

# The effect of a chiral nematic solvent on the orientational order and conformational distribution of a flexible prochiral solute

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Deuterium NMR spectroscopy is used to detect the reduction in symmetry which occurs when a flexible, prochiral molecule, 4-pentyl-4'-cyanobiphenyl, is dissolved in a chiral nematic solvent produced by dissolving poly- $\gamma$ -benzyl-L-glutamate in organic solvents. The quadrupolar splittings obtained are used to investigate whether this phenomenon is the result of a reduction in symmetry of the anisotropic, solute-solvent interaction potential or whether the conformational distribution is also affected. It is demonstrated that the first assumption explains the enantiotopic discrimination in chiral liquid crystals and it is possible in this chiral medium to determine the relative configuration of the deuteriums in the methylene groups.

## Introduction

When a molecule interacts with a chiral environment it can be regarded as having an effective point group symmetry, which will differ from that when the molecule is dissolved in an achiral environment by the absence of reflection symmetry. This phenomenon has been demonstrated by NMR spectroscopy for prochiral solutes which have point group symmetries  $C_s$  and  $C_{2v}$ ,  $S_4$  and  $D_{2d}$ <sup>1-6</sup> when dissolved in the chiral nematic solvent formed by dissolving poly- $\gamma$ -benzyl-L-glutamate (PBLG) in an organic solvent. For these prochiral solutes the change in symmetry may be revealed in the NMR spectra by equivalent enantiotopic nuclei, groups of nuclei, or directions becoming non-equivalent when using a chiral nematic solvent. This is seen very clearly in the deuterium or carbon-13 spectra of such solutes.<sup>4-6</sup> For example, the two deuterium nuclei in the methylene group of deuterated ethanol when dissolved in the chiral nematic solvent PBLG/CHCl<sub>3</sub> show separate quadrupolar doublets.<sup>2,5</sup> A quantitative study<sup>4</sup> of this phenomenon on deuterated acenaphthene dissolved in PBLG/CHCl<sub>3</sub> concluded that the change in effective symmetry for this rigid molecule is caused by a reduction in the symmetry of the anisotropic intermolecular solute-solvent interaction energy.<sup>2,3</sup> The consequence of this symmetry reduction is that the orientational order matrix for this rigid solute changes compared to that in achiral nematic solvents, both in the magnitude of the principal components, and the orientation of the principal axes, whilst it is not necessary to invoke a change in the structure of the molecules. The reduction in symmetry has been also observed for other non-rigid molecules.<sup>1,2,5,6</sup>

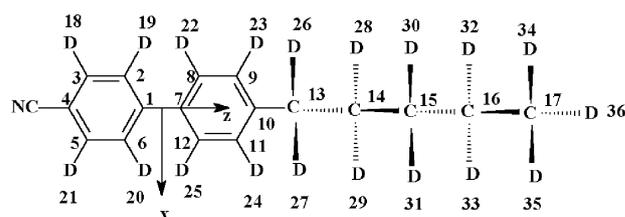
Flexible molecules in a liquid phase will have a distribution amongst the available conformational states, which we can describe by a probability distribution,  $P(\phi_i)$ . The question arises as to whether  $P(\phi_i)$  may also be reduced in symmetry when these molecules are in the chiral nematic phase, and whether this can be detected by NMR. To investigate this question we present here a study of perdeuterated 4-pentyl-4'-cyanobiphenyl (5CB-d<sub>19</sub>) and 4-pentyl-4'-cyanobiphenyl (5CB) embedded in the chiral nematic solvent made of PBLG dis-

solved in an organic solvent. This solute was available from previous studies.<sup>7</sup> The structure of 5CB in its lowest energy conformation is given in Fig. 1. This structure has the alkyl chain orthogonal to the plane of the attached phenyl ring,<sup>8,9</sup> and the chain is in the all-*trans* arrangement.

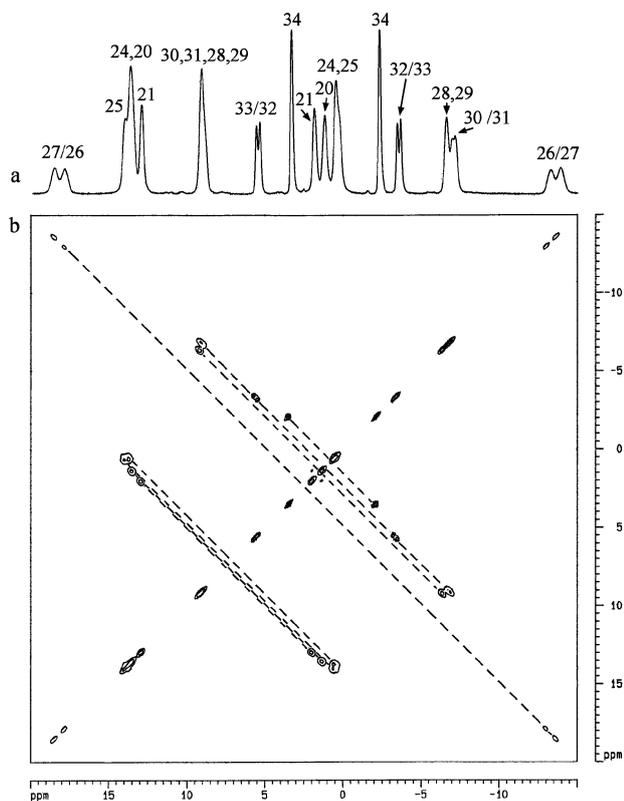
## Results and discussion

### Assignment of the deuterium quadrupolar splittings and determination of their signs

The deuterium 1D spectrum of 5CB-d<sub>19</sub> dissolved in the poly-peptide oriented system can be obtained with a good signal/noise ratio (S/N) after acquiring only a small number of free induction decays. The 1D spectrum is shown for the PBLG/CHCl<sub>3</sub> solvent in Fig. 2a. As the magnitude of <sup>2</sup>H-<sup>2</sup>H scalar and dipolar couplings are very small in the PBLG solvent (generally included inside the linewidth), this 1D spectrum is dominated by quadrupolar splittings,  $\Delta\nu_k$ , and the main task for the spectral analysis is to obtain their magnitude and sign for each deuterium in the molecule. The first step consists of identifying the two components of each quadrupolar doublet, and to assign them to their position in the molecule. This can be achieved using a *Q*-COSY ph 2D experiment.<sup>10</sup> Fig. 2b shows the phased 2D map of 5CB-d<sub>19</sub> in



**Fig. 1** Structure of 5CB in the all-*trans* lowest energy conformation. The cyanylated ring is rotated by about 37° relative to the other ring. The plane containing the carbons C13 to C17 is orthogonal to the plane of the attached ring.



