need to be determined by matching the experimental order parameters to those given by Equations (17), (18) and (19); this is clearly a challenging task. However, with the aid of Excel and experience of solving such mean square fitting problems [16] we have managed to determine the best fit coefficients based on the Correlation-Coefficent. These results are listed in Table 2 and were used to calculate the best fit to the experimental order parameters, S_{zz}, shown as solid diamonds in Figure 11(a-d) and, as is to be expected, the agreement is good.

The coefficients listed in Table 2 for the conical angle (see Equation (19)) were then used to calculate θ_0 as a function of the shifted temperature, $(T_{NI} - T)$. The results for the four mixtures are plotted in Figure 10(a-d) in the twist-bend region. The immediate impression on looking at these is that the variation in θ_0 is a simple continuation of the tilt angle, θ, from the nematic phase. This is in keeping with the weak first-order nature of the $N_{TB} - N$ transition. In addition the similarity in behaviour is emphasised by the common value in the conical angle of about 10 - 12° on formation of the N_{TB} phase. Further the growth of θ_0 in the twist-bend phase is such that at the same shifted temperature $(T_{N_{TB}N} - T)$ the conical angle seems to be essentially the same for all of the four mixtures. For example for a shifted temperature of 30°C the conical angle takes the values DM(36.65): 22°; DM(25.65): 22°; DM(14.70) 22°; DM(5.70) 21°. This is strange given that the nematic ranges of the mixtures differ by 13°C, the addition of 35wt% of 5CB causes the transition temperature $T_{N_{TB}N}$ to decrease by about 48°C [15] and the transitional entropies vary from 0.0214 to 0.0012 (see Table 1).

Comparison with other results for the CB9CB dimer is not particularly straight forward because, in these early studies allowance was not made for the tilt of the director in the nematic phase and different probes were used. Despite these differences the values of θ_0 at corresponding temperatures were, surprisingly, within about 5° of our results for DM(5.70). There are, however, two systems where there the director tilt in the N phase has been measured; they are DTC5C9 [9] and CB6OCB [11] which are discussed in sections (C) and (D) of the Introduction. The tilt and conical angles are given in Figure 18 of [11] which shows some similarity to the results in this paper. Let us start, however, with a difference which is significant; the temperature ranges over which the tilt angle is non-zero is about 20° for both DTC5CP and CB6OCB in contrast to about 10° found here for the CB9CB mixtures. The value of θ_0 at the $(N_{TB} - N)$ transition is ~17° for DTC5C9 and ~14° for CB6OCB. Then the conical angle grows and at 30°C below

$T_{N_{TB}N}$, to 25º for DTC5C9 and 23º for CB6OCB. This is to be compared with a value of the conical angle of about 22º for all of the DM mixtures of CB9CB with the linear monomer 5CB-d_2 in very close agreement with the earlier studies where the molecules studied have a high curvature [9,11].

Table 2. The best fit coefficients for the order parameter and conical angle in the N_{TB} phase

Composition/wt%	5.70	14.70	25.65	36.65
$S_{zz}^n(T)$:				
y	0.923	0.923	0.923	0.924
z	0.208	0.205	0.189	0.170
$\theta_0(T)$:				
$\theta_0(0)$	40.7	40.9	40.9	40.9
y_θ	0.993	0.991	0.991	0.991
z	0.264	0.264	0.265	0.266

