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$^2\text{H-N.M.R.}$ studies of flexibility and orientational order in nematic liquid crystals

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Deuteron magnetic resonance spectroscopy ($^2\text{H-N.M.R.}$) has been used to investigate the effect of the nematic environment on the flexibility and orientational order of two perdeuterated cyanobiphenyl homologues: 4-methyl-4'-cyanobiphenyl (1CB- d_{11}) and 4-*n*-pentyl-4'-cyanobiphenyl (5CB- d_{19}). The systems studied were low concentrations of 1CB- d_{11} and 5CB- d_{19} dissolved in the nematic phases of 5CB, *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline (EBBA), Merck ZLI-1132 (1132) and a 55 wt % mixture of 1132:EBBA. The spectra are dramatically different in these environments. Previous studies on small solutes have suggested that in the 55 wt % 1132:EBBA mixture (at 301.4 K) the dominant orienting mechanism depends on the size and shape of the molecule which suggests that it is a short range repulsive interaction. This interaction has been modelled by treating the liquid crystal as an elastic continuum and the solute as a collection of van der Waals spheres which stretch the liquid crystal in the two dimensions perpendicular to the director. The distortion of the liquid crystal depends on the dimensions of the solute, and the elastic energy is described in terms of a Hooke's law force constant, k . The model is extended to include flexible liquid crystal molecules and quadrupolar couplings are calculated for each conformation of the 5CB chain. Statistical averaging over all conformations gives an excellent fit to the experimental spectrum. The results for 1CB and 5CB show that in the other nematic phases contributions from additional mechanisms must be included. Previous studies of $^2\text{H}_2$ and other solutes indicate that the additional mechanism is the interaction between the solute molecular quadrupole moment and the mean electric field gradient of the liquid crystal.

1. Introduction

The interactions responsible for orientational order in liquid crystals are not well understood. A major problem is that the liquid crystal molecules have little symmetry and normally exist in a number of possible conformations. In order to predict results from experiment it is necessary to average molecular properties over all possible conformations, and to describe properly the interactions present in each conformation.

On the other hand, studies of solutes in liquid crystals have yielded valuable information about the intermolecular forces acting in nematic phases. For example, studies using molecular $^2\text{H}_2$ have demonstrated the existence of an average electric field gradient in many nematic liquid crystals [1,2]. The interaction of this field gradient with the molecular quadrupole moment of $^2\text{H}_2$ explains most of the orientation of this solute in these liquid crystals [1-4]. While this mechanism has also been

found to be important for the orientation of other small solutes [3–7], experiments show that there is at least one additional orienting mechanism. The most convincing experiments involve the use of a mixture of the liquid crystals 1132 and EBBA. The spectrum of $^2\text{H}_2$ in a 55 wt % mixture of 1132 in EBBA at 301.4 K indicates that the electric field gradient at the ^2H nuclei is zero. However, an additional mechanism must be invoked to explain the non-zero orientation of $^2\text{H}_2$ and other solutes in this mixture. A possible candidate for this additional mechanism is the short range repulsive interaction which will become increasingly important for larger molecules. To account for this mechanism we have modelled the solute as a collection of van der Waals spheres which distort the elastic continuum of the liquid crystals [3–5]. Calculations for small solutes of various symmetries are in excellent agreement with experimental results [3–8].

In this paper we shall deal with larger molecules, that is the liquid crystal molecules themselves are treated as solutes. The objective is to see to what extent the theories developed for small solutes can be extended to treat the larger, flexible molecules. The molecule 1CB, which is non-mesogenic and the first homologue of the $n\text{CB}$ series of liquid crystals, is used to bridge the gap between the small solutes and the liquid crystals. The liquid crystal molecule chosen for study is 5CB because it has a limited number of relatively well defined conformations. Additionally, 5CB has been the subject of several previous investigations [9–12]. The axis system used to describe 5CB (and 1CB) is given in figure 1.

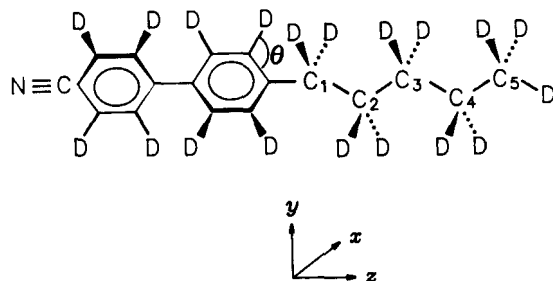


Figure 1. Axis system used to define the 5CB molecule. Calculations are based on the following geometrical parameters: dihedral angle between rings = 30° [11]; the y axis makes an angle of $\pm 15^\circ$ with each ring; the x and y axes for each conformer bisect the two ring planes; the first methylene group of the alkyl chain of 5CB is fixed with the HH direction parallel to the plane of the adjacent benzene ring; aromatic ring angles are taken at 120° ; aliphatic CCC angles = 112.5° ; aliphatic CCH angles = 108.82° ; aliphatic HCH angles = 109.0° ; aliphatic chain gauche rotation dihedral angle = 112.0° ; tetrahedral angles are used for the methyl group.

