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A. L. Bailey[a]; G. S. Bates[a]; E. E. Burnell[a]; G. L. Hoatson[b]
[a] Department of Chemistry, University of British Columbia, Vancouver, British Columbia, Canada [b] Department of Physics, College of William and Mary, Williamsburg, Virginia, U.S.A.

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Orientational ordering in nematic liquid crystals
1CB-d_{11} dissolved in 5CB-d_6

by A. L. BAILEY, G. S. BATES and E. E. BURNELL
University of British Columbia, Department of Chemistry, 2036 Main Mall,
Vancouver, British Columbia, Canada V6T 1Y6

G. L. HOATSON
College of William and Mary, Department of Physics, Williamsburg,
Virginia 23185, U.S.A.

The ^{2}H-N.M.R. spectra of mixtures of the non-mesogenic compound 4-cyano-4′-methylbiphenyl (1CB) and the nematic liquid crystal 4-cyano-4′-*n*-pentylbiphenyl (5CB) are measured as a function of concentration and temperature. Concentrations of up to 25 mol % 1CB have no effect on the N.M.R. spectrum and therefore on the orientational order of 5CB at a given reduced temperature. The order matrix of the 1CB is calculated from the measured quadrupole couplings. The results are analysed in terms of a model for orientational order that includes two anisotropic terms: (*a*) interaction between the molecular quadrupole moment and the mean electric field gradient of the medium, and (*b*) short range repulsive interactions. An estimate of the molecular quadrupole moment tensor of 1CB is obtained from the analysis.

1. Introduction

The intermolecular forces responsible for orientational ordering in liquid-crystalline systems have been the subject of much interest in recent years. Results from N.M.R. experiments in particular have yielded a wealth of experimental information. There is yet, however, no complete description of the mechanisms responsible for the orientational order. One problem is that the interpretation of experimental data is fraught with difficulty because of the asymmetry and flexibility of the liquid crystal molecules.

One very fruitful approach to the problem of orientational order has been the study of small solutes dissolved in nematic liquid crystals. Because of their rigidity and high symmetry, these solutes have provided a useful testing ground for ideas of orientational ordering. Various properties have been used in modelling orientational order, including dispersion forces [1], molecular moments of inertia [2, 3], size and shape [4], polarizability [5] and quadrupole moments [6]. A particularly successful approach has involved a model in which there are two interactions between the liquid crystal and the solute [7–11]. The first interaction is between the average electric field gradient due to the liquid crystal and the molecular quadrupole moment of the solute [6–8, 12, 13]. The second treats short range interactions by modelling the solute as a collection of van der Waals spheres which distorts the assumed elastic continuum of the liquid crystal [7–11, 14, 15].

Of course, the liquid crystal molecules are essentially large, flexible asymmetric solute molecules, and any theory for solutes should be capable of explaining results for liquid crystal molecules themselves. This has been shown to be the case in a preliminary study of the liquid crystal 5CB-d_{19} dissolved in a 55 wt % mixture of Merck ZLI-1132 in *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline (EBBA) [15]. In this special mixture at 301·4 K the electric field gradient/molecular quadrupole moment mechanism is taken as unimportant, and a reasonable fit between experiment and theory is obtained with the short range interaction model.

In order to perform similar calculations on other liquid-crystalline systems in which the mean electric field gradient may not be zero, it is necessary to know the molecular quadrupole moment tensor of each conformation of the liquid crystal molecule of interest. The determination of molecular quadrupole moments, even for small symmetrical molecules, is a notoriously difficult task. Thus, to help extend ideas of orientational ordering of solutes to liquid crystals in general, it seems worthwhile to study a rigid solute molecule of high symmetry that is close in structure to compounds known to have mesogenic properties. For this purpose we have chosen to study 1CB (4-cyano-4′-methylbiphenyl) as a solute in the liquid crystal 5CB (4-cyano-4′-*n*-pentylbiphenyl).

