The Chirality of a Twist−Bend Nematic Phase Identified by NMR Spectroscopy

Laetitia Beguin,[†] James W. Emsley,*[,‡] Moreno Lelli,[†] Anne Lesage,[†] Geoffrey R. Luckhurst,[‡] Bakir A. Timimi,[‡] and Herbert Zimmermann[§]

[†]Université de Lyon, CNRS/ENS Lyon/UCB-Lyon 1, Centre RMN à Très Hauts Champs, 5 rue de la Doua, 69100 Villeurbanne, France

[‡]School of Chemistry, University of Southampton, Highfield, Southampton SO17 1BJ, United Kingdom

[§]Department of Biophysics, Max-Planck-Institut für Medizinische Förschung, D-69120 Heidelberg, Germany

ABSTRACT: One of the defining characteristics of the twist−bend nematic phase, formed by the methylene-linked liquid crystal dimer 1″,7″-bis(4-cyanobiphenyl-4′-yl) heptane (CB7CB), is its chirality. This new nematic phase, predicted by Dozov, is of particular interest because although the constituent molecules are achiral the phase itself is chiral. Here, we describe the use of NMR spectroscopy to determine experimentally whether in reality the phase is chiral or not. The basis of this novel procedure is that the equivalence of the protons or deuterons in a prochiral methylene group in a nematic phase with $D_{\infty h}$ symmetry is lost in a chiral phase because its symmetry is reduced to D_∞ on removal of the mirror plane. Recording proton-enhanced local field (PELF) NMR experiments shows that in the standard nematic phase all of the methylene groups in the heptane spacer have equivalent pairs of C−H groups but this equivalence is lost for the six prochiral methylene groups with their enantiotopic protons on passing to the twist−bend nematic. Strikingly, this equivalence is not lost for the central methylene group where the two protons are homotopic. We also show how the phase chirality can be demonstrated with probe molecules which contain deuteriated prochiral methylene groups, using 4-octyl-4′-cyanobiphenyl-d_2, perdeuteroacenaphthene-d_{10}, and acenaphthene-d_4 as examples. For the standard nematic phase deuterium, NMR shows that the deuterons in these methylene groups are equivalent but, as expected, in the twist−bend nematic phase this equivalence is lost. The deuterium NMR spectra of these probe molecules dissolved in CB7CB have been recorded from the isotropic phase, through the nematic and deep into the supercooled twist−bend nematic.
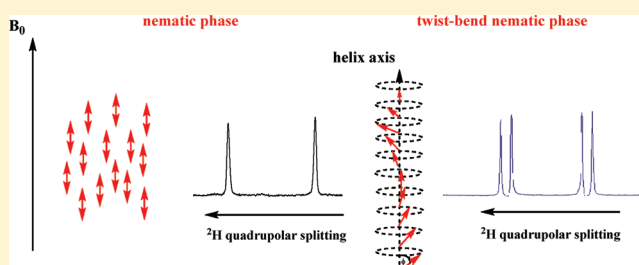
INTRODUCTION

On cooling from the isotropic phase at 116 °C, the symmetric liquid crystal dimer 1″,7″-bis(4-cyanobiphenyl-4′-yl) heptane (CB7CB) forms a nematic phase which persists until 103 °C when there is a second first-order transition to another liquid crystalline phase. Originally this was identified as a smectic phase,[1] but it has also been proposed that it was a biaxial nematic.[2] However, many years later, a detailed investigation of this liquid crystal dimer, involving a wide range of techniques, has suggested that it is a nematic phase having uniaxial symmetry in which the director is not uniformly distributed.[3] It appears that the director has a twist−bend distribution as predicted by Dozov[4] for nematics having a negative bend elastic constant; he further predicted that this is likely for bent-core or V-shaped mesogens. This assignment is consistent with calculations of the elastic constants for CB7CB[3] which indeed predict that the bend elastic constant is negative, whereas the twist elastic constant is predicted to be positive but smaller than the splay elastic constant. We have, therefore, named the new nematic phase the twist−bend nematic and assigned it the mnemonic N_{TB}.[3] The optical texture of this phase has a rope-like appearance with the rope-like stripes having opposite

handedness.[3] This observation is in keeping with Dozov's prediction that the twist−bend nematic should separate into chiral domains also with opposite handedness.[4] A key element in the identification of this new nematic phase was the use of deuterium NMR spectroscopy to show that the twist−bend nematic is chiral.[3] To understand this identification, we note that isolated, single molecules of CB7CB are expected to exist as an interconverting mixture of conformations generated by rotations about the C−C single bonds in the chemical structure shown in Figure 1. Many of these conformations are chiral, but for an isolated molecule, they are expected to exist as an interconverting ± pair, so that the ensemble behavior should be achiral.

This would seem to rule out the formation of a chiral liquid crystalline phase from CB7CB molecules. However, the exchange between conformers with their differing forms could alter the overall molecular shape from that of a single conformer; this shape has been obtained by averaging over all
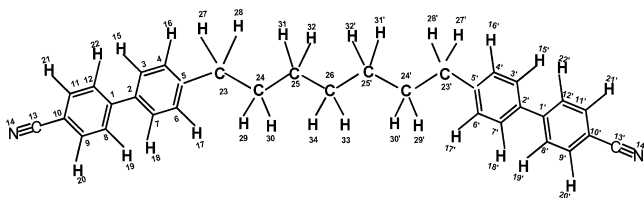
Figure 1. The chemical structure of the symmetric liquid crystal dimer CB7CB.

Figure 2. The structure of a prochiral, molecular fragment; here the X and Y groups are different.

conformers and reveals that the average form in a nematic phase is symmetric and V-like,[5] so that the dimers could form a chiral twist−bend nematic phase.

One of the key experimental results leading to this conclusion was the observation that for the specifically deuterated CB7CB-d_4 the deuterons in the methylene groups at positions C23 and C23′ are equivalent in the nematic but not in the N_{TB} phase. However, although this points strongly to the N_{TB} phase being chiral, the four lines in the two doublets were observed to be unequal in intensity, whereas they must have equal intensities in a phase comprised of domains of the two enantiomorphic states, independently of their relative proportions. Here we undertake a more detailed NMR investigation of the twist−bend nematic which confirms this original proposal concerning the chirality of this unusual phase. In our study, we shall investigate the chirality using CB7CB itself as well as dissolved probes: the mesogenic molecule 4-octyl-4′-cyanobiphenyl deuterated in the first methylene position of the alkyl chain (8CB-d_2), and the perdeuterated rigid probe perdeuteroacenaphthene-d_{10} and its isotopomer acenaphthene-d_4.

NMR spectroscopy has been shown to have the capability of distinguishing between enantiomeric forms of nonmesogenic molecules by recording spectra of samples dissolved in a chiral nematic solvent.[6] The reverse should also be true; that is, a chiral liquid crystalline phase could be recognized through the appearance of different spectra for the two enantiomers in a mixture of chiral solute molecules, although it has not apparently been used for this purpose. Thus, adding a mixture of enantiomers to a chiral nematic phase would demonstrate the chirality of the phase. However, adding a chiral solute to an achiral liquid crystalline phase can induce chirality in the phase, and so this experiment would not necessarily reveal unambiguously the chirality of the uncontaminated phase. This complication can be avoided by examining the NMR spectrum of an achiral solute containing a prochiral group dissolved in the suspected chiral liquid crystal solvent;[7,8] the significance of the term prochiral will become clearer as we proceed. The principle involved can be illustrated by considering a molecule, or molecular fragment having the structure shown in Figure 2. The point group symmetry of this fragment is C_s, with ab as a mirror plane.

NMR spectroscopy can measure the residual dipolar couplings D_{CH1} and D_{CH2} for fragments with the carbon as the isotope ^{13}C, and these are related to C−H bond order parameters, S_{CH1} and S_{CH2}, by

$$D_{CH1} = -K_{CH}S_{CH1} \tag{1}$$

$$D_{CH2} = -K_{CH}S_{CH2} \tag{2}$$

where $K_{CH} = \mu_0\gamma_C\gamma_H h/(16\pi^3\langle r_{CH}^3\rangle)$ with μ_0 as the magnetic constant, γ_C and γ_H the gyromagnetic ratios, h the Planck constant, and r_{CH} the C−H bond length; the angular brackets, $\langle\ \rangle$, denote averaging over vibrational motion.
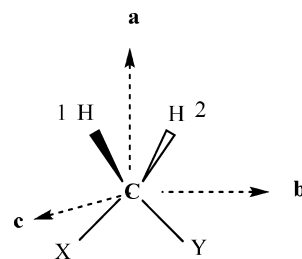
The quadrupolar splittings, $\Delta\nu_1$ and $\Delta\nu_2$, may also be measured when the fragment contains deuterium atoms; these are related, approximately, to the C−D bond order parameters, S_{CD1} and S_{CD2}, by

$$\Delta\nu_1 = (3/2)q_{CD1}S_{CD1} \tag{3}$$

$$\Delta\nu_2 = (3/2)q_{CD2}S_{CD2} \tag{4}$$

with q_{CD1} and q_{CD2} being the components along the C−D bonds of the deuterium quadrupolar tensor, and the quadrupolar asymmetry parameters have been assumed to be zero.