2. Experimental

The liquid crystal ZLI-1132 was obtained from Merck and was not purified prior to use. This is a eutectic mixture of alkylcyclohexylcyanobenzene and alkylcyclohexylcyanobiphenyls [13]. The *N*-(4-ethoxybenzylidene)-4'-*n*-butylaniline (EBBA) was synthesized according to [14]. The preparation of the deuterated cyanobiphenyls was achieved by bromination, followed by cyanation of the appropriately deuterated alkyl biphenyls. The 4-methylbiphenyl- d_{12} was prepared from the sulphonate ester of methanol- d_4 . The aromatic rings were deuterated at high temperature in $^2\text{H}_2\text{O}/^2\text{HCl}$ [15]. The 4-*n*-pentylbiphenyl was perdeuterated at high temperature with $^2\text{H}_2\text{O}$ in the presence of platinum catalyst and NaO^2H [16]. The 4-*n*-(1,1,4,4,5,5,5-heptadeuterio)-pentylbiphenyl (5CB- d_7) was prepared from propargyl chloride [17].

N.M.R. samples were prepared by adding 1CB or 5CB to the liquid crystals in 8 mm o.d. glass tubes. Homogeneous solutions were obtained by heating into the isotropic phase and vortex mixing. These were then subjected to three freeze-pump-thaw cycles and the tubes flame sealed under vacuum. The 5CB- d_7 was used as a solvent for 1CB- d_{11} to avoid problems caused by overlapping resonances. $^2\text{H-N.M.R.}$ spectra were obtained on a modified Bruker BKR-322s spectrometer operating at 30.7 MHz. Quadrupolar echo excitation was used (with a 90° pulse length of 4 μs) and the spectra, obtained after Fourier transformation from the top of the echo, were analysed to obtain quadrupolar splittings of the 5CB- d_{19} , 1CB- d_{11} and 5CB- d_7 . The temperature was regulated by a gas flow unit and controlled to ± 0.5 K.

Sample concentrations were as follows:

5CB- d_{19} : EBBA	5:95 mol %
5CB- d_{19} : EBBA	10:90 mol %
5CB- d_{19} : 55 wt % 1132: EBBA	3:97 wt %
1CB- d_{11} : 55 wt % 1132: EBBA	4:96 wt %
1CB- d_{11} : 5CB- d_7	10:90 mol %

3. Theory

Quadrupolar couplings from $^2\text{H-N.M.R.}$ spectra provide detailed information on the C^{-2}H bond order parameters, S_{CD} , of each specific site of the liquid crystal molecule. In order to relate rigorously these couplings to the orientational order of the molecule the alkyl chain flexibility must be understood.

The rotational isomeric state model [18] has been used extensively to determine the conformational energies and internal rotational partition function of flexible molecules. Gas phase results on n -alkanes indicate that the potential energy for internal rotation about a C-C bond has three minima. The lowest energy state is the trans configuration (t) which differs in energy from the two gauche states ($g+$, $g-$) by $E_{tg} = E_{trans} - E_{gauche} = 2.09 \text{ kJ mol}^{-1}$. We shall assume that the first methylene group of the alkyl chain of 5CB is fixed with the HH direction parallel to the plane of the adjacent benzene ring and we shall neglect rotation of the methyl group. Internal rotations are possible about three C-C bond vectors and thus there are 27 possible conformations. The internal energy of conformer i is given by

$$U_{\text{int},i} = n_g E_{tg} + n_{g+g-} E_{g+g-}, \quad (1)$$

where n_g (n_{g+g-}) is the number of gauche (gauche + gauche -) bonds and E_{g+g-} is the additional energy required to inhibit successive gauche + gauche - bonds which involve large steric interactions between substituents, i.e. the pentane effect [18]. The gas phase conformational partition function is given by

$$Z_{\text{int}} = \sum_i \exp(-U_{\text{int},i}/kT), \quad (2)$$

where i labels the conformer.