1CB is the first in the series of *n*-alkylcyanobiphenyls. It is non-mesogenic, unlike several members of the series, and it is rigid in the sense that it lacks an extended alkyl chain. Yet it is only the length of the alkyl chain which distinguishes 1CB structurally from the liquid crystal 5CB. Our hope was that 1CB would not disturb the 5CB environment, and that the orientation of 1CB in 5CB could be predicted using the two-mechanism model described above. In order to study the system by ^{2}H-N.M.R. we used 1CB-d_{11} and 5CB-d_6 selectively deuterated at the 1, 4 and 5 positions of the alkyl chain to ensure no overlapping signals in the spectra (see figure 1). In addition, perdeuterated 5CB was used to obtain a spectrum of the pure material.

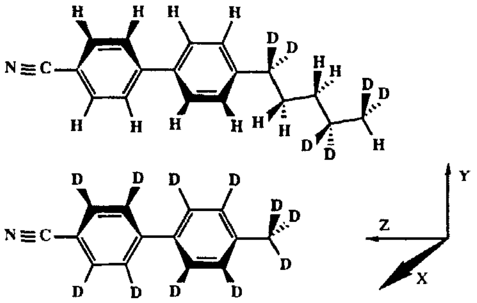

Figure 1. Structures of 5CB-d_6 and 1CB-d_{11} with definition of the molecular axis system used in the determination of the 1CB order matrix. Geometrical parameters used in the calculation are as follows: dihedral angle between the rings = 30° [22]; the y axis makes a 15° angle with each ring; the x and y axes bisect the planes of the two rings; all aromatic ring angles, CCC and CCH = 120°; methyl group angles = 109·47° (tetrahedral); van der Waals radii taken from [23]; bond lengths in Ångströms: C–C ring = 1·397, C–H ring = 1·09, C_{methyl}–C_{ring} and C_{ring}–C_{ring} = 1·52, C–H methyl = 1·09, C–CN = 1·44, C–N = 1·158.

Our approach to studying this problem is to determine first the extent to which the environment of 5CB is disturbed by 1CB. Next the order matrix of 1CB is calculated as a function of temperature and concentration from the ^{2}H-N.M.R. spectra. These results, together with data for 1CB in 55 wt % 1132/EBBA [15], molecular deuterium in 5CB [10], and various small solutes both in 55 wt % 1132/EBBA [11] and in 5CB [10] are used to obtain an estimate of the molecular quadrupole moment of 1CB at a single temperature. The two mechanism model is then tested by comparing its prediction of temperature dependence of the order matrix of 1CB in 5CB with experimental results.

2. Experimental

The 1CB-d_{11}, 5CB-d_6 and 5CB-d_{19} were prepared by coupling copper cyanide and the bromination products of the appropriately deuterated alkylbiphenyls [15]. Samples of 1CB-d_{11} dissolved in 5CB-d_6 were prepared in concentrations of 3, 10 and 25 mol%. Homogeneous dissolution was achieved by vortex mixing in the isotropic phase. The samples were degassed by repeated freeze–pump–thaw cycles and sealed under vacuum in 8 mm o.d. tubes. A pure sample of 5CB-d_{19} was similarly prepared.

The ^{2}H-N.M.R. signals were recorded on a modified Bruker BKR-322s spectrometer operating at 30·7 MHz, using a spin-echo sequence with phase cycling and a $(\pi/2)$ pulse length of 10 μs. Temperature was controlled to within ±0·5 K with an airflow system.

Nematic–isotropic transition temperatures were determined using a Nikon Optiphot Pol polarizing microscope with a heating rate of 4 mK h^{-1}. The temperature was controlled to within 1 mK by a heating wire around the sample cell connected via an integral proportional amplifier to a Wheatstone bridge which compared the resistance from a thermistor in the sample cell to a known resistor. The transition temperatures for 1CB and 5CB mixtures of various compositions are given in table 1.

Table 1. Nematic–isotropic transition temperatures for mixtures of ICB dissolved in 5CB at various compositions. T_{NI}^{+} is the temperature at which the nematic phase is first observed on cooling the isotropic liquid, and T_{NI}^{-} is the temperature at which, upon further cooling, the last of the isotropic phase disappears. Temperatures are accurate to within 0·004°C.