**Fig. 2** Deuterium 1D spectrum (a) and *Q*-COSY Ph 2D spectrum (b) of 5CB-*d*<sub>19</sub> in PBLG/CHCl<sub>3</sub>, both recorded at 300 K. The 2D map was recorded using a data matrix of 1024 (*t*<sub>1</sub>) × 1024 (*t*<sub>2</sub>) data points and the number of free induction decays added for each *t*<sub>1</sub> increment is 48. The 2D spectrum was symmetrized.

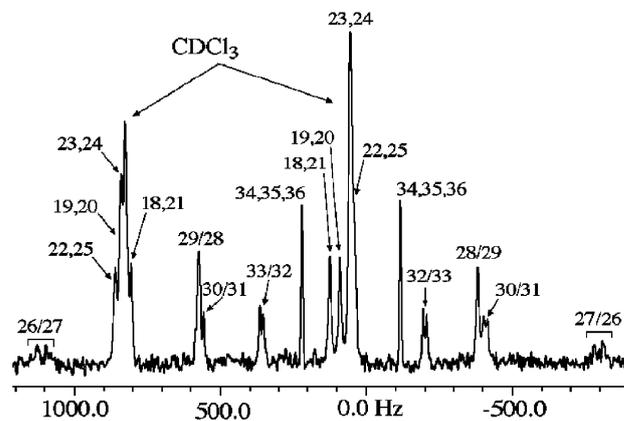
PBLG/CHCl<sub>3</sub>. On this map, the 1D spectrum is on the diagonal whereas the peaks outside of the main diagonal allow the correlation between the two components of a quadrupolar doublet. The chemical shift differences between the isotropic and the liquid crystal samples are expected to be small and can be neglected for the purpose of assignment. It is then possible to assign the quadrupolar doublets of the different deuteriums on the basis of the deuterium chemical shift and this is shown in Fig. 2a. Note here that these spectra exhibit the reduction in nuclear spin symmetry because each pair of deuteriums attached to C-13, C-15, and C-16 (enantiotopic directions) are non-equivalent and have different quadrupolar splittings,  $\Delta\nu_k$  as can be seen in Fig. 2a and 2b.

It is also proved possible to obtain a spectrum of deuteriums at their natural abundance concentration from the sample of 5CB dissolved in the PBLG/CHCl<sub>3</sub> solvent in a 10 mm tube, and this is presented in Fig. 3.<sup>10–12</sup> Although the S/N obtained at natural abundance is much lower than for the enriched sample, a 2D *Q*-COSY experiment, which is more sensitive than the *Q*-COSY ph experiment,<sup>11</sup> could be obtained to correlate the two components of each quadrupolar doublets (not shown).

The second step of the analysis of deuterium spectra in PBLG is to obtain the signs of the quadrupolar splittings. The deuterium spectra are insensitive to the sign of the quadrupolar splittings. This can be done by measuring the <sup>13</sup>C-<sup>1</sup>H dipolar couplings at one bond, <sup>1</sup>*D*<sub>CH</sub>, which can be extracted from the proton-coupled carbon-13 spectrum. The individual proton-coupled carbon signals are dominated by <sup>1</sup>*T*<sub>CH</sub>, the one-bond, total spin-spin coupling, which is related to the scalar and dipolar couplings by

$${}^1T_{CH} = {}^1J_{CH} + 2{}^1D_{CH} \quad (1)$$

Long range proton-carbon couplings only serve to broaden the lines. Nevertheless, we can then determine the signs of <sup>1</sup>*D*<sub>CH</sub>

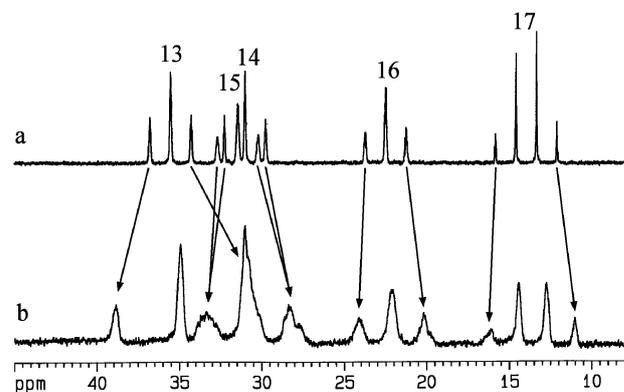


**Fig. 3** 61.4 MHz <sup>2</sup>H-<sup>1</sup>H spectrum of deuteriums at natural abundance level of 5CB dissolved in PBLG/CHCl<sub>3</sub> phase recorded at 310 K in 4.7 h using a recycling delay of 0.5 s. An average of 34000 free-induction decays was obtained.

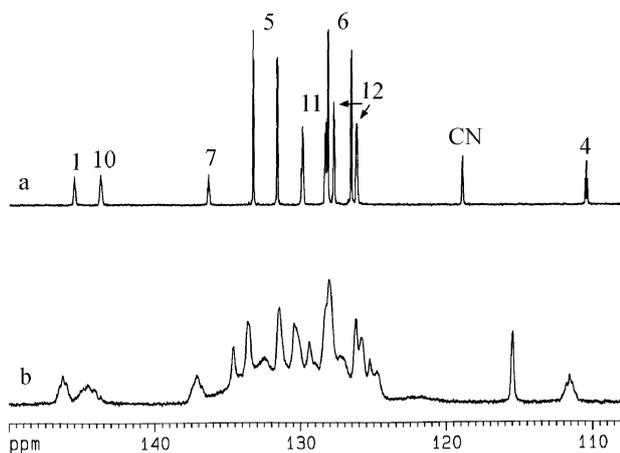
unambiguously, knowing the scalar couplings <sup>1</sup>*J*<sub>CH</sub>, measured on an isotropic sample, which are always positive.<sup>13,14</sup> This is possible because solutes in PBLG are weakly ordered and consequently, in general,  $|{}^1J_{CH}| > |2{}^1D_{CH}|$ .<sup>1,2</sup> Thus, comparing the isotropic and anisotropic <sup>13</sup>C 1D spectra, if the splitting in the isotropic phase is larger (respectively smaller) than in the anisotropic medium, the dipolar couplings is negative (respectively positive). The carbon-13 1D spectra of the aliphatic part for the 5CB dissolved in CDCl<sub>3</sub> solvent and in the PBLG/CHCl<sub>3</sub> phase are shown in Fig. 4a and 4b, respectively. Comparison of the two spectra indicates that the splittings at each site are larger in the PBLG/CHCl<sub>3</sub> solvent than in the isotropic medium, and hence the signs of the one-bond dipolar couplings are all positive. Note that enantiotopic differentiation of the <sup>1</sup>*D*<sub>CH</sub> values is too small to be observed.