An achiral nematic phase has $D_{\infty h}$ symmetry, and as a consequence, the rules for locating the principal axes of the Saupe molecular orientational order matrix, S, depend only on the point group symmetry of the molecule, or molecular fragment. Thus, for this prochiral fragment in a normal, achiral nematic phase, the presence of a molecular mirror plane ab means that c is a principal axis for S, so that the only nonzero off-diagonal elements are $S_{ab} = S_{ba}$, and the bond order parameters, S_{CH1} and S_{CH2}, are governed by

$$S_{CH1} = S_{aa}\cos^2\theta_{CH1a} + S_{cc}\cos^2\theta_{CH1c}$$
$$+ 2S_{ab}\cos\theta_{CH1a}\cos\theta_{CH1b} \tag{5}$$

$$S_{CH2} = S_{aa}\cos^2\theta_{CH2a} + S_{cc}\cos^2\theta_{CH2c}$$
$$+ 2S_{ab}\cos\theta_{CH2a}\cos\theta_{CH2b} \tag{6}$$

The two C−H vectors within the molecular fragment are related by the mirror plane, and so:

$$\theta_{CH1a} = -\theta_{CH2a}$$

$$\theta_{CH1b} = \theta_{CH2b} = 90°$$

$$\theta_{CH1c} = 90° + \theta_{CH1a}$$

$$\theta_{CH2c} = 90° - \theta_{CH1a}$$

Writing $\theta = \theta_{CH1a}$ gives

$$S_{CH1} = S_{aa}\cos^2\theta + S_{cc}\sin^2\theta = S_{CH2} \tag{7}$$

Consequently, in an achiral nematic phase, the two residual dipolar couplings D_{CH1} and D_{CH2} are equal, as are the two deuterium quadrupolar splittings, $\Delta\nu_1$ and $\Delta\nu_2$, in the deuterated fragment. Consider now a chiral nematic phase, and assume that the geometry of the fragment is unchanged, so that the relationships between the angles are also unchanged. However, since the symmetry of the phase is now D_∞, the rules for locating the principal axes of S need to be modified;[8] the absence of a molecular mirror plane no longer allows the normal to this plane to be identified as a principal axis, and the

relationship between the bond order parameters and the molecular order parameters, expressed in the *abc* frame, is

$$S_{CH1} = S_{aa} \cos^2 \theta + S_{cc} \sin^2 \theta - S_{ac} \sin 2\theta \qquad (8)$$

and

$$S_{CH2} = S_{aa} \cos^2 \theta + S_{cc} \sin^2 \theta + S_{ac} \sin 2\theta \qquad (9)$$

As a result, the two residual C−H dipolar couplings are now unequal, as are the quadrupolar splittings for the deuteriated fragment, with their differences, ΔD_{CH} and $\Delta(\Delta\nu)$, proportional to $2S_{ac} \sin 2\theta$. For a methylene group with the tetrahedral angle 109.47° between the C−H bonds, this difference is $1.89S_{ac}$, which is very close to the maximum value of $2S_{ac}$ when the angle between the bonds is 90°.

The inequality of the C−H bond directions within the molecule, implied by the inequality of the dipolar or quadrupolar interactions, produced in a chiral liquid crystalline phase for a group such as that shown in Figure 2, is known as *prochirality*. It is an unambiguous signature that a liquid crystalline phase is chiral, but it has not been used previously in this way.

A chiral phase composed of a single molecular species with the same handedness (+ or −), that is, a single enantiomer, will produce a phase with maximum chirality (+ or −) and a maximum value of ΔD_{CH} and $\Delta(\Delta\nu)$, for a prochiral group: all molecules have the same order parameters, and in particular, this holds for the value of S_{ac} in eqs 8 and 9. Changing the handedness of the constituent molecules will produce a chiral phase of opposite handedness, and now the diagonal elements S_{aa}, S_{bb}, and S_{cc} are unchanged, but S_{ac} has the same magnitude but opposite sign. As a consequence, the magnitudes of ΔD_{CH} and $\Delta(\Delta\nu)$ are unchanged, but they do change sign. This means that the ^{13}C or ^2H spectra for a prochiral group in the + or − chiral phases appear identical. For a homogeneous mixture of equal molar amounts of the two enantiomeric forms, the prochiral splitting vanishes. This has been observed experimentally for small molecules dissolved in the chiral nematic phase formed by dissolving the polypeptides poly-(γ-benzyl-L-glutamate), PBLG, or poly-(γ-benzyl-D-glutamate), PBDG, in a solvent such as chloroform.[9] A scaled, nonzero value of ΔD_{CH} or $\Delta(\Delta\nu)$ occurs for mixtures containing unequal amounts of the enantiomeric forms. If the chiral phase consists of domains having + and − chirality (a racemic conglomerate) with diffusion of the molecules between these two domains which is slow compared with the change produced in either the quadrupolar splitting, $\Delta(\Delta\nu)$, or the C−H dipolar coupling, ΔD_{CH}, then the prochiral splitting is unaffected and the NMR spectra would be identical in either the pure + or − domain. For slow diffusion, therefore, the NMR spectrum is insensitive to the presence of domains.

In this paper, we confirm that CB7CB does form a chiral phase by reinvestigating the deuterium spectrum given by CB7CB-d_4, as well as by recording 2D ^{13}C-detected, ^1H-encoded spectra (known as PELF spectra[10]) on the fully protonated molecule, in both nematic phases and a spectrum of deuterons at natural abundance in the N_{TB} phase.

The NMR spectrum of a solute containing prochiral groups when dissolved in a chiral liquid crystalline phase can also reveal the chirality of the phase, and this too is demonstrated here for CB7CB by NMR experiments with deuteriated samples of acenaphthene and the mesogen 4-octyl-4′-cyanobiphenyl (8CB). The advantage of using a prochiral probe as a diagnostic tool for phase chirality is that the nematogen need not possess a prochiral group. There is also an advantage in choosing a probe which is rigid and of known structure, and a particularly useful molecule in this context is perdeuteroacenaphthene-d_{10} whose structure is shown in Figure 3; the two methylene groups are prochiral, while the other C−
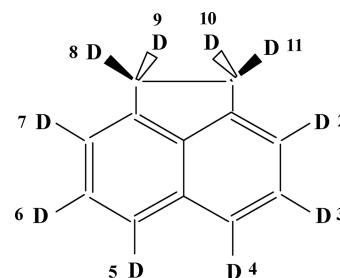

Figure 3. The chemical structure of perdeuteriated acenaphthene-d_{10} and the numbering of the deuterons.

H aromatic equivalent fragments are homotopic because of the molecular C_2 axis. We have studied both perdeuteriated acenaphthene-d_{10} and also acenaphthene-d_4 specifically deuteriated in the methylene groups. The latter probe leads to a simpler NMR spectrum, as we shall see. The other spin probe that we have employed to investigate the chirality of the twist−bend nematic phase of CB7CB was 4-octyl-4′-cyanobiphenyl-d_2 whose structure is given in Figure 4. All of the seven methylene
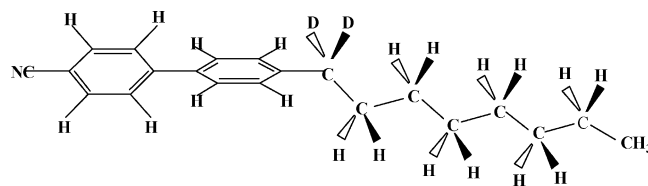

Figure 4. The molecular structure of the mesogen 8CB-d_2.

groups in the octyl chain are prochiral, and for our study, we have chosen that attached to the cyanobiphenyl group to place the two deuterons. This spin probe is, in essence, a monomeric analogue of the liquid crystal dimer CB7CB.

■ EXPERIMENTAL SECTION

A sample of CB7CB was synthesized based on the scheme described previously[1] with the modification that the reduction of 1″,7″-bis(4-bromobiphenyl-4′-carbonyl) pentane to 1″,7″-bis(4-bromobiphenyl-4′-yl) heptane was performed with aluminum trichloride and lithium aluminum hydride. The transition temperatures for CB7CB are $T_{CrN_{TB}} = 102$ °C, $T_{N_{TB}N} = 103$ °C, and $T_{NI} = 116$ °C; the uncertainties in these values are of the order of ± 1 °C.

The sample of perdeuteroacenaphthene-d_{10} was obtained from CDN Isotopes, Quebec, Canada, and used without further purification. It was also used to synthesize acenaphthene-d_4 specifically deuteriated in the two methylene groups by exchanging the aromatic deuterons using several processes for this back exchange. For example, with high pressure tantalum equipment and HCl/H$_2$O at 240 °C, the exchange was found not to be very specific with deuterons being lost from both aromatic and aliphatic positions. Accordingly, the temperature was lowered to 220 °C, then to 180 °C, and finally to 150 °C, but some of the methylene deuterons were still being

exchanged together with the aromatic deuterons. We finally decided to try the exchange by refluxing perdeuteroacenaphthene-d_{10} in trifluoroacetic acid for just 20 h, and this resulted in a perfect back exchange leaving the methylene-deuterons completely intact. Column chromatography was employed to remove small amounts of impurities.

A sample of CB7CB containing 4 wt % perdeuteroacenaphthene-d_{10} was prepared, which had a nematic−isotropic transition temperature of 110 °C. Using 5 wt % acenaphthene-d_4 produced a sample with a comparable transition temperature.