(5CB : 1CB)/mol %	T_{NI}^{-}/°C	T_{NI}^{+}/°C
100 : 0	34·641	34·645
90 : 10	34·690	34·863
82 : 18	36·078	36·306
78 : 22	36·416	36·805
74 : 26	36·827	37·320
69 : 31	37·745	38·008

3. Results and discussion

A typical spectrum of 1CB-d_{11} in 5CB-d_6 is shown in figure 2. The signals for the deuterons on the 1, 4 and 5 positions of the 5CB appear as the more intense peaks lacking fine structure. The remaining two groups of signals come from the 1CB ring and methyl deuterons, the latter having the larger quadrupolar splitting. In determining the order matrix of 1CB, we use the frequencies of the most intense peak in the methyl signal and the ring signal with the largest quadrupolar coupling.

3.1. *5CB*

An important feature of the results is that, other than changes in the nematic–isotropic transition temperature, the average orientation of 5CB appears to be unaffected by the 1CB over the entire nematic temperature range. In fact, except for

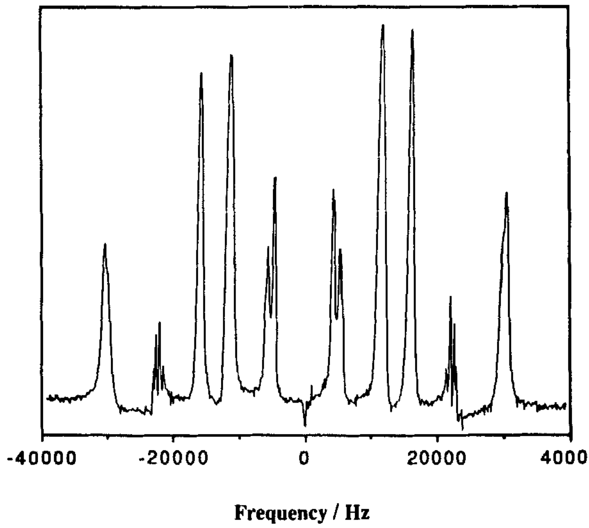

Figure 2. ^{2}H-N.M.R. spectrum of 10 mol % 1CB-d_{11} in 5CB-d_6 at 294 K.

the 25 mol % sample below 296 K, the quadrupolar splittings of deuterons on the 1, 4 and 5 positions of the 5CB-d_6 are constant for a given reduced temperature independent of the concentration of 1CB. A plot of these splittings against reduced temperature is given in figure 3 (*a*). The differences for the 25 mol % sample below 296 K (T_r = 0·96) may be a result of formation of a smectic phase, evidenced by the appearance of the sample and a characteristic change of slope in the order matrix results.

The strongest evidence that the 5CB environment remains relatively unchanged is that the plot of the ratio of quadrupolar splittings of the 4 and 1 positions on the chain versus the splittings for the 1 position is independent of the concentration of 1CB (figure 3 (*b*)). Similar plots for 5CB as a solute [15] have shown such ratios to be very sensitive to: (*a*) changes in the asymmetry of the molecular order matrix and/or (*b*) conformational averaging of the 5CB. Figure 3 (*c*) shows that plots of the quadrupolar couplings in 5CB against the order parameters of the 1CB fall on universal curves consistent with the mean field theory of mixtures [16–18].

3.2. *1CB order matrix*

The two measured quadrupolar couplings of the 1CB-d_{11} can be used to calculate the molecular order matrix using the approximation that 1CB has D_2 symmetry. In fact 1CB has only C_2 symmetry and determination of one off-diagonal element of the order matrix, S_{xy}, in the axis system defined in figure 1, would be required for a rigorous analysis. In this paper we assume that S_{xy} is zero. Indeed, in the calculations for the model reported below, S_{xy} is found to be very small (< 0·3 per cent of S_{zz}), which justifies this assumption.

If the asymmetry parameter, η_q, is zero for a methyl C–D bond, and if the methyl group rotates freely about the molecular z axis, S_{zz} of 1CB can be found directly from the quadrupole splitting of the methyl group deuterons by

$$\Delta\nu_Q = \frac{3}{2}\frac{e^2qQ}{h}P_2(\cos\zeta)S_{zz}, \tag{1}$$

where ζ is the angle between the C–D bond and the z axis, eq is the axially symmetric electric field gradient at the methyl deuteron, eQ is the deuteron nuclear quadrupole moment, P_2 is the second Legendre polynomial, and h is Planck's constant.