The aromatic region of the <sup>13</sup>C spectrum of 5CB in the anisotropic solvent, shown in Fig. 5, is a sum of overlapping lines and it is not trivial to analyse. A so-called *J*-resolved 2D experiment (not presented), which for the PBLG anisotropic solvent depends on the total couplings, *T*<sub>CH</sub>, was recorded to separate these interactions from the <sup>13</sup>C chemical shifts. Each <sup>13</sup>C site shows a spectrum which is the X part of an ABX spin system. Simulation of these spectra shows that again all the one-bond dipolar couplings are positive.

Knowing the sign of the one-bond dipolar couplings, it is now trivial to determine the sign of the quadrupolar splittings  $\Delta\nu_k$ , due to the relationship existing between the two anisotropic data if we assume that the quadrupolar tensor for the



**Fig. 4** 100 MHz proton-coupled carbon-13 spectrum of the aliphatic part of 5CB (a) in CDCl<sub>3</sub> and (b) in PBLG/CDCl<sub>3</sub> both recorded at 300 K.



**Fig. 5** 100 MHz proton-coupled carbon-13 spectrum of the aromatic part (a) in  $\text{CDCl}_3$  and (b) in  $\text{PBLG}/\text{CDCl}_3$  both recorded at 300 K.

deuterium at each site is axially symmetric about the C–D bond direction, namely:<sup>15</sup>

$$\frac{\Delta\nu_k}{^1D_{\text{CH}}} = -\frac{24\pi^3 q_{\text{CD}_k} R_{\text{CH}}^3}{\mu_0 \gamma_C \gamma_H h} \quad (2)$$

From eqn. (2),  $\Delta\nu_k$  and  $^1D_{\text{CH}}$  have always opposite signs, and consequently the sign of all quadrupolar splittings is negative for 5CB. The spectral data are listed in the Table 1.

The composition and temperature of the samples used to obtain the  $^2\text{H}$  spectra of the 5CB-d<sub>19</sub> and 5CB (at natural abundance) are not exactly the same, however, the same ratio was found for the  $^1\text{H}$ – $^{13}\text{C}$  total splitting of the solvent,  $\text{CHCl}_3$ , in the two samples, showing that the orientational order is the same in the two samples. The quadrupolar splittings obtained for these two samples are in a constant ratio of  $1.00 \pm 0.01$ , with maximum deviations from the mean of  $\pm 2\%$ , which is of the order of the error in measuring the peak positions, and so any isotope effect on the 5CB is not distinguishable. This contrasts with the observation by Tabayashi and Akasaka<sup>16</sup> who found a decrease in one quadrupolar splitting of 4% on partial deuteration of the thermotropic liquid crystal 4*N*-propyl-4-(3,4-difluorophenyl) bicyclohexane. They attributed this to a change in the orientational order of the molecules on deuteration, but it is more likely to be a reduction in the quadrupolar splitting produced by a change in the effect of

**Table 1** The quadrupolar splittings,  $\Delta\nu_k$ , in Hz, for the deuterium nuclei in 5CB-d<sub>19</sub> dissolved in the chiral solvents  $\text{PBLG}/\text{CH}_2\text{Cl}_2$  and  $\text{PBLG}/\text{CHCl}_3$ . The splittings obtained for natural abundance deuteriums in 5CB dissolved in the  $\text{PBLG}/\text{CHCl}_3$  solvent are also given. Errors on the quadrupolar splittings are about 6 Hz

	Perdeuterated 5CB		Natural abundance 5CB
	$\text{PBLG}/\text{CH}_2\text{Cl}_2$	$\text{PBLG}/\text{CHCl}_3$	
$\Delta\nu_{18} = \Delta\nu_{21}$	–409	–670	–679
$\Delta\nu_{19} = \Delta\nu_{20}$	–451	–753	–747
$\Delta\nu_{22} = \Delta\nu_{25}$	–458	–796	–790
$\Delta\nu_{23} = \Delta\nu_{24}$	–482	–824	–813
$\Delta\nu_{26}$	–1291	–1887	–1875
$\Delta\nu_{27}$	–1343	–1965	–1937
$\Delta\nu_{28}$	–650	–950	–951
$\Delta\nu_{29}$	–650	–950	–951
$\Delta\nu_{30}$	–664	–970	–956
$\Delta\nu_{31}$	–690	–986	–983
$\Delta\nu_{32}$	–370	–534	–545
$\Delta\nu_{33}$	–395	–558	–570
$\Delta\nu_{34} = \Delta\nu_{35} = \Delta\nu_{36}$	–239	–341	–335

vibrational averaging. Such an effect will be site dependent, and may be either a reduction or an increase in the splittings.

### The relationship between quadrupolar splittings, orientational order and the conformational distribution

**Analysis of quadrupolar splittings.** The analysis of data can be split into two parts corresponding to the quadrupolar splittings for deuteriums in the aromatic rings and in the alkyl chain.

The aromatic part of the molecule is assumed to have a geometry which is independent of the conformations adopted by the alkyl chain. In this case, the four quadrupolar splittings for the ring deuteriums can be related to the angle  $\theta_{\text{CD}_k^z}$ , which the *k*th C–D bond makes with axis *z*, which is fixed in the attached ring, thus we have

$$\Delta\nu_k = 3q_{\text{CD}_k} [S_{zz}(3 \cos^2 \theta_{\text{CD}_k^z} - 1) + (S_{xx} - S_{yy}) \sin^2 \theta_{\text{CD}_k^z}] / 4 \quad (3)$$

where it has been assumed that the quadrupolar tensors are axially symmetric about the CD bond. The observed differences between the quadrupolar splittings for the four equivalent pairs of ring deuterium nuclei could arise because of differences in either the angles  $\theta_{\text{CD}_k^z}$ , or the quadrupolar coupling constants,  $q_{\text{CD}_k}$ . However, neither the  $q_{\text{CD}_k}$  nor the  $\theta_{\text{CD}_k^z}$  values are known.

Deuterium spectra of partially-deuterated samples of pure 5CB show that in the nematic phase the smallest quadrupolar splitting is for one of the pairs in the cyanylated ring, and that the splittings for the other three pairs are very similar, with the larger splittings being assigned to the pair from the alkylated ring.<sup>17</sup> This assignment has been found again here. To investigate the observed non-equivalence of the deuterium nuclei in the chain methylene groups, it is sufficient to consider only the quadrupolar splittings of the deuteriums in the alkylated aromatic ring. For this ring it is assumed that the four C–D bonds are all at an angle of  $60^\circ$  to *z*, and that they have a common value of  $q_{\text{CD}}$  of 185 kHz,<sup>18</sup> and an average quadrupolar splitting of  $-470$  Hz for the  $\text{PBLG}/\text{CH}_2\text{Cl}_2$  solvent for example.