The total energy depends on the conformation, its orientation Ω and its interaction with the external nematic orienting potential,

$$U_{T,i}(\Omega) = U_{\text{int},i} + U_{\text{ext},i}(\Omega), \quad (3)$$

where we assume that $U_{\text{int},i}$ is independent of orientation [19]. The probability of each conformation is

$$P_i = \int \exp(-U_{T,i}(\Omega)/kT) d\Omega / Z_T, \quad (4)$$

where the partition function, Z_T , is the sum over all conformations, i

$$Z_T = \sum_i \int \exp(-U_{T,i}(\Omega)/kT) d\Omega. \quad (5)$$

The independent elements of the ordering matrices are calculated for each conformation by numerically integrating the equation

$$S_{\alpha\beta,i} = \int (3l_\alpha l_\beta - \delta_{\alpha\beta}) \exp(-U_{\text{ext},i}(\Omega)/kT) d\Omega / 2Z_{\text{ext},i}, \quad (6)$$

where

$$Z_{\text{ext},i} = \int \exp(-U_{\text{ext},i}(\Omega)/kT) d\Omega,$$

and l_α is the cosine of the angle between the molecule fixed α axis and the director.

Initial attempts to interpret $^2\text{H-N.M.R.}$ results assumed a single (molecular) orientational order matrix for all conformations and thus reduced the problem to calculating conformational probabilities and the projection of the C-H bond vectors onto the principal axis system of this order matrix [20–24]. While this makes the problem tractable it is clearly incorrect because the external nematic orienting potential must depend on the detailed geometry of each conformation [9, 10, 12, 20, 24–26]. It is necessary to calculate the ordering matrix which contains up to five independent elements for each conformation [27]. The quadrupolar splitting for each conformation is then

$$v_{Q,i} = \sum_\alpha \sum_\beta (e^2 Q/h) q_{\alpha\beta,i} S_{\alpha\beta,i}, \quad (7)$$

where the summations are over geometric coordinates. The experimentally observed quadrupolar splitting is the statistical mechanical ensemble average of these conformer splittings

$$\langle v_Q \rangle = \sum_i v_{Q,i} P_i. \quad (8)$$

In order to calculate these splittings, the external potential, $U_{\text{ext},i}(\Omega)$, must be specified. Since the exact nature of U_{ext} is unknown a model must be used in order to make progress.

Studies on small solutes dissolved in nematic liquid crystals have suggested that there are at least two mechanisms responsible for orientation: (i) the interaction of the molecular quadrupole moment of the solute with the mean electric field gradient present in the liquid crystal; and (ii) the steric interaction between the liquid crystal and the solute. Results for $^2\text{H}_2$ and a number of other small solutes dissolved in 55 wt % 1132:EBBA indicate that, at 301.4 K, the interaction between the molecular quadrupole moment and the mean electric field gradient can be ignored [2–5, 7, 8]. We shall also assume this to be true for the solutes 1CB- d_{11} and 5CB- d_{19} in this particular nematic phase. These molecules are much larger than the solutes studied previously and their molecular quadrupole moments are unknown.

Here the molecule is modelled as a collection of van der Waals spheres (van der Waals radii are taken from Bondi [28]) and the liquid crystal solvent is modelled as an elastic tube aligned parallel to the external Z direction. The tube may be deformed in directions perpendicular to the director by the conformer's size and shape. The mean potential energy arising from the interaction of the conformer with the elastic walls is then

$$U_{\text{ext},i}(\Omega) = kc_i(\Omega)^2/2, \quad (9)$$

where k is the Hooke's law restoring force constant and $c_i(\Omega)$ is the circumference of the deformed tube for some orientation Ω of the solute; $c_i(\Omega)$ is calculated from the projection of the solute onto a plane perpendicular to the director.

4. $^2\text{H-N.M.R. results and discussion}$

Spectra of the flexible $5\text{CB-}d_{19}$ molecule in various nematic environments are shown in figure 2 for a reduced temperature T_R of 0.880 ± 0.006 . Magnetic susceptibility measurements of pure 5CB at this reduced temperature have been correlated to the splitting of the 1 position of $5\text{CB-}d_{19}$ and give a bulk order parameter $S(\Delta\chi)$ of 0.73 [29]. The spectra are characterized by large splittings which result from the quadrupole couplings of the spin 1 deuterons and by fine structure on many of the peaks due to dipolar couplings between deuterons. We shall ignore the dipolar couplings in this paper because they cannot be determined accurately from our results.

