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Chiral solutes can seed the formation of enantiomorphic domains in a twist-bend nematic liquid crystal

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The twist-bend nematic, an enantiomorphic liquid-crystalline phase, exhibited by the structurally symmetric liquid-crystal dimer CB7CB is induced to form a single domain of uniform handedness, in the bulk, by the addition of the dopant chiral solute (S)-1-phenylethanol. Addition of a nonracemic (or scalemic) mixture of both R and S enantiomers of this solute produced equal volumes of P and M chiral domains for the twist-bend nematic phase. This seeding of the domains in an enantiomorphic nematic conglomerate is revealed using deuterium NMR spectroscopy.

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There has been almost 200 years of investigations of the relationship between the chirality of a phase and the symmetry of its components. At the very beginning of this period it was established that single enantiomeric components always produce chiral phases, but also that chiral crystals can be formed from achiral components. Recently, it has been discovered that other enantiomorphic, condensed phases can be prepared from achiral building blocks, such as molecules adsorbed on surfaces, and helical fibers formed by polymerization of achiral monomers [1]. These solid-state systems sometimes form as racemates, that is, intimately mixed enantiomeric forms of opposite chirality, or as conglomerates, which have separate domains of uniform chirality. Until recently there were no known examples of a chiral liquid phase forming without there being an enantiomeric excess amongst the components, and it was therefore very surprising, and intriguing, when an example was discovered of a liquid-crystalline phase which is clearly enantiomorphic, but its constituent molecules are equally clearly achiral [2–4]. A large number of molecules have now been discovered which form these unusual chiral phases and, like the first example, most of them have a bent or V-shaped structure [5]. The majority of the liquid-crystalline phases formed by these V-shaped molecules, including the first example, are chiral, smectic phases. These are true liquid phases, and differ from isotropic liquid phases by having some degree of molecular long-range, orientational order, defined relative to a unit vector, the director, pointing along the preferred direction, and they also possess some degree of long-range translational order. Their enantiomorphism is thought to be determined by the interplay between the bent shape of the mesogenic molecules, a tilt of the directors, and a net polarity within the layers [2–4]. These factors are considered to produce a helical arrangement of the liquid-crystal directors which may be either right (P) or left (M) handed, and in an unconstrained sample these should form with equal probability [2–4]. Even more remarkably, there are also achiral bent-core molecules which show a chiral nematic phase, in which there is no tendency to form layered structures. It was shown that these phases form domains of opposite handedness when grown between glass plates [6–10]. It is not immediately obvious why a nematic phase composed of achiral molecules should form an enantiomorphic phase, since there is no clear constraint on the symmetry of the director distribution, unlike the smectic phases where the presence of layered structures may provide such an effect. One possibility is that the mesogenic, flexible molecules are interconverting between different chiral conformations generated by restricted rotation about their bonds. In the isolated molecule, or one in an isotropic liquid, or a normal nematic phase, the chiral conformations occur in racemic pairs, and hence no net chirality is created. It is possible, however, that in the bent-core nematogens the balance between these pairs is disturbed and a net chirality results. A quite different explanation for why achiral bent-core molecules can form a chiral nematic phase has been proposed by Dozov [11] who pointed out that molecules with a sufficiently bent structure could form nematic liquid-crystalline phases for which the bend elastic constant K_3 is negative, and as a consequence the directors in the nematic phase are predicted to adopt either splay-bend or twist-bend configurations. The twist-bend director configuration has a helical structure with the directors making a constant cone angle ($<90^\circ$) with respect to the helix axis and hence is chiral, while the splay-bend structure is not. The helical structure can adopt a right- or left-handed helicity with equal probability [11]. The bent-core structures have as a "core" a semirigid group, such as a 1,3-disubstituted benzene ring, but although Dozov considered only a rigid, bent molecule, the theory is expected to be applicable to any compound which has, on average, a bent shape. Thus, molecules with a central nonrigid, alkyl chain, and rigid, pendant, mesogenic groups, may also have an average bent shape; for example, the achiral, symmetric molecule CB7CB with its odd spacer, whose molecular structure is shown in Fig. 1(a).