The specifically deuteriated sample of 8CB-d_2 was prepared using the procedure described previously.[11] The transition temperatures for this mesogen are in accord with the literature values; T_{SmAN} = 33.6 °C and T_{NI} = 40.6 °C. About 4 wt % was added to CB7CB, and this depresses T_{NI} by about 1 °C. The N_{TB}−N transition temperature is reduced by ~2 °C, and there appears to be a small biphasic region.

^{13}C−^{1}H PELF Spectra. The PELF NMR spectra were recorded at the high-field NMR Centre in Lyon, France, using the pulse sequence shown in Figure 5. A PELF spectrum was
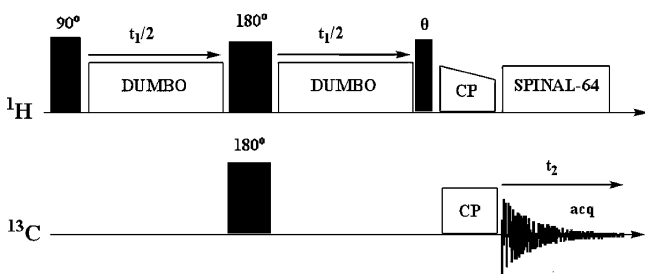

Figure 5. The pulse sequence used to record the PELF spectra of CB7CB.

obtained in the nematic phase at about 104 °C on a sample contained in a stationary 4 mm MAS rotor to give a sample volume of ~92 μL in a MAS probe, and is shown in Figure 6 (top). This arrangement was used because of the good PELF spectra obtained previously for liquid crystalline samples with such a sample holder and probe.[12−14] It proved impossible to record any NMR spectra for the sample in the supercooled N_{TB} phase with the MAS probe. The sample container was therefore changed to an "L" shaped 4 mm o.d. glass tube (i.d. ~2.2 mm, volume ~57 μL), and a Bruker double resonance static probe was used with a fixed, horizontal solenoid (volume ~235 μL). This arrangement gave much better spectra (^{1}H and ^{13}C 1D and PELF 2D), and most importantly, the sample cooled into the N_{TB} phase far below the melting point in the supercooled state. A PELF spectrum was recorded with this probe with the sample in the N_{TB} phase at ~16 °C below the N_{TB}−N transition and is shown in Figure 6 (bottom).

Deuterium Spectra of CB7CB-d_4. In the original deuterium NMR measurements for CB7CB-d_4, the single, quadrupolar split doublet observed when the sample was in the nematic phase becomes two doublets of unequal intensities in the twist-bend phase.[3] The unequal intensities are not consistent with the origin of this splitting, into two doublets, being that the phase is chiral. Equal intensity doublets should be obtained for a phase containing domains of the two enantiomeric forms in any volume ratio providing that diffusion is slow compared with $\Delta(\Delta\nu)$, as discussed previously. It was decided to reinvestigate the spectrum given by the CB7CB-d_4

sample to see if the original result is reproducible. The previous spectra were recorded at 46 MHz (the deuterium Larmor frequency for a magnetic field strength, B_0, of 7.05 T) using a quadrupolar echo sequence, which eliminates badly distorted baselines arising from a small amount of transmitter pulse intensity being picked up by the receiver. However, the quadrupolar echo experiment has been observed to lead to incorrect ratios of the intensities for other deuterium-labeled liquid crystalline samples, and to investigate whether this is the source of the unequal intensities observed previously, a spectrum was obtained using single pulse excitation on the sample in the nematic phase; the spectrometer used operated at a higher field strength of 9.4 T. This gave a quadrupolar doublet with the two lines of equal intensity. It was also found that the same result could be obtained with a quadrupolar echo experiment, and on cooling into the twist−bend phase, two quadrupolar doublets were obtained of equal intensity, within experimental error, as shown in Figure 7. We conclude that an unknown experimental cause was responsible for the unequal intensities in the quadrupolar echo spectra obtained previously,[3] and that the correct result is that shown in Figure 7.

Spectrum of Deuterons at Natural Abundance in CB7CB. An attempt was made to obtain a spectrum from deuterons at natural abundance in CB7CB with the same sample used for the PELF experiments with the "L"-shaped tube at a temperature ~16 °C below the N_{TB}−N transition. Proton decoupling was used, which has the major advantage of simplifying the spectrum, and considerably enhancing the signal-to-noise ratio. Proton decoupling, however, involves the adsorption of heat which can change the sample temperature during the acquisition of the free induction decay, leading to changes in the quadrupolar splittings, and hence to line broadening. To avoid this source of line broadening, the protons were irradiated only during the short acquisition time, and this was followed by a cooling period of 2 s. The result of acquiring ~100 000 free-induction decays, each from a single, 90° pulse excitation, was to produce a spectrum in which the aromatic deuterons are clearly detected, as shown in Figure 8, but not the aliphatic sites. The absence of signals from the aliphatic deuterons can be attributed primarily to a broadening of the resonances caused by the larger quadrupolar splittings combined with a temperature gradient over the sample. The four doublets observed are for the protonated sites in the biphenyl group and are in accord with the symmetry of the biphenyl group and the N_{TB} phase.

The Spectra of Deuteriated Acenaphthene as Solutes in CB7CB. A selection of deuterium NMR spectra of perdeuteroacenaphthene-d_{10} dissolved in CB7CB and measured as a function of temperature, covering both nematic phases, is shown in Figure 9. The spectra were recorded with a quadrupolar echo sequence on a Varian Infinity Plus 300 in the School of Chemistry at the University of Southampton.

We have performed analogous experiments using acenaphthene-d_4 which has some advantages as a spin probe over its perdeuteriated version. A selection of the spectra of the specifically deuteriated probe dissolved in CB7CB is shown in Figure 10 for temperatures within the twist−bend nematic phase.

The acenaphthene-d_4 has the advantage over the perdeuteroacenaphthene-d_{10} isotopomer as a probe of a chiral liquid crystalline phase in that it has the potential to give a simpler deuterium spectrum if the protons are decoupled.
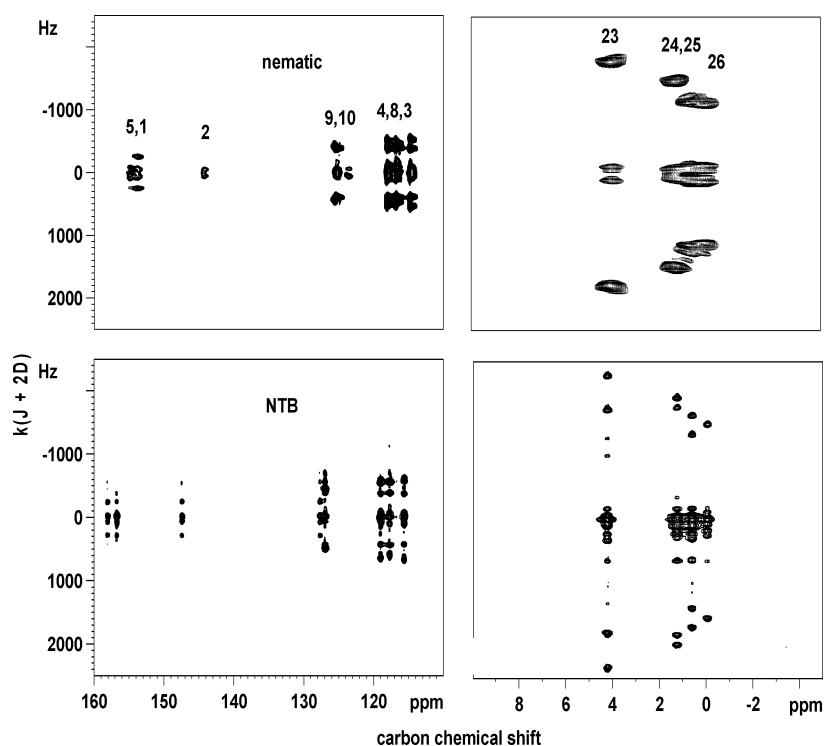
Figure 6. Top: Two-dimensional PELF spectrum of CB7CB in the nematic phase at ~104 °C. The spectrum was recorded on a 500 MHz (proton frequency) Avance III Bruker spectrometer using a double resonance 4 mm MAS probe (static sample). Left, the aromatic region; right, the aliphatic region. The spectrum was acquired with a total of 96 scans and 320 t_1 increments, corresponding to a maximum t_1 evolution period of 19.2 ms and a recycle delay of 7 s. DUMBO-1$_{22}$ decoupling[15] was applied with a RF field strength of 50 kHz (cycle time of 60 μs). SPINAL-64 decoupling[16] was applied with a RF field strength of 50 kHz. The contact time for the polarization transfer step was 2 ms. The spectral width in F_1 was 8333 Hz (experimental time 60 h). Bottom: Two-dimensional PELF spectrum of CB7CB in the N_{TB} phase ~16 °C below the nematic to N_{TB} phase transition. The spectrum was recorded on a 500 MHz (proton frequency) Avance III Bruker spectrometer using a double resonance probe (static horizontal probe 5 mm tube sample). Left, the aromatic region; right, the aliphatic region. The spectrum was acquired with a total of 32 scans and 360 t_1 increments, corresponding to a maximum t_1 evolution period of 21.6 ms and a recycle delay of 5.0 s. DUMBO-1$_{22}$ decoupling was applied at a RF field strength of 50 kHz (DUMBO cycle time of 60 μs). SPINAL-64 decoupling was applied at a RF field strength of 50 kHz. The contact time for the polarization transfer step was 2.5 ms. The spectral width in F_1 was 8333 Hz (experimental time 16 h).
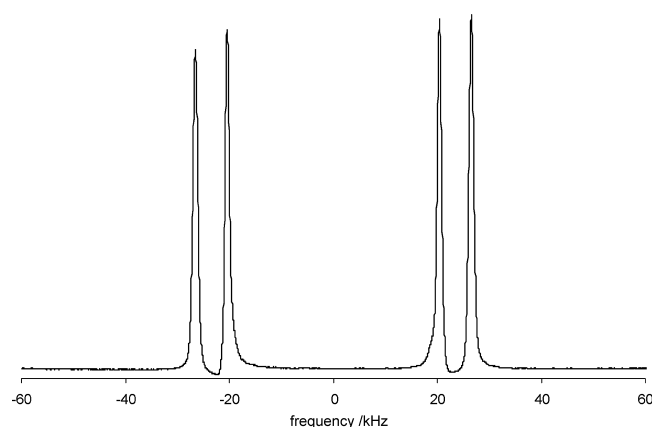