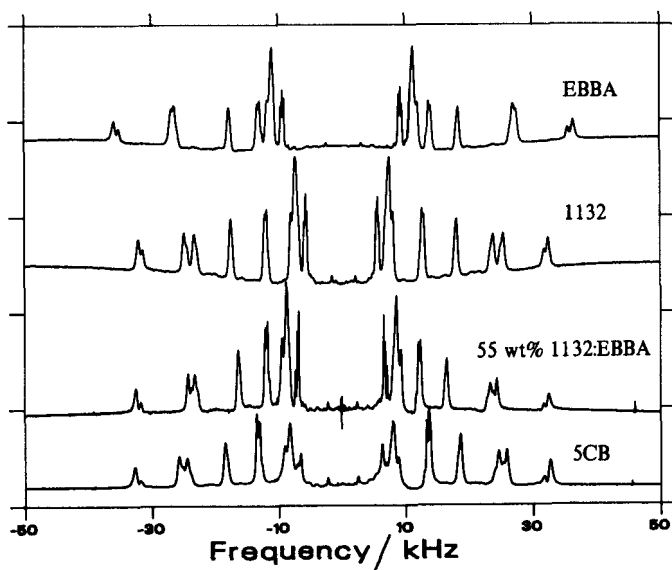


Figure 2. Experimental $^2\text{H-N.M.R.}$ spectra of $5\text{CB-}d_{19}$ dissolved in the liquid crystals indicated.

Examination of the spectra in figure 2 shows a dependence on nematic liquid crystal solvent. For example the central (ring) splittings in the spectrum of 5CB in EBBA are much larger than those in 1132 . To demonstrate the differences we plot in figure 3 the splittings as a function of carbon position. Results for $1\text{CB-}d_{11}$ in the 55 wt % $1132:\text{EBBA}$ mixture are included in this figure for comparison. The splittings

EXPERIMENTAL SPLITTINGS

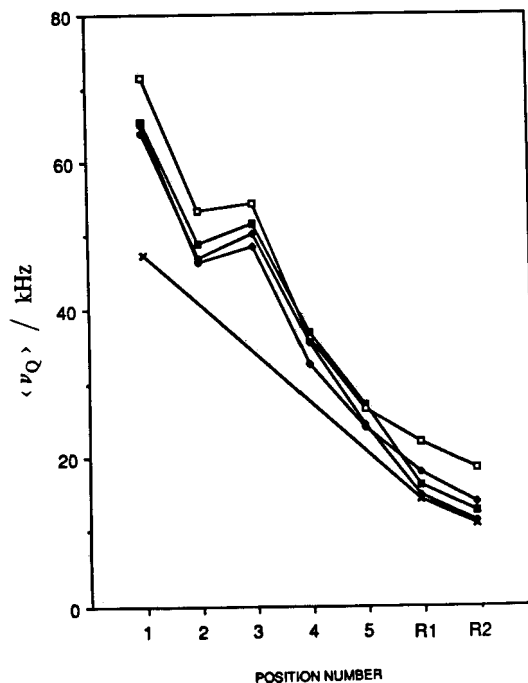


Figure 3. Quadrupolar splittings as a function of molecular position. Results are given for: 5CB- d_{19} in the nematic environments —■—, pure 5CB; —□—, EBBA; —◇—, 1132; and —◆—, 55 wt % 1132:EBBA; and for 1CB- d_{11} in —×—, 55 wt % 1132:EBBA.

are assigned to specific positions in the molecule on the basis of previous studies [9, 10, 30]. There are at least two ring deuteron splittings [9]. Previous studies have shown that the deuterons on the ring adjacent to the aliphatic chain have equal splittings in 5CB [9]. We shall assign the smaller splitting to the deuterons on the other ring. Our calculations below, which treat each conformation separately, are consistent with the same geometry and quadrupolar coupling constant for deuterons on adjacent rings giving rise to unequal quadrupolar splittings. However, the integrated intensity of the second set of peaks accounts for only two deuterons. Thus we cannot distinguish whether our model is correctly predicting different splittings for the two rings or whether the second splitting arises from the deuterons next to the nitrile group. In either case these latter deuterons must have either modified bond angles or a quadrupole coupling constant that deviates from that of the other ring deuterons.

In order to emphasize the differences among liquid crystals, we present in figure 4 plots of ratios of two of the splittings versus the splitting for the chain 1 position, $\langle \nu_Q^{(1)} \rangle$. In this figure results for a range of temperatures are presented, and it is easily seen that for a given $\langle \nu_Q^{(1)} \rangle$ the methyl, $\langle \nu_Q^{(5)} \rangle$, and ring, $\langle \nu_Q^{(R1)} \rangle$, splittings are a function of the nematic environment. These results indicate that the exact form of the ordering potential must also be a function of nematic environment.