In contrast, the observed quadrupolar splittings for the alkyl chain deuteriums are averages over the conformational distribution created by rotations about the C–C bonds. Thus,

$$\Delta\nu_k = \int P_{\text{LC}}(\{\phi_m\}) \Delta\nu_k(\{\phi_m\}) \{d\phi_m\} \quad (4)$$

where the  $\phi_m$  are angles for rotation about the *m*th C–C bonds. The probability,  $P_{\text{LC}}(\{\phi_m\})$ , that the molecule is in the conformation specified by the set of angles  $\phi_m$ ,  $\{\phi_m\}$ , is dependent on  $U_{\text{LC}}(\beta, \gamma, \{\phi_m\})$ , the mean energy for a molecule in conformation  $\{\phi_m\}$  when the liquid crystalline director makes polar angles  $\beta$  and  $\gamma$  with molecule-fixed reference axes. Thus,

$$P_{\text{LC}}(\{\phi_m\}) = Z^{-1} \int \exp[-U_{\text{LC}}(\beta, \gamma, \{\phi_m\})/k_{\text{B}}T] \sin\beta d\beta d\gamma \quad (5)$$

and

$$Z = \int \exp[-U_{\text{LC}}(\beta, \gamma, \{\phi_m\})/k_{\text{B}}T] \sin\beta d\beta d\gamma \{d\phi_m\}. \quad (6)$$

The  $\Delta\nu_k(\{\phi_m\})$  values are determined by the quadrupolar coupling constant,  $q_{\text{CD}_k}$ , for the deuterium at site *k*, which is assumed to be independent of the rotation angles, and  $S_{\text{CD}_k}(\{\phi_m\})$ , an orientational order parameter for the *k*th CD bond, which is dependent on the conformational state:

$$\Delta\nu_k(\{\phi_m\}) = 3q_{\text{CD}_k} S_{\text{CD}_k}(\{\phi_m\}) / 2. \quad (7)$$

Note that eqn. (7) assumes an axially-symmetric quadrupolar tensor. A value of 168 kHz was used for  $q_{\text{CD}_k}$  for all the alkyl chain deuteriums.<sup>18</sup>

The  $S_{\text{CD}_k}(\{\phi_m\})$  values are averages over the motion of the CD bonds relative to the liquid crystalline director. Thus, if  $\theta_{\text{CD}_k}(\{\phi_m\})$  is the angle the CD bond at site *k* makes with the

director when the molecule is in a conformation defined by the set of angles  $\{\phi_m\}$ , then

$$S_{CD_k}(\{\phi_m\}) = Q^{-1} \int (1/2)(3 \cos^2\theta_{CD_k}(\{\phi_m\}) - 1) \exp[-U_{\text{ext}}(\beta, \gamma, \{\phi_m\})/k_B T] \sin\beta d\beta d\gamma \quad (8)$$

with

$$Q = \int \exp[-U_{\text{ext}}(\beta, \gamma, \{\phi_m\})/k_B T] \sin\beta d\beta d\gamma \quad (9)$$

The anisotropic, conformationally-dependent, mean potential,  $U_{\text{ext}}(\beta, \gamma, \{\phi_m\})$ , is related to the total mean potential,  $U_{\text{LC}}(\beta, \gamma, \{\phi_m\})$ , by

$$U_{\text{LC}}(\beta, \gamma, \{\phi_m\}) = U_{\text{ext}}(\beta, \gamma, \{\phi_m\}) + U_{\text{int}}(\{\phi_m\}) \quad (10)$$

where  $U_{\text{int}}(\{\phi_m\})$  is independent of the orientational order and is given by

$$U_{\text{int}}(\{\phi_m\}) = \sum_m V_m(\phi_m) + U_{\text{steric}} \quad (11)$$

$U_{\text{int}}(\{\phi_m\})$  is expected to be close to the same potential for the isotropic phase.  $V_m(\phi_m)$  is a rotational potential for the  $m$ th bond for the molecule in the isotropic phase of the liquid crystalline solvent. The term  $U_{\text{steric}}$  is required to eliminate strongly, sterically-hindered conformations. It was assumed to have the form

$$U_{\text{steric}} = \sum_i \sum_j [(E_i E_j)^{1/2} ((A_i + A_j)/R_{ij})^{12}]. \quad (12)$$

The summation in eqn. (12) was taken only over deuterium atoms, and only those which are separated by four or more bonds, and the atomic parameters  $E_i$  and  $A_i$  are chosen so as to give a significant contribution to  $U_{\text{int}}(\phi_m)$  only for several sterically-hindered conformers.

For 5CB there are rotations about six bonds, but only five of these need to be considered explicitly. Indeed rotation about the inter-ring bond, C1–C7, can be ignored because  $\Delta\nu_{\text{ring}}$ , the average quadrupolar splittings for the four deuteriums in the alkylated aromatic ring, is used in the calculations. It is completely impracticable when fitting calculated to observed quadrupolar splittings to average the quadrupolar splittings over the complete range of values of the  $\phi_m$ , and the approximation is made that only the minimum energy forms need to be considered for each bond rotation, the so-called rotameric state (RIS) model. Rotations about the three bonds C13–C14 ( $m = 2$ ), C14–C15 ( $m = 3$ ) and C15–C16 ( $m = 4$ ) have three minimum energy positions: *trans* ( $t$ ), the lowest energy, corresponding to  $\phi_{m_0} = 0^\circ$  ( $m = 2, 3, 4$ ), and two equivalent energy states, *gauche*  $+(g^+)$  and *gauche*  $-(g^-)$ , with  $\phi_{m_{\pm 1}} = \pm 112^\circ$ .<sup>19</sup> The rotational potential about the bond linking the ring and chain, C10–C13 ( $m = 1$ ), has two equivalent minimum energy states, in which the C13–C14 bond is in the plane orthogonal to the ring ( $\phi_{1_{\pm 1}} = 90^\circ$  and  $270^\circ$ ).<sup>8</sup> The potential about the last bond in the chain, C16–C17 ( $m = 5$ ) is assumed to have three equal minimum energy structures at  $\phi_{5_{0\pm 1}} = 0^\circ, \pm 120^\circ$ .

To calculate the values of  $\Delta\nu_k$  the additive potential (AP) model for  $U_{\text{ext}}(\beta, \gamma, \{\phi_m\})$  was adopted.<sup>20,21</sup> This is simple to apply and computer simulation studies suggest that it is a reasonable approximation.<sup>22</sup> In the AP model  $U_{\text{ext}}(\beta, \gamma, \{\phi_m\})$  is expressed as

$$U_{\text{ext}}(\beta, \gamma, \{\phi_m\}) = -\varepsilon_{2,0}(\{\phi_m\})C_{2,0}(\beta) - 2\varepsilon_{2,2}(\{\phi_m\})\text{Re } C_{2,2}(\beta, \gamma) \quad (13)$$

where the  $C_{2,0}(\beta)$  and  $C_{2,2}(\beta, \gamma)$  are reduced spherical harmonics. The conformationally-dependent, solute-solvent, interaction parameters,  $\varepsilon_{2,0}(\{\phi_m\})$ , are then simplified to being sums of conformationally-independent contributions,  $\varepsilon_{2,p}(j)$ , from rigid fragments,  $j$ :

$$\varepsilon_{2,n}(\{\phi_m\}) = \sum_{p,j} \varepsilon_{2,p}(j) D_{p,n}^2(\Omega_j). \quad (14)$$

The Wigner functions  $D_{p,n}^2(\Omega_j)$  describe the orientation of fragment  $j$  in a reference frame fixed in a rigid part of the molecule.