Figure 7. The 61.370 MHz deuterium NMR spectrum of CB7CB-d_4 recorded in its twist–bend nematic phase at 88 °C, corresponding to a shifted temperature, $T_{N_{TB}N} - T$, of approximately 17 °C. The spectrum was obtained using a quadrupolar spin echo sequence with a delay of 20 μs between the first two pulses and of 35 μs between the second pulse and the acquisition of the FID. The width required for a 90° pulse was determined to be 7.5 μs. 400 FIDs were accumulated into 4096 words of computer memory with a spectral window of 149.925 kHz.

The Deuterium Spectra of 4-Octyl-4′-cyanobiphenyl-d_2 Dissolved in CB7CB. The deuterium NMR spectra of
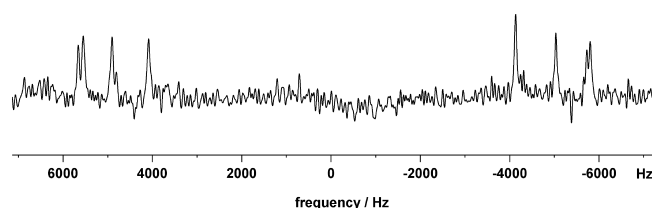

Figure 8. NMR spectrum of deuterons in CB7CB in the N_{TB} phase ~16 °C below the N_{TB}–N transition. The spectrum is the result of accumulating 122 880 free induction decays into 6144 words of computer memory, and with a spectral window of 150 000 Hz. The protons were irradiated during the acquisition time of 20 ms, and there was a delay between acquisitions of 2 s.

8CB-d_2 dissolved in CB7CB were measured for the nematic phase and also deep into the supercooled twist–bend nematic phase. A selection of these spectra is shown in Figure 11.

■ RESULTS AND DISCUSSION

The PELF Spectra of CB7CB. The F_1 cross sections taken at each carbon chemical shift for the two phases are shown in Figure 12. For the nematic phase, they show doublets with a separation, $\Delta_{i,j}$, which depends on the scaled, total spin–spin coupling, $T_{i,j}$, between carbon i and proton j. Thus,

$$T_{i,j} = J_{i,j} + 2D_{i,j} \tag{10}$$

7944

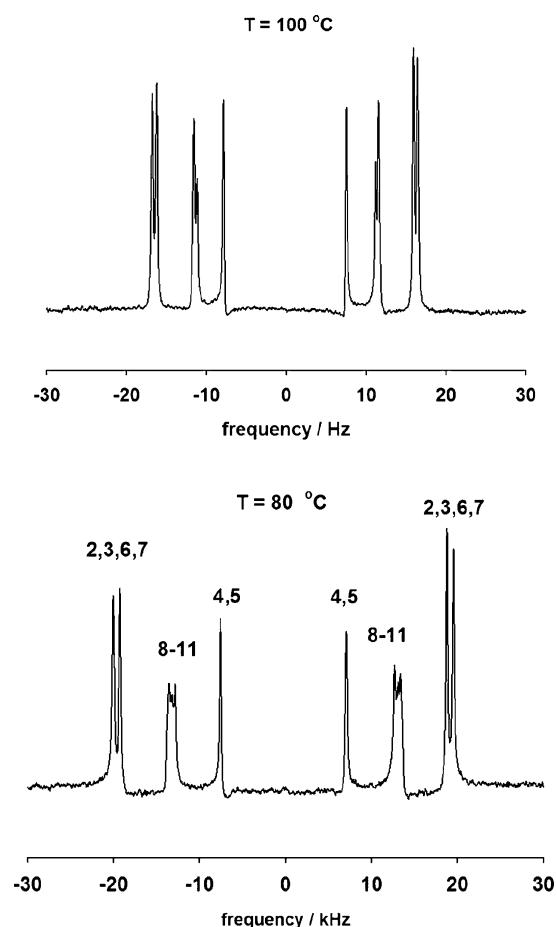dx.doi.org/10.1021/jp302705n | J. Phys. Chem. B 2012, 116, 7940–7951

Figure 9. The deuterium NMR spectra of perdeuteroacenaphthene-d_{10} dissolved in CB7CB, top in the nematic (100 °C) and bottom in the twist−bend nematic (80 °C) phases. The spectra were measured at a frequency of 46.026 MHz using a quadrupolar spin echo sequence with a delay of 20 μs between the first two pulses and of 35 μs between the second pulse and the acquisition of the FID. The 16k FIDs were accumulated into 4k words of computer memory with a spectral window of 149.925 kHz.

where $J_{i,j}$ is the scalar and $D_{i,j}$ is the residual dipolar coupling, and

$$\Delta_{i,j} = k(J_{i,j} + 2D_{i,j}) \tag{11}$$

The scaling factor, k, has a magnitude determined by the nature of the homodecoupling sequence applied in the interval t_1, which has been determined experimentally[13] for the DUMBO sequence to have a value of 0.47.

The F_1 cross sections in a PELF spectrum at the carbon chemical shift positions consist of a set of doublets, one for each equivalent group of protons. The relative intensities of the doublets reflect the number of equivalent protons and the efficiency of transfer of magnetization in the cross-polarization step. The latter depends on the duration of the contact and the strength of the spin−spin coupling between that equivalent group of protons and the carbon-13 nucleus. A 2 ms contact time has been chosen that gives strong intensities for doublets arising from the strongest, usually one-bond C−H interactions, with somewhat weaker intensities for the peaks arising from longer range interactions.

The F_1 cross sections for the aromatic carbons are very similar for the nematic and N_{TB} phases, and are very similar to
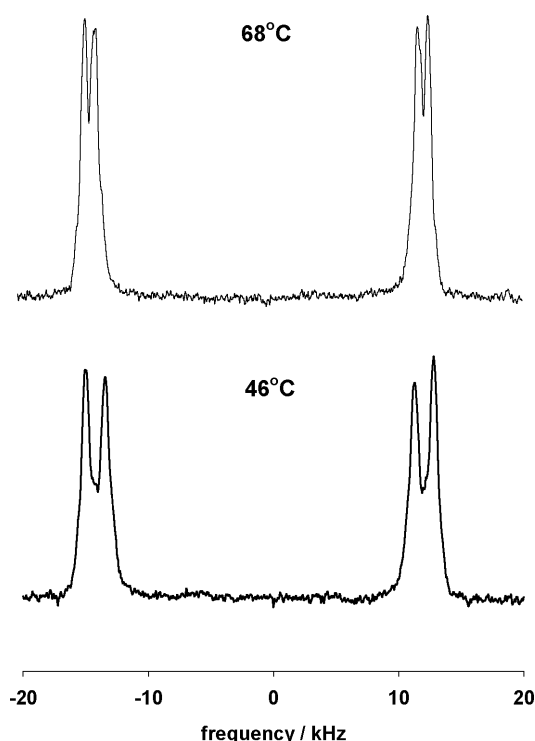

Figure 10. The deuterium NMR spectra of acenaphthene-d_4 dissolved in the twist−bend nematic phase of CB7CB at two temperatures. The spectra were measured at a frequency of 46.028 MHz using a quadrupolar spin echo sequence with a delay of 20 μs between the first two pulses and of 35 μs between the second pulse and the acquisition of the FID. The 16k FIDs were accumulated into 4k words of computer memory with a spectral window of 149.925 kHz.

those observed in the PELF spectrum of 4-pentyl-4'-cyanobiphenyl (5CB).[12] This is to be expected. The equivalence of the protons (15,18,15',18'), (16,17,16',17'), (19,22,19',22'), and (20,21,20',21') and the carbons (C1,C1'), (C2,C2'), (C3,C7,C3',C7'), (C4,C6,C4',C6'), (C5,C5'), (C8,C12,C8',C12'), and (C9,C11,C9',C11') in the two biphenyl groups is because there are 2-fold rotation axes coincident with the para axes in each group, and a 2-fold axis relating the two biphenyl groups which passes through C26, and these relationships are not affected by phase chirality. These results are also consistent with the single doublets observed for the aromatic deuterons in the N_{TB} phase.