This compound does indeed form both a nonenantiomorphic, uniaxial nematic phase N ($T_{\mathrm{NI}} \sim 116\,^\circ\mathrm{C}$) and at $\sim 103\,^\circ\mathrm{C}$ a chiral, twist-bend nematic phase N_{TB}, as shown by a recent, detailed investigation using a wide range of physical techniques [12]. The higher homologs CB9CB and CB11CB also seem to form the N_{TB} phase, although Panov *et al.* [13] did not identify this as such, but denoted it as an unknown nematic phase, N_X. Although the average structures of odd dimers are

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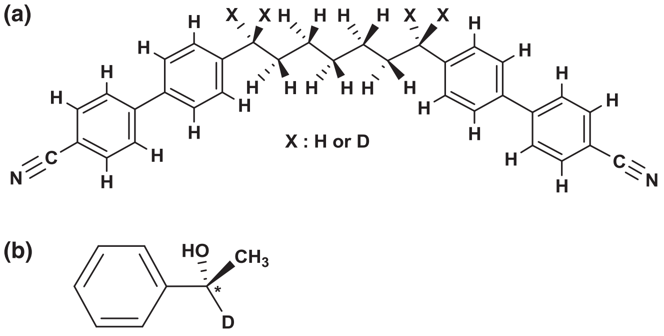

FIG. 1. The structure of (a) 1″,7″-bis(4-cyanobiphenyl-4′-yl) heptane (CB7CB, X = H and CB7CB-d_4, X = D) and (b) (S)-1-phenylethanol-d_1.

bent this is not always sufficient to form the twist-bend nematic phase; what seems to create this are methylene links between the spacer and the mesogenic groups. The relative simplicity of the structure of CB7CB, and similar liquid-crystal dimers, and their ability to form both an achiral nematic as well as the chiral twist-bend phases makes them prime targets for both experimental studies and theoretical modeling.

Most studies on these chiral systems have been concerned with their optical properties, and the thin samples used were contained between glass plates. Their surfaces can align the directors but also influence the formation of the enantiomorphic phase, and examples are known of the formation of samples contained between glass plates with either just one handedness throughout the sample, or in which there are separate domains containing either pure P or M mesophases. There is an advantage in simplifying the system under study by not having the perturbing effects produced by the glass plates, indeed the absence of mirror symmetry for the N_{TB} phase of CB7CB has been unequivocally demonstrated on a bulk sample by both two-dimensional ^{13}C-{^{1}H} proton-encoded local-field NMR experiments, and by ^{2}H NMR [14]. The use of NMR spectroscopy has another major advantage over other methods for studying such samples in that there is a well-defined relationship between the interactions defining the experimental spectra and the structure and orientational order of the constituent molecules. The deuterium NMR spectrum of CB7CB substituted with four deuterons at the 1″,7″ positions in the heptane spacer (CB7CB-d$_4$) is a single quadrupolar doublet when the sample is in the nematic phase, but splits into a pair of doublets when the sample enters the twist-bend phase, which is an unambiguous sign that the latter phase lacks mirror symmetry. These NMR experiments, however, do not reveal whether the sample forms entirely in one of the two, P or M, degenerate helical structures, or whether there are separate regions, so-called domains, of P and M. Using deuterium NMR, we show here that adding a deuterated, chiral solute to a twist-bend nematic phase host does reveal the domain structure of a bulk sample, with a pure enantiomer producing a pure solvent helicity, and a nonracemic mixture of solutes producing equal volumes of both P and M domains.

The expected deuterium NMR spectra given by the solute depends on four possible combinations of solute enantiomorphism and the domain structure of the solvent. For simplicity, but without loss of generality, we consider only a solute, like that used here, which contains just one deuterium site. If the solute is a pure deuterated enantiomer, there are two possible NMR spectra (A1 and A2) which could be observed.

(A1) *The solvent exists in a single domain of either handedness.* A single quadrupolar doublet would be observed with a value for the quadrupolar splitting of either $\Delta\nu_1$ or $\Delta\nu_2$ dependent on the anisotropic, solute (S or R) -solvent (P or M) potential energy, which in general will differ for the combinations: $SM \equiv RP$ and $SP \equiv RM$. It is not possible from these spectra to identify which combinations of solute and solvent enantiomorphism produce which splitting.

(A2) *The solvent has domains of opposite handedness.* A pair of doublets would be observed with quadrupolar splittings of $\Delta\nu_1$ and $\Delta\nu_2$, provided that diffusion of the solute between the solvent domains is slow on the spectroscopic time scale (diffusion rates $\ll |(\Delta\nu_1 - \Delta\nu_2)|$). In this case, the relative doublet intensity I_1/I_2 is determined by how the solute is partitioned between the domains. The relative amounts n_S^M/n_S^P and n_R^P/n_R^M of the enantiomeric solutes S and R in the mirror-image domains M and P are given by

$$n_S^M/n_S^P = K(V^M/V^P) \tag{1}$$

and

$$n_R^P/n_R^M = K(V^P/V^M). \tag{2}$$

Here V^P and V^M are the volumes of the two domains and K is the partition coefficient for the solutes between them. In the limit that K is unity, which is likely given the similar structures of the two solutes and of the two solvent domains, then the relative intensity is equal to the relative volumes of the domains.

If the solute is a mixture of n_S moles of S isomers and n_R moles of R isomers, and again making the reasonable assumption of slow molecular diffusion, then two possible spectra (B1 and B2) may be observed.