## The conformation of the alkyl chain and the conformationally-dependent order parameters of 5CB-d<sub>19</sub> for an achiral nematic environment

Two quadrupolar splittings,  $\Delta\nu_{k,A}$  and  $\Delta\nu_{k,B}$  are expected for each methylene group in the alkyl chain for 5CB in the chiral nematic phase formed by PBLG dissolved in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>. These correspond to the *pro-R* and *pro-S* deuteriums which are discriminated in this chiral oriented phase, but it is not possible to assign these splittings by NMR spectroscopy, and therefore the labels A and B are used. Taking the average  $\langle \Delta\nu_k \rangle_{A,B} = (\Delta\nu_{k,A} + \Delta\nu_{k,B})/2$  gives the value of the splittings that would be expected for 5CB embedded in an achiral nematic solvent formed by equimolar amounts of PBLG and PBDG, the enantiomer of PBLG, dissolved in CHCl<sub>3</sub>.<sup>23</sup> These average splittings were then used to determine the conformational distribution, and conformationally-dependent order parameters expected for 5CB in an achiral ‘‘PBG’’ nematic phase, and then to repeat the calculations, using the values of  $\Delta\nu_{k,A}$  and  $\Delta\nu_{k,B}$  to determine the effect of lowering the symmetry of the chiral phase. For all calculations it was necessary to assume a geometry for the alkyl chain, and this is given in Table 2, and is based on a X-ray diffraction study of 5CB in the solid, crystalline phase for the positions of the carbon and nitrogen atoms.<sup>24</sup> The deuterium positions are such that the CD<sub>2</sub> planes bisect the CCC angle, and the all DCD angles are 109.47°.

In order to fit calculated and observed values of  $\langle \Delta\nu_k \rangle_{A,B}$ , it is necessary to vary the parameters defining the conformational distribution, which are the energy differences  $E_{ig}(m)$ , and the fragment interaction parameters,  $\varepsilon_{2,p}(j)$ . The C–C bonds in the alkyl chain are assumed to be cylindrically symmetric, thus only  $\varepsilon_{2,0}(\text{CC})$  is non-zero, and this is assumed to be the same for each bond. Similarly the C–D bonds in the chain each contribute just  $\varepsilon_{2,0}(\text{CD})$ . The ring is assumed to have  $C_{2v}$  symmetry and contributes  $\varepsilon_{2,0}(\text{R})$  and  $\varepsilon_{2,2}(\text{R})$ . In fact, it is more convenient in the calculations to use a cartesian rather than a spherical tensor representation, and so the fragment interaction parameters are:

$$\varepsilon_{\text{CC}} = (3/2)^{1/2} \varepsilon_{2,0}(\text{CC})$$

$$\varepsilon_{\text{CD}} = (3/2)^{1/2} \varepsilon_{2,0}(\text{CD})$$

$$\varepsilon_{zz} = (3/2)^{1/2} \varepsilon_{2,0}(\text{R})$$

$$\varepsilon_{xx} - \varepsilon_{yy} = 2\varepsilon_{2,2}(\text{R})$$

The potentials,  $V_m(\phi_m)$ , for rotation about bonds C13–C14, C14–C15 and C15–C16 were assumed to be equal so that the energy of a conformer specified by the three bond rotation angles is given by

$$E(\phi_{13,14}\phi_{14,15}\phi_{15,16}) = V(\phi_{13,14}) + V(\phi_{14,15}) + V(\phi_{15,16}) + U_{\text{steric}} \quad (15)$$

**Table 2** Bond lengths and angles assumed for the alkyl chain of 5CB. The CD<sub>2</sub> planes bisect the CCC angles in the chain

$i,j$	$R(i,j)/\text{\AA}$	$i,j,k$	$\theta(i,j,k)/^\circ$
10,13	1.501	10,13,14	115.0
13,14	1.515	13,14,15 <sup>a</sup>	113.5
14,15	1.529	10,13,26 <sup>b</sup>	108.07
15,16	1.480	26,13,27 <sup>c</sup>	109.47
16,17	1.503	13,14,28 <sup>d</sup>	108.45
All C–D	1.10	16,17,34 <sup>e</sup>	109.47

<sup>a</sup> Equals 14,15,16 and 15,16,17. <sup>b</sup> Equals 10,13,27. <sup>c</sup> All DCD angles are equal to the tetrahedral angle 109.47°. <sup>d</sup> Equals 13,14,29 = 14,15,30 = 14,15,31 = 15,16,32 = 15,16,33. <sup>e</sup> The methyl group has all angles equal to 109.47°.

For each bond, the bond rotation angles associated to each gauche forms have identical value so that there is a contribution  $E_{tg}$  to each conformation for every  $g\pm$  configuration in the conformer. The steric term was calculated from eqn. (12).

There are six observed values of  $\langle\Delta\nu_k\rangle_{A,B}$  for 5CB in "PBG", and so only two parameters defining the conformational distribution can be varied. The steric parameters are not independent, and so the fitting procedure proceeded by varying  $\varepsilon_{zz}$ ,  $\varepsilon_{xx} - \varepsilon_{yy}$ ,  $\varepsilon_{CC}$ ,  $\varepsilon_{CD}$ ,  $E_{tg}$  and  $A_D$  with  $E_D$  fixed, which gives a finite, minimum RMS value, and the procedure was then repeated using the variables  $\varepsilon_{zz}$ ,  $\varepsilon_{xx} - \varepsilon_{yy}$ ,  $\varepsilon_{CC}$ ,  $\varepsilon_{CD}$ ,  $E_{tg}$  and  $E_D$  with  $A_D$  fixed at the previously optimised value. Starting with values of  $A_H$  and  $E_H$  given by Allen and Tildesley,<sup>25</sup> and considering  $A_H = A_D$  and  $E_H = E_D$ , the best fit to the mean quadrupolar splittings,  $\langle\Delta\nu_k\rangle_{A,B}$ , for 5CB-d<sub>19</sub> in "PBG"/CH<sub>2</sub>Cl<sub>2</sub> is obtained with  $A_D = 0.85$  Å, and  $E_D = 0.15$  kJ mol<sup>-1</sup>. These values of  $A_D$  and  $E_D$  were then kept fixed when fitting the values of  $\langle\Delta\nu_k\rangle_{A,B}$  for 5CB-d<sub>19</sub> in "PBG"/CHCl<sub>3</sub> and 5CB in "PBG"/CHCl<sub>3</sub> by varying just  $\varepsilon_{zz}$ ,  $\varepsilon_{xx} - \varepsilon_{yy}$ ,  $\varepsilon_{CC}$ ,  $\varepsilon_{CD}$ , and  $E_{tg}$  with the results shown in Table 3.