The largest splittings observed in each case for the equivalent groups (C3,C7,C3',C7'), (C4,C6,C4',C6'), and (C8,C12,C8',C12') can be assigned, unambiguously, to being from the one-bond C−H interactions, with the next largest from the two-bond couplings. For (C9,C11,C9',C11'), these two splittings are very similar in magnitude, and are unresolved in 5CB and in the nematic phase of CB7CB, and barely resolved in the N_{TB} phase.

The aliphatic carbons (23,23'), (24,24'), and (25,25') each have $F1$ cross sections for the nematic phase showing a large doublet corresponding to the one-bond coupling, which in the N_{TB} phase clearly splits into two. The $F1$ cross-section for the central carbon, C26, shows a single doublet for the one-bond interactions in both phases. The splittings, and derived residual dipolar couplings for CB7CB in the two phases are given in Table 1.

The Deuterium Spectra of Perdeuteroacenaphthene-d_{10} Dissolved in CB7CB. The spectra in the nematic phase,
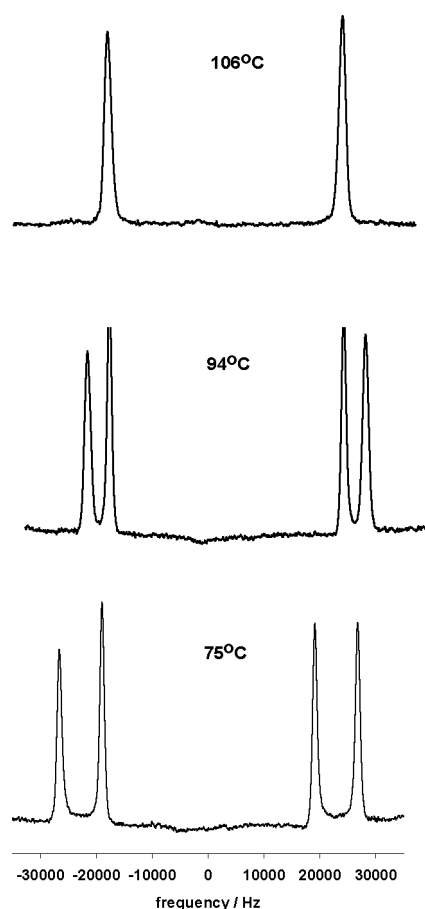
Figure 11. The deuterium NMR spectra of 8CB-d_2 dissolved in CB7CB and recorded in both the nematic (at 46.0 MHz) and twist–bend nematic phase (at 61.4 MHz). The spectra were measured using a quadrupolar spin echo sequence with a delay of 20 μs between the first two pulses and of 35 μs between the second pulse and the acquisition of the FID. The 16k FIDs were accumulated into 4k words of computer memory with a spectral window of 149.925 kHz.

shown in Figure 9, consist of three quadrupolar doublets originating from the three pairs of equivalent aromatic deuterons (see Figure 3). The smallest of these doublets is assigned to the 4,5 deuterons in keeping with measurements of the deuterium NMR spectra of acenaphthene dissolved in the nematic host ZLI 1132.[17] By the same token, the largest splitting is assigned to deuterons 3,6 and the next largest splitting to deuterons 2,7. The similarity of these quadrupolar splittings results from the closeness of the angles made by the C–D bonds with the principal axes of the Saupe ordering matrix for acenaphthene. There are four aliphatic deuterons, 8, 9, 10, 11, and these are equivalent in the nematic phase. However, there is a moderate dipolar coupling, D, between the two deuterons on each methylene group. This is responsible for the splitting of the aliphatic peaks into pairs of lines of unequal intensity. In fact, the dipolar coupling should split the quadrupolar doublet into three components,[18] but the smallest of these is not resolved, as shown in Figure 13. For these spectra, it is possible to obtain the quadrupolar splitting and the dipolar coupling directly from the positions of the resolved peaks, which are at $\pm(\Delta\nu/2 - 3D)$, intensity 1, $\pm(\Delta\nu/2 - D)$, intensity 3, and $\pm(\Delta\nu/2 + 3D)$, intensity 2.

As the temperature is lowered within the nematic phase, there is a slight increase in all of the quadrupolar splittings. On

entering the twist–bend nematic phase, the peaks from the aromatic deuterons do not change except for an increase in the splittings. However, there is a clear change in the appearance of the NMR peaks associated with the aliphatic deuterons, which is illustrated by the spectra at 80 °C shown in Figure 14. These spectra are consistent with the two deuterons in the methylene groups having different quadrupolar splittings, as shown by the simulated spectra shown in Figure 14. The simulated spectra were obtained using the spin Hamiltonian:

$$H = D(3I_{1z}I_{2z} - \mathbf{I}_1\mathbf{I}_2) + \Delta\nu_1(3I_{1z}^2 - \mathbf{I}_1^2)/6 + \Delta\nu_2(3I_{2z}^2 - \mathbf{I}_2^2)/6$$

where D is the residual dipolar coupling between the two deuterons in the methylene group. The nuclear spin operators, $\mathbf{I}_1$ and $\mathbf{I}_2$, have components I_{1z} and I_{2z} along the field direction, z. The simulations were realized with a Mathematica program "Spin Dynamica" kindly provided by M. H. Levitt (www.mhl.soton.ac.uk/public/Main/index.html). Further into the N_{TB} phase, the aliphatic lines shift and broaden with a net result that they appear as a broad doublet, with unresolved dipolar coupling, and the lines have equal intensity. This is entirely in keeping with the chirality of the twist–bend nematic phase as is the fact that for the pairs of homotopic, aromatic deuterons the quadrupolar doublets are not split.

We have been able to measure such spectra over a very wide temperature range because the N_{TB} phase is readily super-cooled. The temperature dependence of the quadrupolar splittings is shown in Figure 15 as a function of the shifted temperature, $T_{NI} - T$. At the nematic–isotropic transition there is a pronounced jump in all of the quadrupolar splittings in keeping with the first order nature of this transition.[1,3] At first, the splittings increase slowly with decreasing temperature, caused by a small biphasic region resulting from the low concentration of the spin probe. All of the quadrupolar splittings then increase rapidly with further decrease in temperature until the transition to the twist–bend nematic phase is reached. At this transition, there is a clear jump in the splittings for the two pairs of aromatic deuterons with the larger splitting; again, this is in keeping with the first-order nature of this transition.[1,3] For the pair of aromatic deuterons with the smallest splitting, the change at the N_{TB}–N transition is negligible, while in the N_{TB} phase the quadrupolar splitting decreases with decreasing temperature. The two quadrupolar splittings for the aliphatic deuterons behave differently. One quadrupolar splitting grows, while the other decreases until at the lowest shifted temperature of 80 °C the difference in these is about 3 kHz. Although significant, this difference is small in comparison with that found for the prochiral deuterons in CB7CB-d_4 of about 19 kHz at a comparable shifted temperature.[3]

The expressions for the two quadrupolar splittings for a pair of deuterons attached to a prochiral fragment in a chiral phase (see eqs 3, 4, 8, and 9) show that their mean depends on the diagonal elements of the ordering matrix, S_{aa} and S_{cc}, as for the achiral phase (see eq 7). We have, therefore, shown the temperature variation of this mean in Figure 15; we can see that at first it increases and then decreases but the changes are small. Such behavior is in contrast to the increase in the difference of the quadrupolar splittings which indicates a significant variation in the off-diagonal order parameter, S_{ac}. The weak temperature variation in the mean quadrupolar splitting for the aliphatic deuterons does, however, compare well with that found for the temperature dependence for the quadrupolar splittings for the aromatic deuterons (3,6 and 2,7). We should note that this
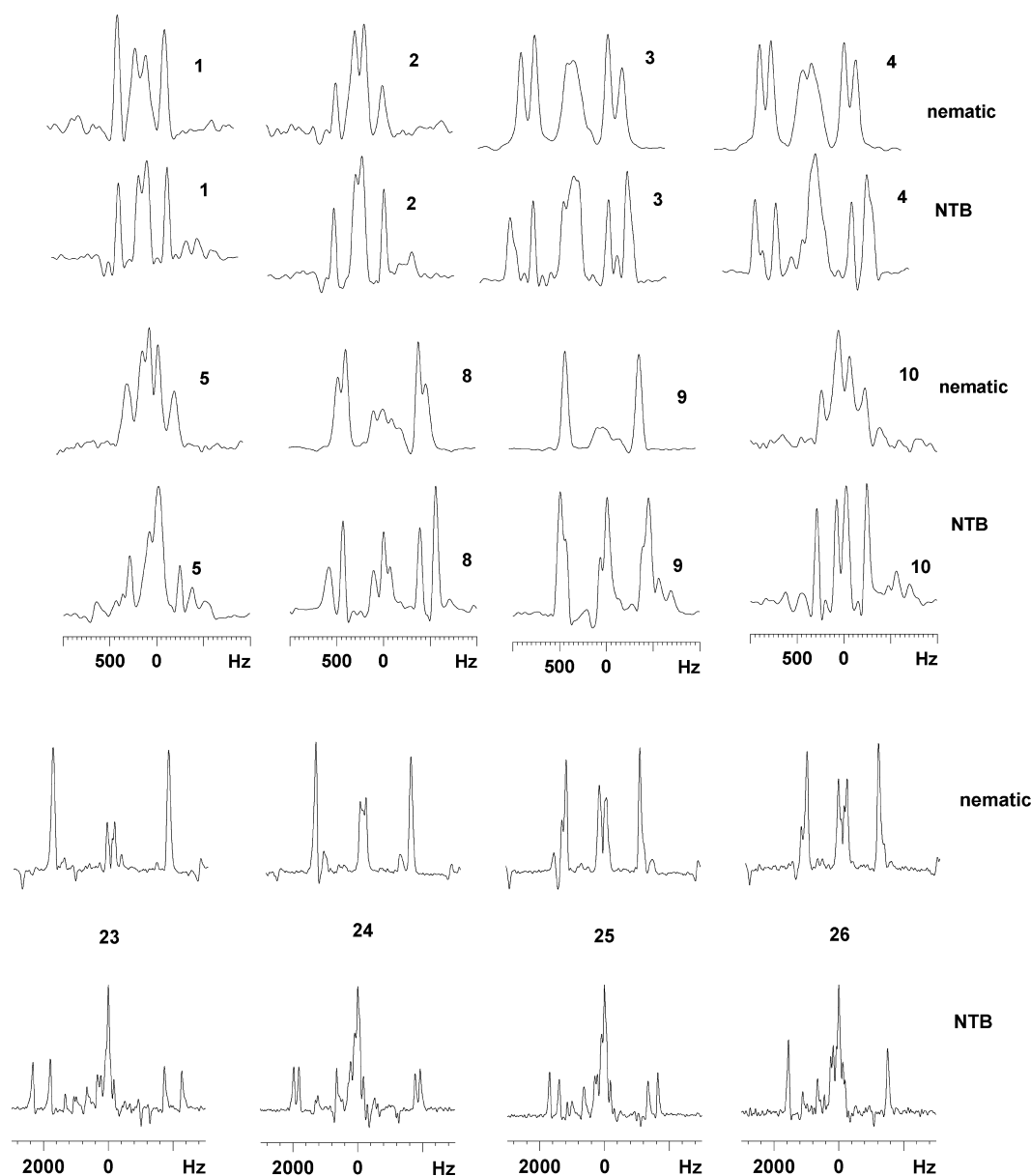
Figure 12. The F_1 cross sections from the PELF spectra for the nematic phase at ~104 °C and the N_{TB} phase at ~87 °C.