(B1) *The solvent is a single domain.* There will be a pair of doublets with quadrupolar splittings $\Delta\nu_1$ and $\Delta\nu_2$ and their relative intensity will equal the ratio n_S/n_R.

(B2) *The solvent exists in two domains with volumes V^M and V^P*. The NMR spectrum will exhibit the same two doublet splittings. Based on the model used in (A2) their relative intensity I_1/I_2 is given by

$$\begin{aligned} I_1/I_2 = {}& \{K n_R V^P/(V^M + KV^P) + K n_S V^M/(V^P + KV^M)\}/ \\ & \times \{n_R V^M/(V^M + KV^P) + n_S V^P/(V^P + KV^M)\}. \end{aligned} \tag{3}$$

If we make the same reasonable assumption concerning the partition coefficient the ratio of intensities is simplified considerably to

$$I_1/I_2 = (n_R V^P + n_S V^M)/(n_R V^M + n_S V^P), \tag{4}$$

and from Eq. (3), when the volumes of the domains are the same, irrespective of the amounts of the enantiomers, the spectral intensities will be equal. In the limit that the domain volumes are the same, then I_1/I_2 is equal to the partition coefficient as we found for case (A2) when there was just a pure enantiomeric solute.

The solvent used in the experiments is CB7CB containing a small amount of CB7CB-d_4; the presence of the deuterated solvent allows the nematic and twist-bend nematic phases to

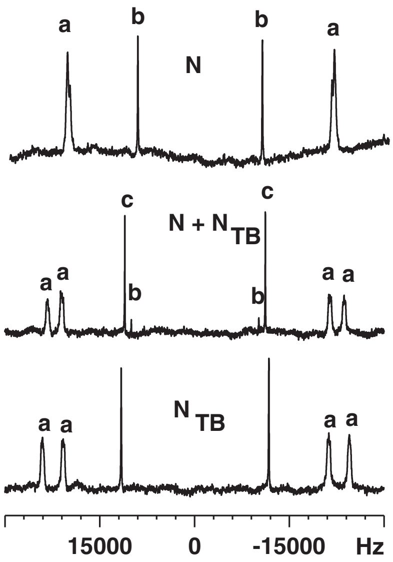

FIG. 2. 61.4 MHz ^{2}H-{^{1}H} spectrum of 2 mg of (S)-1-phenylethanol-d_1 dissolved in 80 mg of the solvent CB7CB + 3 mg of CB7CB-d_4 in (top) the nematic (N) phase at 100 °C; (middle) at the nematic to twist-bend nematic ($N_{\rm TB}$) phase transition at 97 °C; and (bottom) in the twist-bend nematic phase at 95 °C. The labels on the peaks refer to **a**, the solvent CB7CB-d_4; **b**, the solute in the nematic phase; and **c**, the solute in the twist-bend nematic phase. Each spectrum is the result of acquiring 4096 free-induction decays into 29 994 words of computer store, applying an exponential window function of width 30 Hz, zero-filling to 64k before Fourier transformation. The cooling rate was ~1 °C per 10 min.

be clearly distinguished from the deuterium NMR spectra. A sample of (S)-1-phenylethanol-d_1, whose structure is shown in Fig. 1(b), and whose enantiomeric purity (>98%) has been established [15,16], was used to demonstrate the effect of adding a pure enantiomeric solute to CB7CB. A small amount, ~2 mg, was added to 80 mg of the CB7CB + 3 mg of CB7CB-d_4. After raising the temperature of the sample to the isotropic phase it was thoroughly mixed mechanically while being heated outside the spectrometer magnet. The limited amount of sample available dictated the choice of a 3-mm i.d. tube filled to a length of ~10 mm, which was inserted into a normal 5-mm o.d. sample tube. ^{2}H spectra were recorded on a Bruker DRX 400 spectrometer equipped with a ^{2}H selective probe. The deuterium spectra shown in Fig. 2 were obtained for this sample in the N and $N_{\rm TB}$ phases. Note that there is a region of <2 °C when the N and $N_{\rm TB}$ phases coexist, and <1 °C for coexistence of the N and I phases. The three spectra shown in Fig. 2 are consistent with case (A1), namely, that the solvent exists entirely in one domain in the twist-bend nematic phase.

A new sample was prepared by adding 6.3 ± 1 mg of a racemic mixture of the solute to 106 ± 1 mg of (CB7CB + CB7CB-d_4) + 2 ± 1 mg of (S)-1-phenylethanol-d_1; again this was thoroughly mixed outside the magnet. Figure 3 shows spectra of this sample in the pure nematic, in the biphasic, and in the pure twist-bend nematic phases.

The nematic and twist-bend nematic phases coexist in this sample over ~7 °C, and this large biphasic region contrasts with a coexistence region for the nematic and isotropic phases of <2 °C.