The values of  $E_{tg}$  obtained for the three sets of values of  $\langle\Delta\nu_k\rangle_{A,B}$  for 5CB in the "PBG" solutions are essentially identical, and similar in magnitude to the value of 2.1 kJ mol<sup>-1</sup> suggested by Flory<sup>26</sup> for use in calculations involving alkyl chains by the RIS model, and so can be regarded as appropriate for 5CB dissolved in CH<sub>2</sub>Cl<sub>2</sub> or CHCl<sub>3</sub>, with perhaps a small contribution from the presence of the "PBG" molecules. The value of  $E_{tg}$  found for pure 5CB is considerably larger, so that *trans* configurations are favoured more strongly.

The discrete conformational distributions,  $P_{LC}(n)$  with  $n = 27$ , for 5CB in these samples is affected by the  $E_{tg}$  values, and also by the steric repulsion term. In principle, the  $P_{LC}(n)$ 's are also dependent on the orientational order of the molecules. Thus, the conformational probabilities for the molecule in the ordered phase,  $P_{LC}(n)$  for a discrete number of conformations is given by

$$P_{LC}(n) = Z^{-1} \int \exp[-U_{LC}(\beta, \gamma, n)/k_B T] \sin\beta d\beta d\gamma \quad (16)$$

with

$$Z = \sum_n \int \exp[-U_{LC}(\beta, \gamma, n)/k_B T] \sin\beta d\beta d\gamma. \quad (17)$$

In general this will differ from  $P_{iso}(n)$ , the probability for a conformation in an isotropic phase of the same solvent, which is given by

$$P_{iso}(n) = Z_{iso}^{-1} \exp[-U_{int}(n)/k_B T] \quad (18)$$

with

$$Z_{iso} = \sum_n \exp[-U_{int}(n)/k_B T]. \quad (19)$$

Note first that including the steric repulsion term in eqn. (15) dramatically reduces the probabilities,  $P_{LC}(n)$ , of the conformers  $tg \pm g\mp$ ,  $g\pm g\mp g\pm$ , and  $g\pm g\pm g\mp$  for both pure 5CB and 5CB in the achiral "PBG" solutions, as shown in Figs. 6a and 6c.

**Table 3** The energy differences,  $E_{tg}$ , and the fragment interaction parameters, both in kJ mol<sup>-1</sup> which produce the best agreement between calculated and observed values of the averaged quadrupolar splittings,  $\langle\Delta\nu_k\rangle_{A,B}$  for samples of 5CB-d<sub>19</sub> dissolved in the solvents (a) "PBG"/CH<sub>2</sub>Cl<sub>2</sub> and (b) "PBG"/CHCl<sub>3</sub>, and (c) for deuteriums at natural abundance for 5CB in the achiral solvent "PBG"/CHCl<sub>3</sub>. Data is also shown, (d) for pure 5CB-d<sub>15</sub> in the nematic phase at 286 K

Parameters (a)	(b)	(c)	(d)	
$\varepsilon_{zz}$	0.340±0.003	0.450±0.005	0.450±0.003	14.51±0.02
$\varepsilon_{xx} - \varepsilon_{yy}$	-0.021±0.003	-0.042±0.003	-0.040±0.003	2.93±0.01
$\varepsilon_{CC}$	0.440±0.005	0.555±0.01	0.562±0.005	18.11±0.04
$\varepsilon_{CD}$	0.222±0.005	0.278±0.005	0.282±0.005	8.93±0.02
$E_{tg}$	2.61±0.002	2.61±0.002	2.58±0.01	3.27±0.001

If the orientational order is large, then these two probabilities are significantly different, but for low order, as is the case for the "PBG" solutions, then they are essentially the same. The results obtained for 5CB-d<sub>19</sub> in the "PBG"/CH<sub>2</sub>Cl<sub>2</sub> and "PBG"/CHCl<sub>3</sub> solutions shows that the conformational distributions  $P_{iso}(\phi_{im})$  for 5CB in these two solvents have a small, but significant difference, which is certainly a reasonable result given that rotational potentials in general are solvent dependent, and that the two solvents are quite similar.

However, it should be noted that these conformers are of low probability even without inclusion of the steric term, and the improvement in the fit of the data is dependent more on how the probabilities are re-distributed amongst the other conformers. If the orientational order is large, then  $P_{LC}(n)$  and  $P_{iso}(n)$  are significantly different, as shown in Fig. 6b for pure 5CB, but for low order, as is the case for the achiral "PBG" solutions, then they are essentially the same. Note too that the distributions derived from values of  $\langle\Delta\nu_k\rangle_{A,B}$  for 5CB in the three different "PBG" samples are essentially equal, and only data for the "PBG"/CH<sub>2</sub>Cl<sub>2</sub> solution are shown in Fig. 6.

Fig. 6d compares  $P_{iso}(n)$  for pure 5CB and 5CB in achiral "PBG"/CH<sub>2</sub>Cl<sub>2</sub>. The two distributions are clearly different which is attributed to an intermolecular effect. The largest difference is in the probabilities of the all-*trans* conformer, for which there is a reduction from 0.311 in pure 5CB to 0.222 for 5CB in achiral "PBG"/CH<sub>2</sub>Cl<sub>2</sub>, which is a consequence of the differences noted earlier between the values of  $E_{tg}$  obtained for 5CB in these two samples.

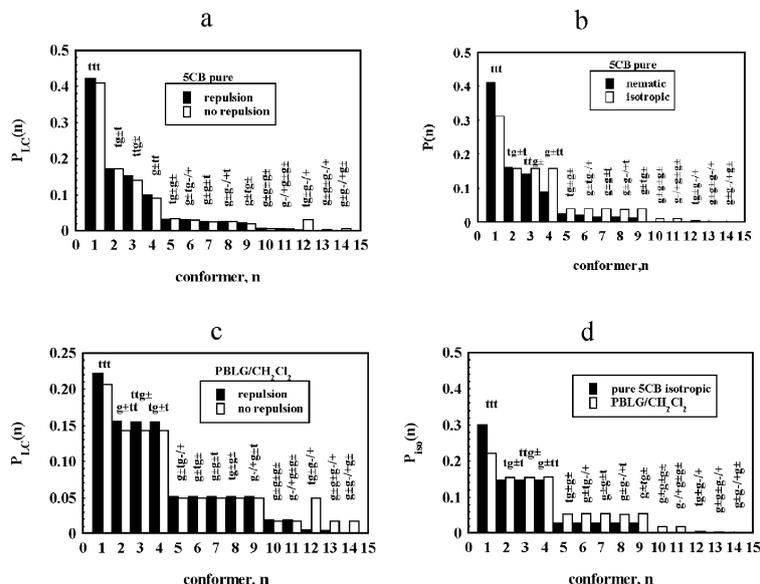
#### Fitting the calculated to the observed quadrupolar splittings $\Delta\mu_{k,A}$ and $\Delta\mu_{k,B}$ for 5CB-d<sub>19</sub> dissolved in the PBLG chiral nematic solvents.