behavior contrasts with that found for perdeuteroacenaphthene-d_{10} dissolved in the chiral nematic phase formed by PBLG dissolved in chloroform.[17] There, both the difference in the quadrupolar splittings of the aliphatic deuterons and their mean decrease with increasing temperature, although the ratio of these two quantities is approximately constant. Thus, for the twist−bend nematic, the mean of the quadrupolar splittings appears to be insensitive to the orientational order, whereas for the chiral nematic formed from PBLG it is not.[17]
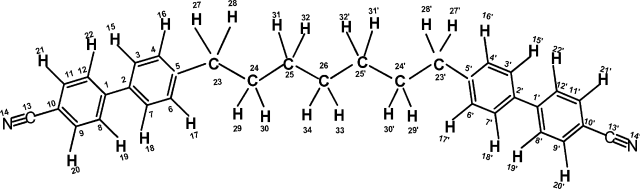
The Deuterium Spectra of 8CB-d_2 Dissolved in CB7CB. In the nematic phase, the spectrum consists of a single quadrupolar doublet; the linewidths are too large for the dipolar coupling between the two deuterons to be resolved. At the transition to the twist−bend nematic phase, a second quadrupolar doublet of low intensity appears which grows in intensity while the original is reduced. This behavior is suggestive of a small biphasic region, reminiscent of that observed for CB7CB-d_4[3] and consistent with the chirality of the twist−bend nematic phase. As the temperature is lowered

further so the difference in the two quadrupolar splittings increases. The dependence of the quadrupolar splittings for 8CB-d_2 in CB7CB on the shifted temperature, $T_{NI} - T$, is shown in Figure 16. As we had expected, the quadrupolar splitting changes discontinuously at T_{NI} in keeping with the first-order character of this phase transition. The splitting then increases fairly rapidly with decreasing temperature until the transition to the N_{TB} phase occurs, when there is a discontinuous change to a spectrum showing two sets of quadrupolar doublets. This behavior is analogous to that found for CB7CB-d_4, and is consistent with the chirality of the N_{TB} phase.[3]

The nature of the discontinuity at $T_{N_{TB}N}$ is revealed by comparing the splitting in the nematic phase, $\Delta\nu(N)$, with the mean, $\Delta\nu_{mean}$, of the two splittings in N_{TB}, as shown in Figure 16. The ratio $\Delta\nu_{mean}/\Delta\nu(N)$ is 1.06 at the transition, while the difference in the quadrupolar splittings, $\Delta(\Delta\nu)$, which appears in the twist−bend phase is about 3 kHz, which is 8% of $\Delta\nu(N)$, and is similar in magnitude to that observed for CB7CB-d_4. The

Table 1. Splittings, $\Delta_{i,j}$/Hz, and Residual Dipolar Couplings, $D_{i,j}$/Hz, Obtained for CB7CB in the Nematic Phase, and $\Delta_{i,j}(1)$/Hz, $\Delta_{i,j}(2)$/Hz, $\Delta_{i,j}(\text{mean})$/Hz, $D_{i,j}(1)$/Hz, and $D_{i,j}(2)$/Hz for the Twist−Bend Nematic Phase

i,j	$J_{i,j}$[a]	nematic		twist−bend nematic					
		$\Delta_{i,j}$	$D_{i,j}$	$\Delta_{i,j}(1)$	$\Delta_{i,j}(2)$	$\Delta_{i,j}(\text{mean})$	$D_{i,j}(1)$	$D_{i,j}(2)$	$D_{i,j}(\text{mean})$
1,19		510	543	519		519			552
1,?		121	129						
2,15		500	532	533		533			567
2,?		107	114						
3,15	157	1082	1073	1249					1250
3,16		−781	−831	−803		−803			−854
3,?		102	109	153		153			163
4,15		−788	−838			−810			−862
4,16	157	1024	1016			1193			1191
4,?		185	197						
4,?		123	131						
5,16		499	531			535			569
5,?		170	181						
8,19	162	930	908			1140			1132
8,20		−778	−828			−822			−874
8,?		191	203						
8,?		40	43						
9,19		−792	−843			−827			−880
9,20	166	792	760			941			918
9,?		115	122						
10,20		472	502			533			567
10,?		114	121			105			112
23,27	126	3570	3735	4598	3523	4061	4828	3685	4257
23,?		234	249						
23,?		78	83						
24,29	126	2911	3034	3896	3586	3741	4082	3752	3917
24,?		178	189						
25,31	125	2257	2339	3335	2736	3036	3485	2848	3167
25,?		204	217						
26,33	125	2187	2264	3059		3059			3192
26,?		272	289	441		441			469
26,?				306		306			326

[a]The values of $J_{i,j}$ were obtained from a spectrum of CB7CB dissolved in CDCl$_3$.

value of $\Delta(\Delta\nu)$ increases very slightly over the next 6 °C, and we tentatively attribute this near constancy of this difference to the biphasic nature of the system caused by the addition of the spin probe. The value of $\Delta\nu_{\text{mean}}$ remains almost constant down to $T_{\text{NI}} - T = 74$ °C. However, in the same temperature range, there is a rapid increase in $\Delta(\Delta\nu)$ with decreasing temperature until it reaches a value of about 26 kHz at the lowest shifted temperature. This behavior is similar to that observed for CB7CB-d_4[3] but is significantly larger than that found for the rigid spin probe perdeuteroacenaphthene-d_{10}. The question as to the cause of this difference in behavior is an intriguing one. The sum, and hence also the mean, of the two quadrupolar splittings in the twist−bend nematic is independent of the off-diagonal ordering matrix element, $S_{a\sigma}$, and is related directly to the quadrupolar splitting observed in the nematic phase. The mean is plotted in Figure 16, and it shows the expected jump at the N$_{\text{TB}}$−N transition but then changes only slightly and

decreases at low temperatures. As for acenaphthene, the effect of the phase chirality on the quadrupolar splittings for 8CB-d_2 clearly increases significantly with decreasing temperature, whereas the orientational order first increases slightly but then passes through a maximum before decreasing by a small amount.