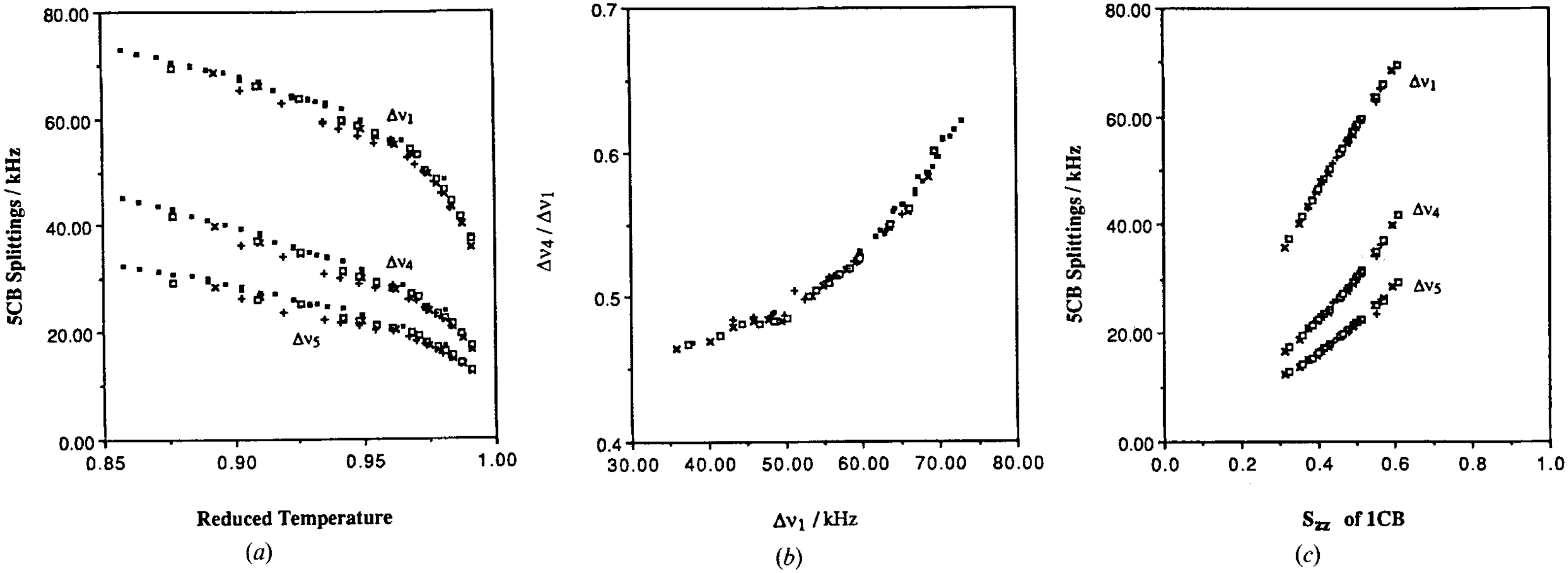

Figure 3. (*a*) Plots of the three measured quadrupolar splittings of 5CB-d_6 against reduced temperature (T/T_{NI-}): x, 3 mol % 1CB-d_{11}; □, 10 mol % 1CB-d_{11}; +, 25 mol % 1CB-d_{11}. Splittings for pure 5CB-d_{19} are shown as ■. (*b*) Ratios of the quadrupolar splitting of the 4 to the 1 position of the 5CB alkyl chain against the splitting of the 1 position: ■, pure 5CB-d_{19}; a5CB-d_6 with: x, 3 mol % 1CB-d_{11}; □, 10 mol % 1CB-d_{11} and +, 25 mol % 1CB-d_{11}. (*c*) Plots of the three measured quadrupolar splittings of 5CB-d_6 against the order parameter S_{zz} of 1CB-d_{11}: x, 3 mol % 1CB-d_{11}; □, 10 mol % 1CB-d_{11}; +, 25 mol % 1CB-d_{11}.