It is not certain what is the origin of the doubling of some splittings observed in the deuterium spectrum of 5CB-d<sub>19</sub> dissolved in the chiral nematic solvent. Assuming that the origin is a reduction in symmetry of the anisotropic, solute-solvent potential,  $U_{ext}(\beta, \gamma, \{\phi_m\})$ , then the question arises of how to introduce this into the AP model? The simplest way to do this is to make the values of  $\varepsilon_{CD}$  differ for C–D bonds on each methylene group, that is having  $\varepsilon_{CD26} = \varepsilon_{CD28} = \varepsilon_{CD30} = \varepsilon_{CD32}$ , and  $\varepsilon_{CD27} = \varepsilon_{CD29} = \varepsilon_{CD31} = \varepsilon_{CD33}$ , whilst the three values for the C–D bonds in the CD<sub>3</sub> group are equal. This gives a good, but not perfect agreement between observed and calculated quadrupolar splittings for each of the three sets of data, with the assignment of the splittings shown in Table 1. The mean square error obtained is equal to 2.6 Hz. Reversing any one of the assignments at the methylene groups produces an unacceptably poor fit to the data. Reversing all assignments together is equivalent to re-labelling the deuteriums since the data cannot distinguish between the directions  $x$  and  $-x$ . It is possible, therefore, to determine the relative, but not absolute, configuration (*pro-R* or *pro-S* character) of the deuteriums.

An exact fit to the data is obtained by allowing the interaction parameters to be different for all C–D bonds, with the values given in Table 4.

#### Is the symmetry of the bond rotational potentials reduced in a chiral environment?

Although the non-equivalence of the deuterium nuclei in the methylene groups of 5CB-d<sub>19</sub> dissolved in the chiral nematic solvent can be explained in terms of a fixed conformational distribution, but with a reduction in symmetry of the solute-solvent anisotropic potential, it is interesting to explore an alternative explanation. Indeed, it is possible that the rotation potentials could also be influenced by the environment, and could be reduced in symmetry. The reduction in symmetry has to destroy the reflection symmetry within the methylene groups. For the bond C10–C13 this symmetry reduction could



**Fig. 6** The conformational distributions obtained for: (a) pure 5CB in the nematic phase at 286 K, showing the effect of the inclusion of a steric repulsion in the intermolecular interaction potential; (b)  $P_{LC}(n)$  and  $P_{iso}(n)$  pure 5CB at 286 K demonstrating the effect of the orientational order on the distributions; (c) 5CB dissolved in the achiral "PBG"/ $\text{CH}_2\text{Cl}_2$  nematic phase; (d)  $P_{iso}(n)$  for pure 5CB and for 5CB dissolved in the achiral "PBG"/ $\text{CH}_2\text{Cl}_2$  solvent.

be a shift in the position of the energy minima from  $90^\circ$  and  $270^\circ$ . This alone does not explain the data. Thus an attempt to fit the data by varying the angle of twist,  $\alpha$ , away from  $90^\circ$  and  $270^\circ$ , and the interaction parameter set  $\epsilon_{zz}$ ,  $\epsilon_{xx} - \epsilon_{yy}$ ,  $\epsilon_{CC}$ , and  $\epsilon_{CD}$  equal for all C–D bonds, produces an unacceptably large error.

An asymmetry was introduced also in the potentials for the bonds C13–C14, C14–C15 and C15–C16 by making the two gauche forms non-equivalent in energy by raising one and lowering the other by the same amount,  $\Delta E_{ig}(i,j)$ , giving two values,  $E_{ig+}(i,j) \neq E_{ig-}(i,j)$  for each bond rotation, but keeping their positions fixed at  $\pm 112^\circ$ . Varying the eight parameters  $\alpha$ ,  $\Delta E_{ig}(13,14)$ ,  $\Delta E_{ig}(14,15)$ ,  $\Delta E_{ig}(15,16)$ ,  $\epsilon_{zz}$ ,  $\epsilon_{xx} - \epsilon_{yy}$ ,  $\epsilon_{CC}$ , and  $\epsilon_{CD}$  equal for all C–D bonds, gives almost exact agreement between the 10 observed and calculated quadrupolar splittings, for each of the three sets of data. The results for the three sets of data are very similar, and in Table 5 only the results for the PBLG/ $\text{CH}_2\text{Cl}_2$  are given.

The changes in  $E_{ig}$  for bonds C14–C15 and C15–C16 are both about 15%, which compares with changes in the values of  $<1\%$  in  $\epsilon_{CH}$  required to produce the observed differences in

**Table 4** The fragment interaction parameters, in  $\text{kJ mol}^{-1}$ , obtained by bringing the calculated values of the quadrupolar splittings into best agreement with those observed for 5CB- $d_{19}$  dissolved in the chiral nematic solvents PBLG/ $\text{CH}_2\text{Cl}_2$  and PBLG/ $\text{CHCl}_3$  and deuterium at natural abundance for 5CB dissolved in PBLG/ $\text{CHCl}_3$

	5CB- $d_{19}$ in PBLG/ $\text{CH}_2\text{Cl}_2$	5CB- $d_{19}$ in PBLG/ $\text{CHCl}_3$	5CB in PBLG/ $\text{CHCl}_3$
$\epsilon_{zz}$	0.340	0.450	0.450
$\epsilon_{xx} - \epsilon_{yy}$	-0.021	-0.042	-0.040
$\epsilon_{CC}$	0.450	0.555	0.562
$\epsilon_{CD26}$	0.2235	0.2796	0.2831
$\epsilon_{CD27}$	0.2212	0.2764	0.2803
$\epsilon_{CD28}$	0.2217	0.2803	0.2833
$\epsilon_{CD29}$	0.2203	0.2786	0.2818
$\epsilon_{CD30}$	0.2237	0.2771	0.2823
$\epsilon_{CD31}$	0.2217	0.2756	0.2801
$\epsilon_{CD32}$	0.2217	0.2803	0.2831
$\epsilon_{CD33}$	0.2200	0.2789	0.2813
$\epsilon_{CD34} = \epsilon_{CD35} = \epsilon_{CD36}$	0.2225	0.2784	0.2821