Magnetic Field Alignment of the Twist−Bend Nematic Phase. The primary aim of this investigation was to demonstrate that the twist−bend nematic phase of CB7CB is indeed chiral, and this we have achieved. However, the NMR experiments also allow us to comment on the effect of a magnetic field on the structure of this phase. First, we note that in the nematic phase the director is aligned parallel to the magnetic field, showing that the diamagnetic anisotropy, $\Delta\chi$, defined relative to the director, must be positive. This is apparent because the orientational order parameter of the cyanobiphenyl mesogenic group calculated from the quad-
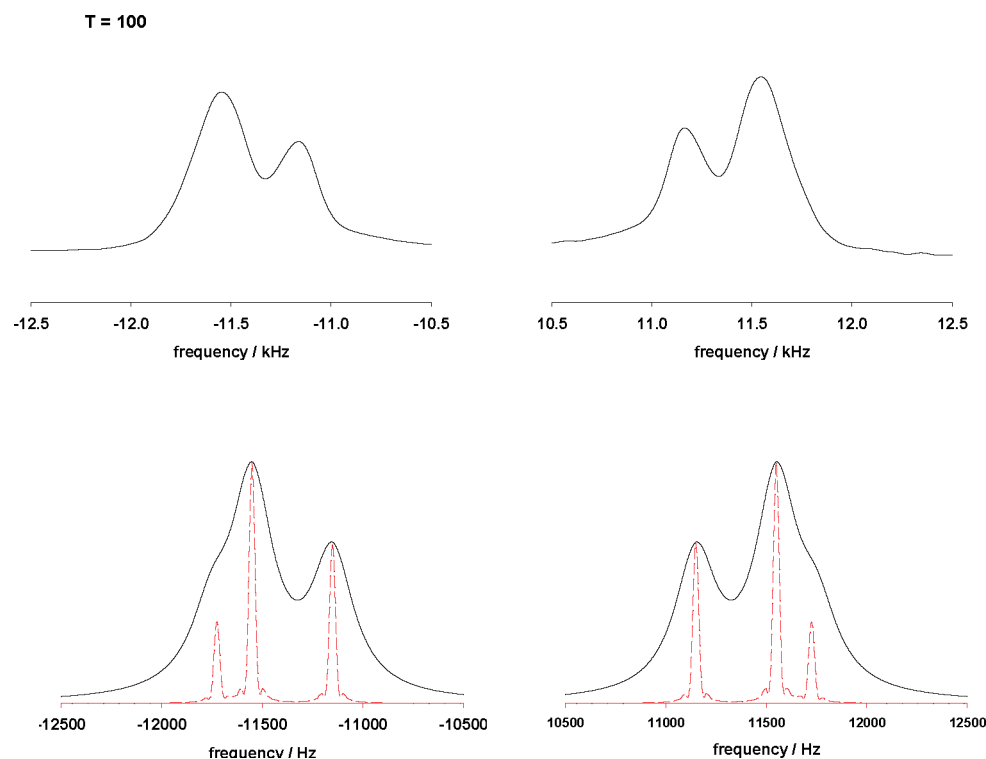
T = 100

Figure 13. The peaks from the aliphatic deuterons in the spectrum of perdeuteroacenaphthene-d_{10} dissolved in CB7CB in the nematic phase at 100 °C. Top, experiment; bottom, simulation with linewidths of 251 Hz (black, continuous) and 25 Hz (red, dashed).
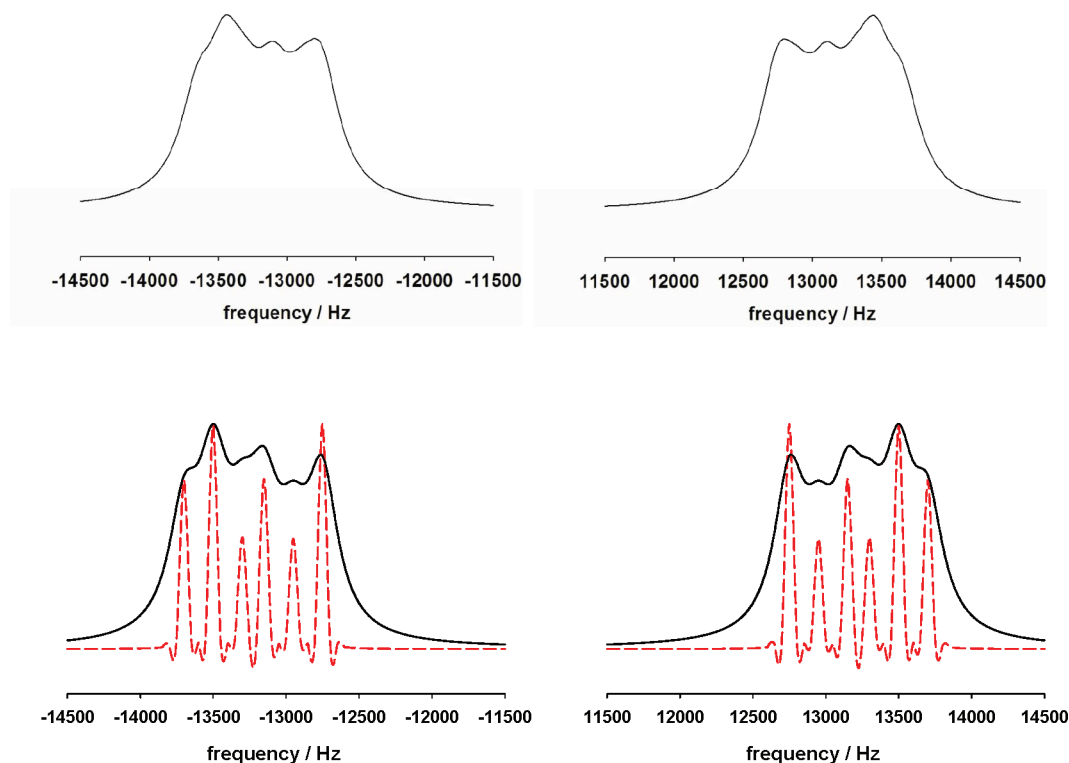

Figure 14. The peaks from the aliphatic deuterons in perdeuteroacenaphthene-d_{10} when the sample is in the twist−bend nematic phase at 80 °C. Top, experiment; bottom, simulations with $\Delta\nu_1 = -27\,000$ Hz, $\Delta\nu_2 = -25\,965$ Hz, $D = 95$ Hz, and linewidths of 251 Hz (black, continuous) and 25 Hz (red, dashed).

rupolar splittings in CB7CB-d_4 is greater than 0.5 and so must be positive.[3] Second, the deuterium NMR lineshapes are symmetric and the widths relatively small for a deuteriated species within the nematic and twist−bend nematic phase of

CB7CB. This is consistent with the uniform alignment of the director with respect to the magnetic field in both phases. The fact that the dipolar splittings determined in the PELF experiments are consistent with those first measured[3] from
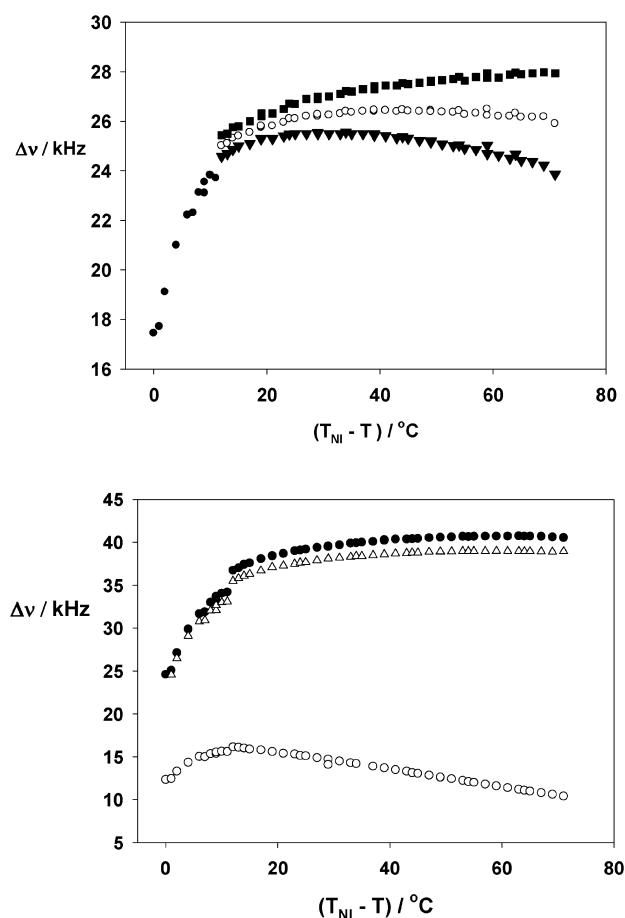
Figure 15. The temperature dependence of the quadrupolar splittings for perdeuteroacenaphthene-d_{10} dissolved in CB7CB shown as a function of the shifted temperature ($T_{NI} - T$). Top: aliphatic deuterons in the nematic phase (●), and then in the twist−bend nematic phase (■ and ^{2}) with ○ the mean of the two splittings. Bottom: aromatic deuterons in both phases for D3 and D6 (●), D2 and D7 (△), and D4 and D5 (○).
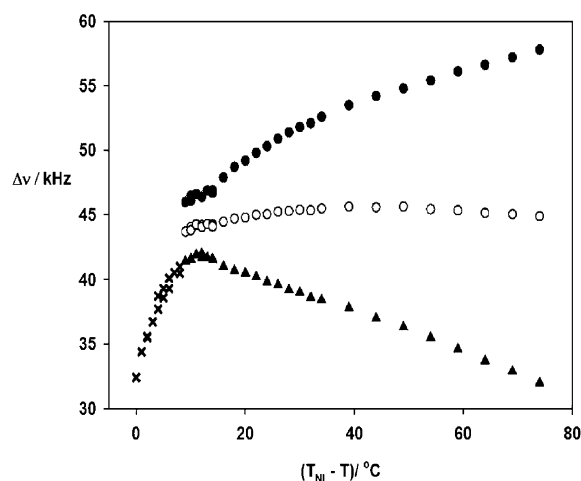

Figure 16. The temperature dependence of the quadrupolar splitting for 8CB-d_2 dissolved in CB7CB, shown as a function of the shifted temperature ($T_{NI} - T$). The splitting in the nematic phase is given as ×. In the N_{TB} phase, the splittings are denoted as ● and ▲, while their mean is shown as ○.

the quadrupolar splittings is important because the magnetic fields are significantly different in magnitude. In the former experiments, the field strength, B_0, is 11.75 T, while in the latter experiments B_0 is 7.05 T. This difference in field strengths corresponds to a factor of about 2.8 in the magnetic torques, and our results show that this major change has not influenced the director distribution with respect to the field. While this is to be expected in the nematic phase, it is of significance for the structure of the N_{TB} phase. Such behavior is, however, consistent with the director distribution predicted by Dozov[4] for a chiral domain of the twist−bend nematic phase. Here the components of the director take the form $(\sin\theta_0 \cos\varphi(z)$, $\sin\theta_0 \sin\varphi(z)$, $\cos\theta_0)$, where z is the position along the helix axis and $\varphi(z)$ is the azimuthal angle. The tilt of the director with respect to the helix axis is θ_0 and does not vary with the position along this axis; it will reduce the anisotropy of the magnetic susceptibility, $\Delta\chi_{cd} = \chi_{cd}(\parallel) - \chi_{cd}(\perp)$, for a chiral domain (cd), where $\parallel$ and $\perp$ refer to the helix axis to $\Delta\chi P_2(\cos\theta_0)$, where $P_2(\cos\theta_0)$ is the second Legendre function. When θ_0 is <54.47°, the anisotropy in the magnetic susceptibility of a domain is positive, and the helix axis should align parallel to the magnetic field direction. This anisotropy becomes negative when θ_0 is >54.47°, and now the helix axis will tend to align orthogonal to the field.