The quadrupolar splittings are calculated in terms of the particular form chosen for the internal and external potentials. The internal rotational potential depends on

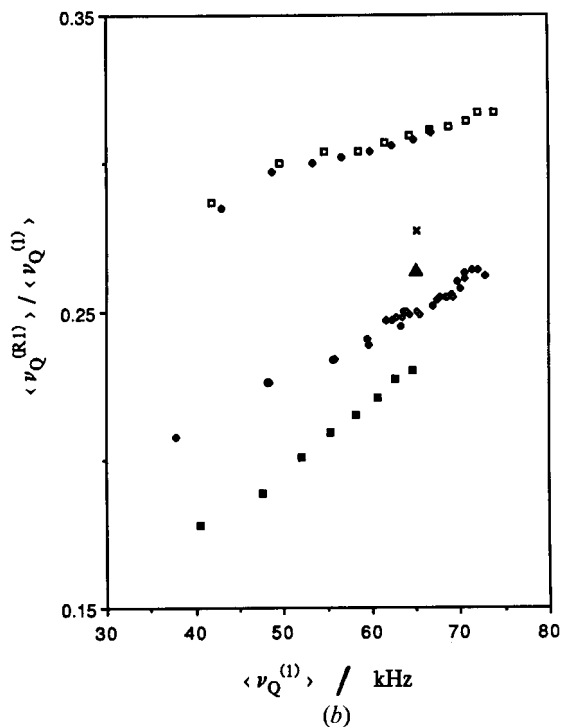
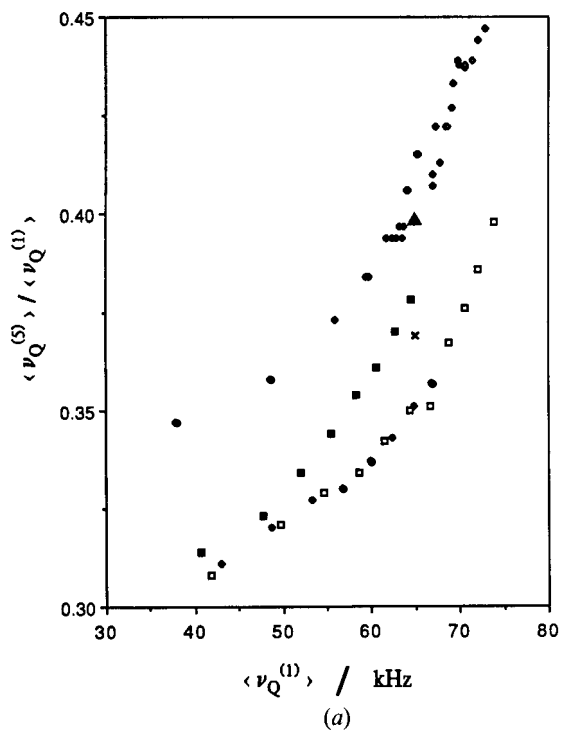


Figure 4. (a) Ratio of the quadrupolar splittings $\langle \nu_Q^{(5)} \rangle / \langle \nu_Q^{(1)} \rangle$ of the alkyl chain deuterons plotted against $\langle \nu_Q^{(1)} \rangle$ of 5CB-*d*₁₉ in \square , EBBA (5 mol %); \blacklozenge , EBBA (10 mol %); \blacksquare , 1132; \blacklozenge , 5CB; \times , 55 wt % 1132:EBBA; \blacktriangle , theory. (b) Ratio of the quadrupolar splittings of the aromatic deuterons (larger of the two observed aromatic splittings) and the 1 position of the alkyl chain plotted against $\langle \nu_Q^{(1)} \rangle$ of 5CB-*d*₁₉ in \square , EBBA (5 mol %); \blacklozenge , EBBA (10 mol %); \blacksquare , 1132; \blacklozenge , 5CB; \times , 55 wt % 1132:EBBA; \blacktriangle , theory.

the parameter E_{tg} . In the absence of an external electric field gradient the external potential depends only on the liquid crystal force constant, k . To demonstrate the effect of the parameters E_{tg} and k , quadrupolar splitting profiles calculated from equation (8) are shown in figure 5 for combinations of the following values: $k = 2.5$ or 2.9 dyn cm^{-1} and $E_{\text{tg}} = 2.09$ or 4.45 kJ mol^{-1} . From the figure it is seen that high values of E_{tg} are needed to generate profiles similar to the experimental ones in figure 3. The probabilities of the conformations of the alkyl chain of 5CB and the ordering matrices for the best fit values of the parameters reported here are given for both the nematic and gaseous phases in table 1. In order to predict the ensemble average of any physical observable of a flexible molecule these probabilities must be known.