3.3. Twist-bend nematic: chirality

One of the most significant features of the twist-bend nematic phase, predicted by Dozov [2] and Meyer [1], is that although the constituent molecules are achiral the phase itself would be chiral, composed of degenerate domains having opposite handedness. Indeed one of the key properties used in the NMR study which revealed that CB7CB-d_4 did form the N_{TB} phase was that the prochiral deuterons in the 1" and 7" positions in the heptane spacer lost their equivalence; thus demonstrating the chirality of the phase [4]. This is essentially qualitative information which supports the identification of the twist-bend nematic phase. However, there is also the opportunity to obtain some quantitative information about the N_{TB} structure. This obtains because the prochiral splittings, of the order of several kHz, come from the interaction of the deuteriated molecule with the heliconical structure. Subsequently, Chen *et al.* [5] confirmed the chirality of the N_{TB} phase using FFTEM images where the heliconical pitch was found to be surprisingly small, about 8.3nm, and increasing only slightly with decreasing temperature. In our present study we have observed analogous behaviour where the equivalence of the α-deuterons in the pentyl chain of 5CB-d_2 has been lost. As a consequence the difference in the chiral quadrupolar splittings, $\Delta|\Delta\nu|$, provides a pragmatic measure of the phase chirality which we now discuss.

The results for the four mixtures of 5CB-d_2 dissolved in CB9CB are shown in Figure 12 where they are plotted as a function of the shifted temperature, $(T_{N_{TB}N} - T)$ because the results seemed to show universality. This is clearly apparent from Figure 12; the chiral quadrupolar splittings for DM(5.70) and DM(14.70) fall on essentially a common curve which runs from zero at the phase transition and reach a value of just under 10kHz. The next two mixtures, DM(25.65) and DM(36.65), also follow an essentially common curve but at a slightly lower value. This may result

from the higher concentration of 5CB-d_2 with its significantly lower curvature in comparison with CB9CB. The traces themselves are of interest in that after the initial growth at the phase transition the increase is less rapid and more linear. We have also explored another representation of the four sets of $\Delta|\Delta\nu|$ to help understand them. This is to plot them against the orientational order parameters, S_{zz}^n, with respect to the director; these were extracted from the order parameters determined from the mean quadrupolar splitting, $(\Delta\nu_1 + \Delta\nu_2)/2$, as described in the previous section. These results are shown in Figure 13 and there is a significant difference to those in Figure 12. First the universality in behaviour is not so apparent; thus the two mixtures DM(25.65) and DM(36.65) exhibit different behaviour while DM(5.70) and DM(14.70) do possess a similarity.

These results for the shifted temperature and order parameter dependence of $\Delta|\Delta\nu|$ certainly present a challenge. In addition the fact that the chiral quadrupolar splitting does change significantly with temperature provides a marked contrast with results for the weak temperature variation of the helical pitch found for CB7CB [4]. In addition an X-ray study of a mixture of the dimer, DTC5C7 with DTSe in the N_{TB} phase shows that the heliconical pitch decreases from ~9nm to ~12nm over about 15°C gap [25]. Although the results for CB7CB might suggest a fundamental difference between the heliconical pitch of the N_{TB} phase and its chiral splitting those for DTC5C7 might imply a similarity in behaviour.

Just as the results for the mean of the quadrupolar splittings,$(\Delta\nu_1 + \Delta\nu_2)/2$, in the N_{TB} phase can be analysed to yield the diagonal order parameter of the Saupe matrix so the difference can be used to determine an off-diagonal of the same matrix as we have seen from Equation (15). This methodology has been employed by Jokisaari *et al.* [7] and we have followed their procedure here for the four mixtures in the N_{TB} phase using the conical angle, θ_0, determined previously. The results of these calculations for S_{ac} as a function of the shifted temperature are shown in Figure14. The results are clearly comparable to the results in Figure 13 for the primary data, that is the chiral quadrupolar splitting, $\Delta|\Delta\nu|$. However, the growth in the off-diagonal element shown in Figure 14 seems to steepen slightly because S_{ac} depends on the conical angle which grows with decreasing temperature. The largest value for the off-diagonal element is about 0.05 when the shifted temperature $(T_{N_{TB}N} - T)$ is about 50K. This result can be compared with the value of S_{ac} determined for CB7CB-d_4 using the same procedure [7]. Thus at a shifted temperature also of 50°C the off-diagonal element is about 0.06 which is close to the result found for 5CB-d_2 in its four mixtures with CB9CB.