For the twist−bend phase of CB7CB, the optics suggest that the tilt angle is about 10°,[3] and this would reduce $\Delta\chi_{cd}$ to about $0.95\Delta\chi$; it is therefore expected that the helix axes in the two domains of the twist−bend phase will align along the magnetic field direction. Note that it is not possible to align the directors along the field direction without destroying the helical twist, and hence the chirality of the phase. Alignment of the directors will be in competition with the helical twist, and so at high enough field strengths, the helix should unwind. Such behavior is well-known for the chiral nematic phase[19] which can be viewed as a special case of the twist−bend nematic when θ_0 is 90°. A tilt of the directors in the chiral domain will also influence the magnitudes of the anisotropic magnetic NMR interactions, such as the dipolar and quadrupolar splittings, which are also reduced by a factor of $P_2(\cos\theta_0)$. If the only change on going from the nematic to the twist−bend nematic phase is the creation of a tilt of the director relative to the magnetic field direction, then the dipolar or quadrupolar splittings would decrease by about 0.95 at the N to N_{TB} transition, whereas an *increase* of $\Delta\nu_{mean}$ relative to $\Delta\nu_N$ of about 1.06 is observed at this temperature. This increase suggests that there is an increase in molecular orientational ordering on going from the nematic to the twist−bend nematic phase of about 10%, which is compensating for the reduction resulting from the tilt of the director.

■ CONCLUSIONS

The forms of the *F1* cross sections in the $^{13}C-^1H$ PELF spectrum taken in the N_{TB} phase show that this phase is chiral. The chirality is revealed very clearly and unambiguously by the nonequivalence of the two C−H directions in each of the alkyl chain methylene groups, except for the pair in the central group, which retain their equivalence because of its 2-fold symmetry axis. The other six methylene groups are prochiral, and as such, their pairs of C−H directions are related by a mirror plane in achiral phases, but this reflection symmetry is lost in a chiral phase. The PELF experiment also yields residual dipolar couplings, $^1D_{CH}$, for all other carbons in the CB7CB molecule, and the total set of C−H couplings measured,

including some over two bonds, are potentially a very rich source of data with which to test models for the molecular structure, the conformational distribution, and how these affect the molecular orientational order. However, the PELF spectrum takes about 12 h to record, and hence is an impractical method for following the temperature dependence of these important molecular properties. The deuterium spectrum of CB7CB-d_4, which contains two equivalent deuterated prochiral methylene groups at positions 23 and 23′, has also been used to show the chirality of the twist−bend nematic phase via the deuterium quadrupolar splitting, and now the spectra take just minutes to record, and hence can be used to follow how the prochiral splitting changes with temperature.

The molecular prochirality test of phase chirality, as revealed by deuterium NMR, has also been demonstrated by recording the spectra of probe molecules containing prochiral groups dissolved in the suspected chiral phase. This probe prochirality test of a chiral phase should be easily applicable for identifying other proposed chiral liquid crystal phases, such as the twist−bend nematic phase formed by other compounds.

It should be noted that the NMR spectra reported here show definitely only that the nematic phase formed on cooling from the isotropic phase is not chiral, while the lower temperature nematic phase is. The spectra in the chiral phase are consistent with the formation either of a uniformly handed phase, or a mixture of right- and left-handed domains with slow interdomain diffusion. Both of these possibilities have been suggested to explain the results of optical experiments on thin film twist−bend phases formed by similar molecules to CB7CB[20] and also on bent-core mesogens.[21] It is planned to investigate whether NMR experiments can distinguish between these two important possibilities.

It is also of interest to speculate on the possibility of using the nematic twist−bend phase as a medium for distinguishing between enantiomers of dissolved chiral molecules via their different NMR spectra.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: J.W.Emsley@soton.ac.uk.

Notes

The authors declare no competing financial interest.

■ REFERENCES

(1) Barnes, P. J.; Douglass, A. G.; Heeks, S. K.; Luckhurst, G. R. *Liq. Cryst.* **1993**, *13*, 603.

(2) Toriumi, H. Private communication to G. R. Luckhurst (1985).

(3) Luckhurst, G. R. NMR of Oriented Phases, Tropea, Italy, 2009. Cestari, M.; Diez-Berart, S.; Dunmur, D. A.; Ferrarini, A.; de la Fuente, M. R.; Jackson, D. J. B.; Lopez, D. O.; Luckhurst, G. R.; Perez-Jubindo, M. A.; Richardson, R. M.; Salud, J.; Timimi, B. A.; Zimmermann, H. 21ˢᵗ International Liquid Crystal Conference, Krakow (2010) Abstract of oral 62(2); *Phys. Rev. E* **2011**, *84*, 011704.

(4) Dozov, I. *Europhys. Lett.* **2001**, *56*, 247.

(5) Luckhurst, G. R. *Macromol. Symp.* **1995**, *96*, 1.

(6) Bayle, J. P.; Courtieu, J; Gabetty, J. E.; Loewenstein, A.; Pechine, J. M. *New J. Chem.* **1992**, *16*, 837.

(7) Czarniecka, K; Samulski, E. T. *Mol. Cryst. Liq. Cryst.* **1981**, *63*, 205.

(8) Meddour, A.; Canet, I.; Loewenstein, A.; Pechine, J. M.; Courtieu, J. *J. Am. Chem. Soc.* **1995**, *116*, 9652. Merlet, D.; Loewenstein, A.; Smadja, W.; Courtieu, J.; Lesot, P. *J. Am. Chem. Soc.* **1998**, *120*, 963. Merlet, D.; Emsley, J. W.; Lesot, P.; Courtieu, J. *J. Chem. Phys.* **1999**, *111*, 6890.

(9) Courtieu, J.; Aroulanda, C.; Lesot, P.; Merlet, D. *Liq. Cryst.* **2010**, *37*, 903.

(10) Hong, M.; Pines, A.; Calderelli, S. *J. Phys. Chem.* **1996**, *100*, 14815. Calderelli, S.; Hong, M.; Emsley, L.; Pines, A. *J. Phys. Chem.* **1996**, *100*, 18696.

(11) Emsley, J. W.; Long, J. E.; Luckhurst, G. R.; Pedrielli, P. *Phys. Rev. E* **1999**, *60*, 1831.

(12) Emsley, J. W.; Lesot, P.; De Luca, G.; Lesage, A.; Merlet, D.; Pileio, G. *Liq. Cryst.* **2008**, *35*, 443.

(13) Emsley, J. W.; Lesot, P.; Lesage, A.; De Luca, G.; Merlet, D.; Pileio, G. *Phys. Chem. Chem. Phys.* **2010**, *12*, 2895.

(14) De Luca, G.; Emsley, J. W.; Salager, A.; Lesage, A. *Phys. Chem. Chem. Phys.* **2010**, *12*, 7968.

(15) Sakellariou, D.; Lesage, A.; Hodgkinson, P.; Emsley, L. *Chem. Phys. Lett.* **2000**, *319*, 253.

(16) Fung, B. M.; Khitrin, A. K.; Ermolaev, K. *J. Magn. Reson.* **2000**, *142*, 97.

(17) Merlet, D.; Emsley, J. W.; Jokisaari, J.; Kaski, J. *Phys. Chem. Chem. Phys.* **2001**, *3*, 4918.

(18) Luz, Z.; Hewitt, R. C.; Meiboom, S. *J. Chem. Phys.* **1974**, *61*, 1758.

(19) Meyer, R. B. *Appl. Phys. Lett.* **1968**, *12*, 281. de Gennes, P. G. *Solid State Commun.* **1968**, *6*, 163.

(20) Panov, V. P.; Balachandran, R.; Nagaraj, M.; Vij, J. K.; Tamba, M. G.; Kohlmeier, A.; Mehl, G. H. *Appl. Phys. Lett.* **2011**, *99*, 261903.

(21) Görtz, V.; Southern, C.; Roberts, N. W.; Gleeson, H. F.; Goodby, J. W. *Soft Matter* **2009**, *5*, 463.