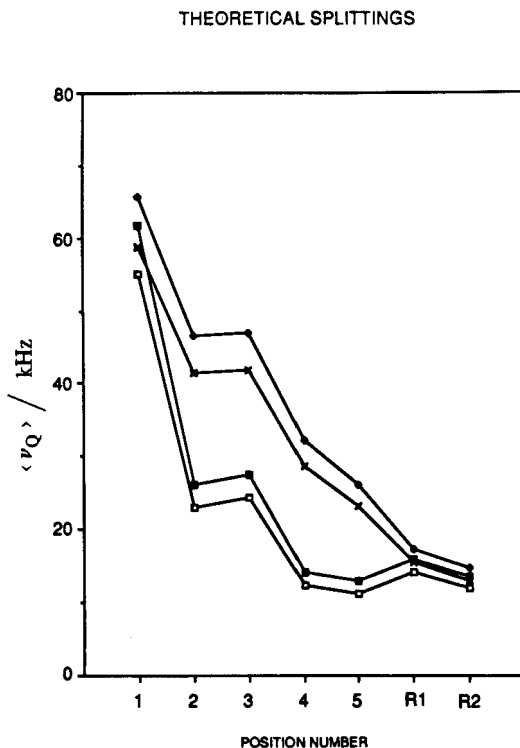


Figure 5. Theoretical order parameter profiles calculated using an orienting potential characterized by the following parameters: \square , $E_{\text{tg}} = 2.09 \text{ kJ mol}^{-1}$, $k = 2.5 \text{ dyn cm}^{-1}$; \times , $E_{\text{tg}} = 4.45 \text{ kJ mol}^{-1}$, $k = 2.5 \text{ dyn cm}^{-1}$; \blacksquare , $E_{\text{tg}} = 2.09 \text{ kJ mol}^{-1}$, $k = 2.9 \text{ dyn cm}^{-1}$; \blacklozenge , $E_{\text{tg}} = 4.45 \text{ kJ mol}^{-1}$, $k = 2.9 \text{ dyn cm}^{-1}$.

The spectrum calculated from a least squares fitting of this size and shape theory to the experimental results for 5CB- d_{19} in 55 wt % 1132:EBBA is compared with the experimental spectrum in figure 6. To achieve reasonable agreement with the aromatic ring deuteron splitting it was essential to vary the ring CCD bond angle θ (see figure 1) [9, 11] in addition to k and E_{tg} [9]. Best agreement between experiment and theory was obtained with $k = 2.9 \text{ dyn cm}^{-1}$, $E_{\text{tg}} = 4.45 \text{ kJ mol}^{-1}$ and $\theta = 119.0^\circ$. As can be seen from figure 6, the experimental quadrupolar splittings are reproduced very well. The value of E_{tg} disagrees with the gas phase estimate, which is to be expected

Table 1. Order parameter components† and internal and external probabilities calculated from the best fit parameters for 5CB-*d*₁₉ in 55 wt % 1132:EBBA. $k = 2.9 \text{ dyn cm}^{-1}$, $E_{\text{ig}} = 4.45 \text{ kJ mol}^{-1}$ and $\theta = 119.0^\circ$.