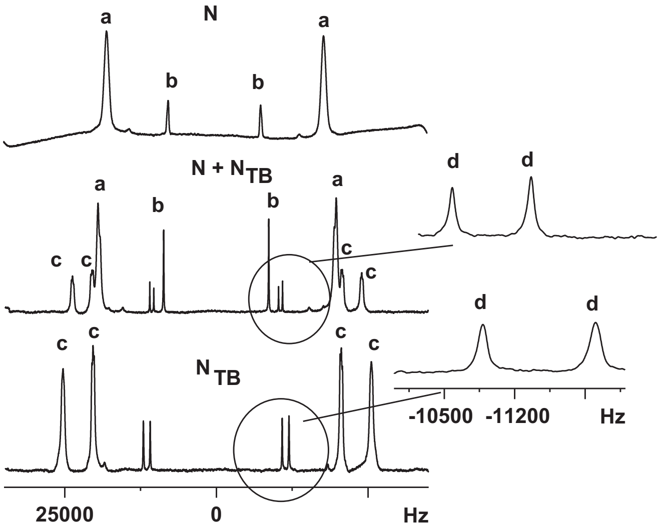

FIG. 3. 61.4 MHz ^{2}H-{^{1}H} spectra of nonracemic (R)- + (S)-1-phenylethanol-d_1 in CB7CB + CB7CB-d_4 in (top) the nematic at 93 °C, (middle) the biphasic at 85 °C, and (bottom) the twist-bend nematic phase at 78 °C. Peaks **a** are from CB7CB-d_4 in the nematic phase; peaks **b** are from the solute in the nematic phase; peaks **c** are from CB7CB-d_4 in the twist-bend nematic phase; and peaks **d** are from the solute in the twist-bend nematic phase. The spectra were each the result of averaging 1024 scans, accumulated into 8k of computer store, an exponential window function of 30 Hz was applied, and the decay was zero filled to 32k before Fourier transformation.

Comparison of the values of the quadrupolar splitting for (S)-1-phenylethanol-d_1 in the twist-bend nematic phase (see Fig. 2) with the two splittings for the solute in the nonracemic mixture of R and S solutes allows us to identify the single splitting for the pure solute in Fig. 2 with the larger of the two splittings for the mixture in Fig. 3. Furthermore, the ^{2}H spectrum recorded for the mixture at the high temperature end of the $N + N_{\rm TB}$ biphasic region, when the concentration of $N_{\rm TB}$ is much less than that of N, has the two peaks for the solute in the $N_{\rm TB}$ phase with the intensity ratio close to the ratio n_S/n_R, which identifies the larger quadrupolar splitting as being for the S solute in either the M or P domains, depending on which combination, SM or SP, has the stronger anisotropic interaction in the mixed sample, and the same combination in the sample containing the pure S solute.

The spectrum in Fig. 3 for the mixture of R and S solutes in the pure twist-bend nematic phase shows two doublets which have a value for I_1/I_2 of 1.04 ± 0.01 (average of the two doublets) compared to the ratio of the amounts of the two enantiomers of 1.62 ± 0.5. From Eq. (1) this value of I_1/I_2 corresponds to a domain volume ratio V^P/V^M of 1.17 ± 0.3, which is equal to unity within experimental error. This demonstrates that the presence of both the R and S enantiomers promotes the formation of two domains for the pure $N_{\rm TB}$ phase, but does not affect their relative volumes.

In conclusion, we have shown that deuterium NMR spectroscopy is a powerful new way of studying how a chiral additive can influence the structure of a chiral liquid-crystalline phase composed of achiral molecules. It is shown that the presence of ~2.4% (~10% mole fraction) by weight of the pure S enantiomer of a chiral compound in the mesogen

CB7CB causes the twist-bend nematic phase to form from the nematic phase as a single *M* or *P* domain on lowering the temperature. This contrasts with the influence of a chiral additive on the domain structure in a chiral smectic phase formed by an achiral, bent-core mesogen [17]. In this case adding ∼30% by weight (∼30% mole fraction) produced a single domain, but smaller amounts gave proportionate amounts of both domains.

There is a more complex development of the solvent domains in the twist-bend nematic phase towards equilibrium for the sample containing a nonracemic mixture of the solute enantiomers as the sample temperature is reduced from the start of the biphasic region until finally the sample is entirely in the twist-bend nematic phase. However, there are equal volumes of the two solvent domains in the pure N_{TB}, which shows, perhaps surprisingly, that domain stability is not affected by the ratio of the amounts of the *S* and *R* forms of the solute when thermal equilibrium has been achieved.

Panov *et al.* [18] have suggested that the potential electro-optic applications of the twist-bend nematic phase require a reliable technique for controlling the domain handedness to be developed. Our results suggest that the addition of a chiral solute would satisfy this need.

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