For the ring deuterons, the asymmetry in the electric field gradient tensor must be considered and the splitting is given by

$$\Delta\nu_Q = \frac{3}{2}\frac{e^2 q_{bb} Q}{h}\left[S_{bb} + \tfrac{1}{3}\eta_q(S_{aa} - S_{cc})\right], \tag{2}$$

where η_q is the asymmetry parameter $(q_{aa} - q_{cc})/q_{bb}$ taken as 0·041 [19], and (a, b, c) is a coordinate system with b along the C–D bond and a in the plane of the ring. The required values of the order matrix in the (a, b, c) coordinate system are related to those in the (x, y, z) molecular system by a coordinate transformation. The signs of the quadrupolar splittings are chosen to give values of $S_{zz} > 0{\cdot}5$ at low temperature and reasonably small values of $S_{yy} - S_{xx}$.

For each concentration and temperature the diagonal elements S_{xx}, S_{yy} and S_{zz} of the order matrix of 1CB have been determined using equations (1) and (2) with values of e^2qQ/h equal to 168 kHz for methyl and 188 kHz for ring deuterons, the geometrical parameters given in the caption to figure 1, and the fact that the order matrix is traceless. The resultant values of S_{zz} and $S_{yy} - S_{xx}$ are given in table 2. If identical reduced temperatures are considered, the order matrix is independent of concentration.

Table 2. Experimental order parameters for 1CB-d_{11} in 5CB-d_6.

	3 mol % 1CB-d_{11}		10 mol % 1CB-d_{11}		25 mol % 1CB-d_{11}	
T/K	$S_{yy} - S_{xx}$	S_{zz}	$S_{yy} - S_{xx}$	S_{zz}	$S_{yy} - S_{xx}$	S_{zz}
305	0·063	0·313	0·065	0·324	0·070	0·376
304	0·070	0·352	0·069	0·359	0·072	0·395
303	0·072	0·376	0·073	0·385	0·073	0·413
302	0·074	0·396	0·074	0·402	0·074	0·428
301	0·075	0·411	0·075	0·417	0·074	0·440
300	0·076	0·427	0·077	0·432	0·075	0·452
298	0·077	0·464	0·076	0·467	0·075	0·483
296	0·079	0·479	0·079	0·481	0·078	0·480
294	0·079	0·492	0·079	0·493	0·076	0·490
292	0·079	0·501	0·076	0·505	0·078	0·501
290	0·078	0·510	0·076	0·514	0·078	0·511
285	0·068	0·550	0·072	0·552	0·079	0·552
280	0·071	0·571	0·068	0·572	0·073	0·566
275	0·069	0·593	–	–	–	–
270	–	–	0·066	0·608	–	–

3.3. *The model*

The orientation of solutes in liquid-crystalline systems has been successfully modelled by a potential involving long and short range interactions:

$$U_{\text{tot}} = U_{\text{lr}} + U_{\text{sr}}.$$

The long range force is taken as the interaction of the mean electric field gradient of the liquid crystal **F** and the molecular quadrupole moment of the solute **Q**:

$$U_{\text{lr}} = -\frac{1}{3}\sum_{\beta,\gamma=x,y,z} F_{\beta\gamma}Q_{\beta\gamma}.$$

The average electric field gradient of a uniaxial liquid crystal with director along the space-fixed Z direction is completely determined by F_{ZZ}, which can be estimated from the N.M.R. spectrum of $^2H_2$ dissolved in the liquid crystal [6, 20]. We assume that all solutes experience the same F_{ZZ} as $^2H_2$.

The short range interaction is modelled as a hard body repulsive force between the solute, represented by a collection of van der Waals spheres, and the liquid crystal medium, represented by an elastic continuum:

$$U_{sr}(\Omega) = \tfrac{1}{2}kc^2(\Omega).$$

Here k is a Hooke's law force constant and c is the circumference of the solute for some orientation Ω projected into the XY plane of the liquid crystal. The order matrix of the solute is calculated by numerical integration over all orientations and conformations [15].