4. Conclusions

One of the aims here was to help understand, using NMR spectroscopy, the structure of the nematic phase prior to the formation of the twist-bend nematic phase. Several studies have shown the difference in the phase structure in which the nematic director is tilted with respect to an aligning field. The origin of the tilt could be pretransitional related to the N_{TB} phase or has also been suggested to result from the introduction of a new phase [11] such as the splay-bend nematic [2].To provide the systems for this study we have used binary mixtures of the dimer CB9CB to which is added the monomer 5CB-d_2; it is the specifically deuteriated pentyl chain which also provides the NMR probe. The addition of the monomer, depending on its concentration, clearly perturbs the system, thus it reduces the entropy change at the $N_{TB} - N$

transition, this transition is also significantly depressed; the N – I phase transition is also depressed such that the nematic range is reduced although this is slight. The change in the nematic behaviour grows with the concentration of 5CB-d_2 and at its largest value the quadrupolar splitting exhibits a maximum just before the N_{TB} phase is formed. However, even for lower concentrations the addition of the monomer still causes the behaviour of the nematic phase to be altered, in that the Haller function does not predict the temperature dependence of the quadrupolar splitting towards the end of the nematic phase for all of the mixtures. That is the nematic director is observed to tilt even without passing through a maximum, as found for other twist-bend mesogens [24]. For all of our mixtures the temperature dependence of the tilt angles appears to exhibit a similar variation implying universality when plotted against the shifted temperature $(T - T_{N_{TB}N})$. Despite careful examination there was no indication of the identity of another phase except the N phase based on our NMR measurements and the adiabatic scanning calorimetry also in the N phase [15]. For all of the mixtures there was a clear continuation of the tilt angle into the conical angle when studying the N_{TB} phase [13]. The detailed fit of the quadrupolar splitting in the N_{TB} phase gave the orientational order parameter with respect to the director and the conical angle with respect to the tilt angle. Most noticeable the results for the four mixtures are very similar especially when plotted as a function of the shifted temperature $(T_{N_{TB}N} - T)$. However, there was a small reduction in orientational order when the concentration of the monomer is low although it is not quite clear why this should be. In addition to the conical angle and order parameter with respect to the tilted director in the N_{TB} phase there is the phase chirality. This comes from the loss of equivalence of the two C - D bonds which results in the quadrupolar splittings being significantly different. This difference which is related to an off-diagonal order parameter in the Saupe matrix grows as the temperature in the N_{TB} phase falls. This contrasts with the pitch of the heliconical angle in CB7CB measured by Chen *et al.* [5] which grows with decreasing temperature. However, measurements by Stevenson *et al.* [25] for a selenium dimer and DTC5C7 found that the pitch decreased with decreasing temperature. It will be important to relate the chiral quadrupolar splitting to the pitch of the heliconical helix; in fact a start has been made with this challenging problem [6]. The results for the chiral quadrupolar splitting for the four mixtures are found to exhibit a close similarity when plotted as a function of the shifted temperature, $(T_{N_{TB}N} - T)$. The origin of such universality would clearly benefit from careful analysis.

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to the deep and wide ranging discussion between David and Claudio who were equally stimulated both by the questions and the answers.

Much has happened since then although initially Claudio did return to help teach on the undergraduate course in Liquid Crystals and Liquids made possible by his abilities as an extremely able lecturer. Such skills have undoubtedly developed over the years and it is always a real privilege to listen to one of his lectures. Related to this is the true diversity of his research as is evident by his recognition by a wide range of learned societies, the journals that they publish and the management of the science with which he is involved.

Those of us from Southampton and, no doubt, elsewhere are truly impressed, but not surprised, by his amazing achievements. We now look forward to seeing how his interests will develop further, to reading his papers and, as in the past, discussing science with him.

Disclosure agreement

No potential conflict of interest was reported by the authors.