conf‡	S_{xx}	S_{yy}	S_{zz}	S_{xy}	S_{xz}	S_{yz}	$P_{\text{int},i}$ §	$P_{\text{tot},i}$ ¶
111	-0.3069	-0.3312	0.6381	-0.0134	0.1764	-0.0524	0.4414	0.4428
112	-0.2769	-0.2945	0.5715	-0.0308	0.1757	-0.0967	0.0747	0.0722
113	-0.2607	-0.3104	0.5711	-0.0028	0.1959	-0.0135	0.0747	0.0709
121	-0.3370	-0.3214	0.6585	0.0032	0.0859	0.0608	0.0747	0.0809
122	-0.3012	-0.2900	0.5911	0.0158	0.1257	0.0736	0.0126	0.0131
123	-0.3133	-0.2912	0.6044	-0.0051	0.0497	0.0625	0.0010	0.0011
131	-0.3418	-0.3169	0.6587	-0.0052	0.0471	-0.1006	0.0747	0.0814
132	-0.3092	-0.2948	0.6041	0.0009	0.0150	-0.0821	0.0010	0.0011
133	-0.3190	-0.2735	0.5925	-0.0141	0.0757	-0.1340	0.0126	0.0134
211	-0.2337	-0.2179	0.4516	-0.0666	0.1569	-0.1509	0.0747	0.0704
212	-0.2036	-0.2483	0.4519	-0.0438	0.1663	-0.0937	0.0126	0.0127
213	-0.2594	-0.2674	0.5268	-0.0451	0.1694	-0.1268	0.0126	0.0133
221	-0.2858	-0.1891	0.4749	-0.0279	0.0749	-0.1799	0.0126	0.0129
222	-0.3038	-0.2454	0.5491	-0.0206	0.0720	-0.1611	0.0021	0.0025
223	-0.2716	-0.2162	0.4878	-0.0061	0.0413	-0.1394	0.0002	0.0002
231	-0.2399	-0.1916	0.4315	-0.0441	0.0886	-0.0921	0.0010	0.0013
232	-0.2455	-0.2174	0.4629	-0.0259	0.0793	-0.0665	0.0000	0.0000
233	-0.2199	-0.2249	0.4448	-0.0311	0.0913	-0.0657	0.0002	0.0002
311	-0.1795	-0.2711	0.4506	0.0285	0.2038	0.0431	0.0747	0.0675
312	-0.2289	-0.2971	0.5260	0.0083	0.2036	0.0154	0.0126	0.0129
313	-0.1843	-0.2670	0.4514	-0.0093	0.1859	-0.0118	0.0126	0.0125
321	-0.1970	-0.2323	0.4293	0.0303	0.1159	0.0284	0.0010	0.0012
322	-0.2019	-0.2416	0.4435	0.0012	0.1073	0.0042	0.0002	0.0002
323	-0.2229	-0.2378	0.4607	0.0125	0.0968	0.0119	0.0000	0.0000
331	-0.2436	-0.2297	0.4733	0.0445	0.1452	0.1135	0.0126	0.0125
332	-0.2590	-0.2285	0.4875	0.0160	0.0976	0.0974	0.0002	0.0002
333	-0.2775	-0.2700	0.5475	0.0245	0.1344	0.0988	0.0021	0.0024

† The axis system used is defined in figure 1. The axes are fixed in the aromatic part of the molecule. The physical data used in the analysis are e^2qQ/h (chain) = 168 kHz (axial symmetry assumed along C²H bonds); e^2qQ/h (ring) = 185 kHz; $(q_{aa} - q_{bb})/q_{cc} = 0.04$ for ring deuterons where the *c* axis is along the CD bond direction and the *b* axis is perpendicular to the ring plane.

‡ 1 = trans; 2 = gauche +; 3 = gauche -.

§ $P_{\text{int},i} = \exp(-U_{\text{int},i}/kT)/Z_{\text{int}}$ is the free molecule conformer probability in the absence of an external potential (gas phase).

¶ $P_{\text{tot},i} = P_i$ in equation (4) is the probability of conformer *i* in the presence of an anisotropic external potential (nematic phase).

in condensed matter, and may reflect the neglect of isotropic contributions to the external potential [31]. Space filling molecular models suggest that steric interference between aromatic ring deuterons and those in the 2 position can occur. Inclusion of an additional term in the internal energy to correspond to an increased energy of a gauche link at C₁-C₂ was found to decrease the value of E_{ig} slightly. The least squares fitting procedure gave a value of 290 J mol⁻¹ for the additional term and a value of 4.26 kJ mol⁻¹ for E_{ig} . Thus the additional parameterization does not seem well justified. Similar anomalously high values for E_{ig} have been found in other mean field theories in condensed matter [10].

A convenient method of comparison of results in various liquid crystals can be effected by inspection of the ²H quadrupolar splitting ratio plots [9, 20-22, 25, 26].