3.4. *Application of the model to solutes*

Without knowledge of the molecular quadrupole moment of 1CB, the above model cannot be applied directly to 1CB as a solute in 5CB, since both mechanisms contribute to the orientational order. However, for 1CB in 55 wt % 1132/EBBA only the short range mechanism operates, and a fit yields a value of $k_{1132/\mathrm{EBBA}}(1\mathrm{CB})$. For solutes with known molecular quadrupole moments, optimal values of k can be found in both 5CB and 55 wt % 1132/EBBA. By comparison of the average ratio of $k_{5\mathrm{CB}}/k_{1132/\mathrm{EBBA}}$ for various solutes with the value for $k_{1132/\mathrm{EBBA}}(1\mathrm{CB})$, an estimate of $k_{5\mathrm{CB}}(1\mathrm{CB})$ can be calculated.

The mean electric field gradient, F_{ZZ}, in 5CB has previously been determined as a function of temperature using molecular deuterium [10]. The orientational behaviour of a series of small solutes in 5CB has also been studied [10]. Using molecular quadrupole moments of the solutes from the literature (references given in [11]), an optimal value of the force constant, k, in 5CB for each solute was found. In addition, these same solutes have been studied in 55 wt % 1132/EBBA at 301·4 K where the electric field gradient at the ^{2}H nucleus of molecular deuterium is zero [12]. We assume that in this system only the short range mechanism contributes to orientation of the solute, and values for $k_{1132/\mathrm{EBBA}}(\mathrm{solute})$ have been determined.

The individual values for the force constant necessary to fit the order parameters of eight solutes in 55 wt % 1132/EBBA at 301.4 K [12] and in 5CB at 294 K [10] are given in table 3. The values of $k_{5\mathrm{CB}}(\mathrm{solute})$ are corrected for the changes which the solutes induce on the 5CB. The effect is quantified by the change in quadrupolar splitting from deuterons in the α position on the chain, using the α splitting of 5CB with 1CB as a solute of 294 K (56·88 kHz) as a reference. The correction term is taken as $dk/d\Delta\nu_\alpha = 0{\cdot}1141 \times 10^{-3}\,\mathrm{N\,m^{-1}\,kHz^{-1}}$ [10]. The values for $k_{1132/\mathrm{EBBA}}$ are not adjusted, since all solutions have similar splittings for the EBBA ring deuterons [11].

The ratio $k_{1132/\mathrm{EBBA}}/k_{5\mathrm{CB}}$ is also given for each solute in table 3. The average ratio (1·13 ± 0·19) is in good agreement with the individual ratios for a number of the solutes. Of particular interest is the proximity of the average to the value for 1,3,5-trichlorobenzene, for which the dependence dependence of the force constant in 5CB has been studied [10]. We use this average to determine the value of $k_{5\mathrm{CB}}(1\mathrm{CB})$.

3.5. *Application of the model to 1CB*

The experimentally determined molecular order matrix of 1CB in 55 wt % 1132/EBBA at 301·4 K [15] is used in the model to find a value of $k_{1132/\mathrm{EBBA}}(1\mathrm{CB}) = 4{\cdot}0 \times 10^{-3}\,\mathrm{N\,m^{-1}}$. Using the average ratio of $k_{1132/\mathrm{EBBA}}/k_{5\mathrm{CB}}$ reported above, the value

Table 3. Calculated values of k ($10^{-3}\,\mathrm{N\,m^{-1}}$) for solutes in 55 wt % 1132/EBBA and 5CB, corrected values in 5CB, and ratios.

Solute	$k_{1132/\mathrm{EBBA}}$ (*a*)	$k_{5\mathrm{CB}}$ (*b*)	$\Delta\nu_\alpha$ 5CB/kHz (*c*)	$k_{5\mathrm{CB}}$ (*d*)	$\dfrac{k_{1132/\mathrm{EBBA}}}{k_{5\mathrm{CB}}(d)}$
Benzene	8·58	4·37	44·03	5·82	1·47
1,3,5-Trichlorobenzene	6·47	5·06	53·61	5·42	1·19
1,3,5-Tribromobenzene	4·38	4·54	50·05	5·31	0·82
2,4-Hexadiyne	4·63	4·15	55·68	4·28	1·08
2-Butyne	5·23	4·05	48·04	5·05	1·04
Allene	5·99	4·48	52·20	5·00	1·20
Acetylene	7·45	7·36	58·11	7·21	1·03
Propyne	6·49	5·15	53·17	5·56	1·17
1CB	4·00 (*e*)		56·88	3·6 ∓ 0·6 (*f*)	avg 1·13(±0·19)

(*a*) Calculated from order matrix data taken at 301·4 K in 55 wt % 1132/EBBA [11].