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Appendix

In the present investigation of CB9CB mixed with 5CB based on ^{2}H NMR spectroscopy we have taken advantage of the ability to prepare 5CB-d$_2$ with its near uniaxiality about the para-axis. An earlier study of the dimer CB9CB [16] did not have this option and instead the deuterium source was provided by the specifically deuteriated dimer, CB7CB-d$_4$. In view of the significant difference in the molecular structure of the two probes we can now explore the consequences of this choice. In both studies the quadrupolar splittings of the prochiral deuterons were used to obtain the order parameters for the para-axis of a cyanobiphenyl group; the comparison with CB7CB-d$_4$ was made with the DM(5.70) mixture so that the concentrations of the two probes 5CB-d$_2$ and CB7CB-d$_4$ are comparable.

We start with the nematic phase. The order parameter for CB7CB-d$_4$ ranges over the nematic phase from 0.35 to 0.57 and for 5CB-d$_2$ this is comparable, namely from 0.34 to 0.55. In addition as the N$_{TB}$ phase is approached for both probes the order parameters tend to form a plateau.

For the twist-bend nematic phase the CB7CB-d$_4$ order parameter grows slightly from 0.57 to 0.58. The order parameter for 5CB-d$_2$ covers a similar small range but now decreases from 0.55 to 0.54. These order parameters are defined with respect to the magnetic field of the NMR spectrometer. Allowance can be made for the tilt of the director and this gives the order parameters with respect to the director for CB7CB-d$_4$ as about ~0.6 to ~0.7 and for 5CB-d$_2$ the results are remarkably similar, namely 0.59 to 0.69. In both cases the plots are just slightly curved.

The final quantity that can be compared is the conical angle, θ_0, that calculated from the order parameter in the N$_{TB}$ phase is 0º at phase transition and when the end of the phase it has reached a value of 19º. For the probe 5CB-d$_2$, the starting point is quite different the conical angle starts at 11º and ends at 24º. This difference clearly results from the inclusion of a tilt angle in the nematic phase prior to the start of the N$_{TB}$ phase but such an analysis was not used for the probe CB7CB-d$_4$ [16].

The net conclusion is certainly intriguing with most of the results from the two probes, the dimer and the monomer, being surprisingly similar; the origin of this remains to be discovered.

Figure Captions

Figure 1. (Colour online) The variation of the quadrupolar splittings, $\Delta\nu$, with shifted temperature, $(T_{NI} - T)$, for the 1",7"-deuterons in the heptane spacer in the N and N_{TB} nematic phases of CB7CB-d_4 [4] are shown as($\blacklozenge$ and $\blacklozenge$) The mean of the splittings in the N_{TB} phase is shown as the open symbol ($\lozenge$).

Figure 2. (Colour online) The dependence of the deuterium quadrupolar splittings, $\Delta\nu$, for CB7CB-d_4 used as a spin probe, on the shifted temperature, $(T_{NI} - T)$ [8]. The results for the mixture of ether-linked, odd dimers, KA, are indicated by ($\square$) for the nematic phase and for this mixture with a 0.2 mole fraction of a methylene-linked dimer to induce the N_{TB} phase, KA(0.2), by ($\blacksquare$). In the N_{TB} phase the two inequivalent prochiral quadrupolar splittings are shown as ($\lozenge$) and ($\blacklozenge$).Reproduced with permission from Ref [8].

Figure 3. (Colour online) The temperature dependence of the orientational order parameter, S_{zz}, measured for the para-axis of the trimer groups, using ^{13}C-NMR, of the dimer DTC5C9 in both the nematic and twist-bend nematic phase as a function of $(T_{NI} - T)$; also shown is the variation predicted by the Haller function [10]. Reproduced from Ref [9] with permission from the PCCP Owner Societies.

Figure 4. The reduced temperature dependence of the order parameter determined for the para-axis of the cyanobiphenyl group attached through a methylene link in CB6OCB-d_2 are shown by ($\bullet$). The open circles shown are those estimated from the Haller function fitted to the experimental data [10]. Reproduced with permission from Ref [11].