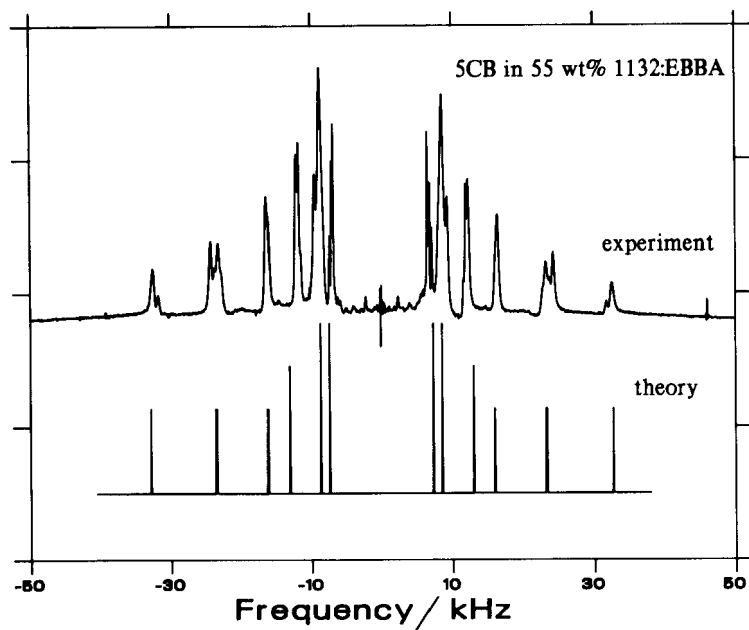


Figure 6. Experimental spectrum of 5CB- d_{19} in 55 wt % 1132:EBBA compared with the spectrum calculated for $E_{ig} = 4.45 \text{ kJ mol}^{-1}$, $k = 2.9 \text{ dyn cm}^{-1}$ and $\theta = 119.0^\circ$. The two smallest splittings in the calculated spectrum are ring splittings. The smaller of these is from the ring containing the nitrile group, and the larger from the ring attached to the aliphatic chain.

Theory and experiment for 55 wt % 1132:EBBA are shown in figure 4. Reasonable agreement is found for the ratio of the ring to the 1 position in figure 4(b), but not for the methyl to the 1 position in figure 4(a). It is interesting to note that the trends in figure 4(b) follow the relative values of the electric field gradients in the liquid crystals [5, 6], which are EBBA < 55 wt % 1132:EBBA < 5CB < 1132. The main reason for inclusion of these plots is that if the same single mechanism were acting in all nematic liquid crystals, plots for 5CB as solute in all nematic phases should be identical. These ratio plots indicate that more than one mechanism is required to explain the N.M.R. results for 5CB- d_{19} in 5CB, 1132 and EBBA. This is expected since for other solutes the electric field gradient molecular quadrupole moment mechanism contributes to the solute ordering in these nematic solvents.

The size and shape model has also been used to explain the results of 1CB- d_{11} in 55 wt % 1132:EBBA giving $k = 4.2 \text{ dyn cm}^{-1}$. Experimental and theoretical results for 1CB are summarized in table 2. Note that the theory for the biaxiality, $\eta = (S_{yy} - S_{xx})/S_{zz}$, agrees with the value observed for 1CB in 55 wt % 1132:EBBA, and not with the value observed for 1CB in 5CB. This is expected because the molecular quadrupole moment electric field gradient mechanism contributes to solute ordering in 5CB [6] but not in 55 wt % 1132:EBBA [5, 7]. The results are also consistent with those previously observed for smaller solutes where larger values of k were required [7].

A quantitative description of contributions to the ordering of 1CB and 5CB from the molecular quadrupole moment electric field gradient interaction is difficult because the quadrupole moment tensors for these molecules have not been determined.

Table 2. The principal values of the ordering matrix of 1CB-*d*₁₁ as solute†.

Nematic phase	$\eta = (S_{yy} - S_{xx})/S_{zz}$	S_{zz}
5CB	0.109	0.608
55 wt % 1132:EBBA	0.092	0.571
Theory ($k = 4.2 \text{ dyn cm}^{-1}$)	0.078	0.567

† The axis system and geometrical parameters used are defined in figure 1. The axes are fixed in the aromatic part of the molecule. S_{zz} is obtained from the C²H₂ quadrupolar splitting using e^2qQ/h (methyl) = 168 kHz (axial symmetry assumed along C²H bonds); S_{xx} and S_{yy} are obtained from the aromatic quadrupolar splittings using the parameters: all aromatic bond angles taken as 120°, e^2qQ/h (ring) = 185 kHz, $(q_{aa} - q_{bb})/q_{cc} = 0.04$ for ring deuterons where the *c* axis is along the CD bond direction and the *b* axis is perpendicular to the ring plane.

However, the results are consistent with a mean anisotropic electric field gradient interacting with the molecular quadrupole moment, provided that Q_{zz} is negative and *z* is along the long axes of the two molecules.

5. Conclusions

²H-N.M.R. results have proved useful in understanding the flexibility, biaxiality and orientational order of 1- and 5-cyanobiphenyl molecules at low concentrations in a number of nematic environments. The observed modifications of the quadrupolar splitting profile are a direct consequence of changes in the external nematic orienting potential and the internal conformational probabilities. In the 55 wt % 1132:EBBA mixture good agreement between theory and experiment indicates that the steric interaction model, originally developed for small solutes, is capable of predicting the orientational order of the larger 1CB and 5CB molecules. In the other solvents where F_{zz} is non-zero the steric interaction is not capable of explaining the results and this is interpreted as evidence for additional orienting mechanisms.

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