**Table 5** The values of  $\alpha$ , the angle of twist about the bond C10–C13, the energy differences (in  $\text{kJ mol}^{-1}$ )  $E_{ig+}(i,j)$  and  $E_{ig-}(i,j)$  for rotation about bonds C13–C14, C14–C15 and C15–C16, and the interaction parameters,  $\epsilon_{zz}$ ,  $\epsilon_{xx} - \epsilon_{yy}$ ,  $\epsilon_{CC}$ , and  $\epsilon_{CD}$  equal for all C–D bonds, in  $\text{kJ mol}^{-1}$  obtained by fitting calculated to observed quadrupolar splittings of deuteriums in 5CB- $d_{19}$  dissolved in the chiral nematic solvent PBLG/ $\text{CH}_2\text{Cl}_2$

$\alpha/^\circ$	4.3
$E_{ig+}(13,14)$	2.610
$E_{ig-}(13,14)$	2.613
$E_{ig+}(14,15)$	2.401
$E_{ig-}(14,15)$	2.822
$E_{ig+}(15,16)$	2.809
$E_{ig-}(15,16)$	2.415
$\epsilon_{zz}$	0.3400
$\epsilon_{xx} - \epsilon_{yy}$	-0.0210
$\epsilon_{CC}$	0.4400
$\epsilon_{CD}$	0.2217

quadrupolar splittings at each methylene group. This suggests that the non-equivalencies in the quadrupolar splittings at the methylene groups can be attributed mainly to a change in the anisotropic potential rather than to a change in the structure and conformer distribution.

## Conclusion

We have shown that it is possible to analyse the  $^2\text{H}$  and  $^{13}\text{C}$  NMR spectra given by samples of 5CB dissolved in liquid crystalline solutions of PBLG/organic solvents to yield the magnitude and signs of the deuterium quadrupolar splittings. The conformational distributions derived from the average quadrupolar splittings,  $(\Delta\nu_A + \Delta\nu_B)/2$  for 5CB in the PBLG/ $\text{CH}_2\text{Cl}_2$  and PBLG/ $\text{CHCl}_3$  nematic solvents, that is, for an achiral environment, are found to be significantly different from the distribution derived in the same way for pure 5CB in the nematic phase. Thus,  $P_{LC}(tt)$  the probability of the all-*trans* conformer in the nematic phase is 0.42 for pure 5CB at 286 K, and 0.22 when 5CB is dissolved in the PBLG solutions. A considerable part of this difference is attributable to the effect of the orientational order of 5CB in these different solvents, which is large for the strongly ordered pure 5CB and small for the weakly ordered PBLG samples. The theoretical model used

to derive the conformer distributions also provides values of  $P_{\text{iso}}(n)$ , the probabilities at the same temperature but without the contribution from orientational order of the molecules. Now,  $P_{\text{iso}}(\text{all-trans})$  reduces to 0.31 for pure 5CB, whilst the values of  $P_{\text{iso}}(\text{all-trans})$  and  $P_{\text{LC}}(\text{all-trans})$  are essentially equal at 0.22 for the PBLG solutions. The differences in  $P_{\text{iso}}(n)$  for 5CB in the pure nematic and PBLG solutions is attributed to a solvent effect on the isotropic, intermolecular potentials. This hypothesis should be tested by obtaining conformational distributions for 5CB in other, different environments and phases.

It should be noted that the conformational distributions obtained are subject to systematic errors arising from both the geometrical assumptions invoked, and, more importantly, the assumption that only *trans* and *gauche* forms are populated. However, the effect of these assumptions on the distributions obtained will be similar for pure 5CB and 5CB dissolved in the PBLG solutions. Hence the differences in the distributions for these different environments are more significant than the absolute values of the probabilities of individual conformers.

The reduction in symmetry of the nuclear spin system of 5CB and 5CB- $d_{19}$  when dissolved in the chiral nematic phase can be explained as being either a reduction in symmetry only of the solute-solvent, anisotropic interaction potential, or a change in symmetry only of the bond rotational potentials, or indeed of a combination of the two effects.

The reduction in symmetry of the anisotropic, intermolecular interaction potential was achieved by making the interaction parameters  $\epsilon_{\text{CH}}$  at each methylene site differ by only about 1%. In contrast, attributing the observed differences in quadrupolar splittings at the methylene sites entirely to changes in the bond rotational potentials requires changes of up to 15%, and hence is the less likely source of the observed changes in symmetry. Further support for attributing the observed reduction in symmetry of the methylene deuterium sites to changes only in the anisotropic, intermolecular interaction potential,  $U_{\text{ext}}(\beta, \gamma, \phi_m)$ , is the observation of similar effects in rigid molecules, which can be explained by changes in  $U_{\text{ext}}(\beta, \gamma, \phi_m)$  by similar orders of magnitude.

Finally, we note that using the additive potential model for the conformation dependence of the anisotropic, intermolecular mean potential allowed the determination of the relative configuration of the deuteriums of the alkyl chain in 5CB. This suggests that the relative configuration of other flexible pro-chiral compounds can be determined in the same way. Such results could be extended to the determination of relative configuration in flexible molecules which are chiral by virtue of isotopic substitution (R-CHD-CHD-R').<sup>27</sup>

## Experimental section

A sample of the perdeuterated compound was prepared, which contained 5CB- $d_{19}$  (106 mg, *i.e.* 14.5% w/w), PBLG (100 mg, DP = 1279) and  $\text{CH}_2\text{Cl}_2$  (525 mg) in a 5 mm NMR tube. To obtain the results in another co-solvent, after evaporation of the  $\text{CH}_2\text{Cl}_2$ , the same sample was used but with  $\text{CHCl}_3$  (353 mg, *i.e.* 18.9% w/w of 5CB- $d_{19}$ ). Another oriented sample was prepared to study 5CB using the natural abundance deuterium NMR spectroscopy. For this, 5CB (430 mg, *i.e.* 14.4% w/w), PBLG (450 mg, DP = 1352) and  $\text{CHCl}_3$  (2110 mg) were mixed in a 10 mm NMR tube, and the tube was sealed to avoid solvent evaporation. For carbon-13 studies, a sample of 5CB

(100 mg, *i.e.* 18.2% w/w), PBLG (100 mg) and  $\text{CDCl}_3$  (350 mg) was prepared in a 5 mm NMR tube. In order to achieve spectra with narrow lines, for each sample, the tubes were centrifuged back and forth several times. Various practical details for the sample preparation and NMR spectroscopy in PBLG can be found in ref. 28.

The deuterium NMR spectra were obtained with a Bruker MSL 200 spectrometer and a Bruker DRX 400 (for the natural abundance experiment), the  $^{13}\text{C}$  NMR spectra were recorded at 100 MHz with a Bruker DRX 400 spectrometer. Other experimental details are given in the figure captions.

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