Figure 5. (Colour online) The entropy of transition, $\Delta S_{NtbN}/R$, shown as a function of the reduced transition temperature, $T_{N_{TB}N}/T_{NI}$, for mixtures of 5CB with CB9CB obtained from data in Tripathi *et al.* [15].]. The wt% of 5CB in the mixtures with CB9CB is (a) 0% (b) 5% (c) 12.5% (d) 25% (e) 30% (f) 35% and (g) 40%.

Figure 6. (Colour online) The deuterium NMR spectra of the monomer 5CB-d_2 in the mixture DM(25.65) determined as a function of temperature in the nematic (N) and twist-bend nematic (N_{TB}). The N_{TB}- N transition occurs at about 69°C

Figure 7. The coordinate system, *a,b,c,* for the α-methylene group in the pentyl chain of 5CB-d_2, the two deuterons are prochiral and the axis *a* bisects the $D\hat{C}D$ bond angle. Axis *b* is orthogonal to the $D\hat{C}D$ plane and axis *c* is orthogonal to the plane formed by cyanobiphenyl group and the conformationally averaged butyl chain.

Figure 8. (Colour online) The variation of the order parameter, S_{zz}, for the para-axis of 5CB-d_2 in mixtures with CB9CB as a function of the reduced temperature, T/T_{NI}, in the nematic phase. The experimental results are shown as (●) and the results obtained by fitting to the Haller function by (○).The plots for the four mixtures are (a) DM(36.60) (b) DM(25.65) (c) DM(14.70) and (d) DM(5.70) and the associated fitting parameters are given in Table 1.

Figure 9. (Colour online) The dependence of the difference, $\Delta(S_{zz})$, between the best-fit Haller function for the order parameter, S_{zz}, and the experimental value shown as a function of the shifted temperature, $(T_{NI} - T)$.

Figure 10. (Colour online) The dependence on the shifted temperature, $(T_{NI} - T)$, of the tilt angle, θ, in the N phase (●) and the conical angle, θ_0, in the N_{TB} phase (●) for the mixtures (a) DM(36.65) (b) DM(25.65) (c) DM(14.70) and (d) DM(5.70). The fitting parameters are listed in Table1.

Figure 11. (Colour online) The dependence, on the shifted temperature $(T_{NI} - T)$, of the experimental order parameter, S_{zz}, (●) and the Haller function fitted to the bulk of the N phase data (○). In addition the experimental $S(T)$ in the N_{TB} phase measured with respect to the magnetic field are shown as a function of $(T_{NI} - T)$ (■). The best fit to this, using the methodology developed by Jokisaari *et al.* [7], in which the director order parameter and the conical angle are varied is shown as (♦). The fitted director order parameter, S_{zz}, in the N_{TB} nematic is shown as (□). The plots for the four mixtures are given in (a)DM(36.65) (b) DM(25.65) (c) DM(14.70) and (d) DM(5.70). The fitting parameters can be found in Table 2.

Figure 12. (Colour online) The dependence of the chiral quadrupolar splitting, $\Delta|\Delta\nu|$, determined for the monomer 5CB-d_2 dissolved in the dimer CB9CB in the N_{TB} nematic phase on the shifted temperature, $(T_{N_{TB}N} - T)$, in the mixtures (a) DM (5.70) (b) DM(14.70) (c) DM (25.65) (d) DM (36.65).

Figure 13. (Colour online) The variation of the chiral quadrupolar splitting, $\Delta|\Delta\nu|$, of 5CB-d_2 with its orientational order, S_{zz}, for the four mixtures (a) DM(5.70) (b) DM(14.70) (c) DM(25.65) (d) DM (36.65). The order parameter was extracted from the mean quadrupolar splitting, $(\Delta\nu_1 + \Delta\nu_2)/2$, in the twist-bend nematic phase.

Figure 14. (Colour online) The dependence of S_{ac}, the off-diagonal element of the Saupe ordering matrix, for 5CB-d_2 dissolved in the dimer CB9CB in its twist-bend nematic phase on the shifted temperature, $(T_{N_{TB}N} - T)$ for the mixtures (a) DM(5.70) (b) DM(14.70) (c) DM(25.65) (d) DM (36.65).