(*b*) Calculated using order matrix data at 294 K from [10], field gradients as determined by molecular deuterium in [10] and molecular quadrupole moments given in [11].

(*c*) Quadrupolar splittings of the α-deuterons of 5CB at 294 K.

(*d*) Values corrected for differences in electric field gradient as determined from the α-deuteron splittings. The values reported correspond to $\Delta\nu_\alpha = 56{\cdot}88$ kHz, the value with 1CB as the solute (see text).

(*e*) Calculated assuming zero field gradient using order matrix data given in [15].

(*f*) Predicted value based on the average ratio and standard deviation for other solutes relative to those in 55 wt % 1132/EBBA.

of $k_{5CB}(1CB)$ at 294 K is predicted to be $(3{\cdot}6 \mp 0{\cdot}6) \times 10^{-3}\,N\,m^{-1}$, where the error limits used throughout reflect the sign and value of the standard deviation in the average $k_{1132/EBBA}/k_{5CB}$.

In order to predict the behaviour of 1CB in 5CB at other temperatures, we assume that $k_{5CB}(1CB)$ has the same dependence on $\Delta\nu_\alpha$ as the force constant for 1,3,5-trichlorobenzene, $k_{5CB}(TCB)$:

$$\frac{dk_{5CB}(1CB)}{d\Delta\nu_\alpha} = \frac{dk_{5CB}(TCB)}{d\Delta\nu_\alpha}\,\frac{k_{5CB}(1CB)_{294\,K}}{k_{5CB}(TCB)_{294\,K}}.$$

We also assume that the electric field gradient in 5CB is the same for a given $\Delta\nu_\alpha$ as measured in experiments with $^2H_2$ as a solute. The resulting values of $k_{5CB}(1CB)$ and F_{ZZ} at various temperatures are given in table 4.

Table 4. Calculated values of the electric field gradient [10] and force constant of 1CB in 5CB and predicted values of the order matrix.

T/K	$\Delta\nu_\alpha$ (5CB)/kHz	$F_{zz}/10^4\,V\,m^{-1}$	$k/10^{-3}\,N\,m^{-1}$	S_{zz} (calc.)	$S_{yy} - S_{xx}$ (calc.)
304	40·86	4·29	2·35	0·3230	0·0676
300	49·90	6·09	3·02	0·4182	0·0762
294	56·88	7·47	3·54	0·4916	0·0782
290	59·47	8·01	3·73	0·5202	0·0781
285	63·70	8·85	4·05	0·5629	0·0769

For given values of $k_{5CB}(1CB)$ and F_{ZZ} the calculated order matrix can be fitted exactly to the experimental value by adjusting the principal components of the molecular quadrupole moment tensor. At 294 K the values obtained are $Q_{zz} = (-1{\cdot}4 \pm 3{\cdot}2) \times 10^{-5}\,C\,m^{-2}$ and $Q_{yy} - Q_{xx} = (3{\cdot}5 \pm 0{\cdot}7) \times 10^{-5}\,C\,m^{-2}$. Note that $Q_{yy} - Q_{xx}$ is much better determined than Q_{zz}, which is closely correlated to the value of k. However, the value of $Q_{yy} - Q_{xx}$ depends on the ability of the model for short range forces to predict $S_{yy} - S_{xx}$. The estimate of $Q_{yy} - Q_{xx}$ may be too large, since the short range model predicts a value of $S_{yy} - S_{xx} = 0{\cdot}040$, which is smaller than that observed in 55 wt% 1132/EBBA (=0·053).

Using the fit for the quadrupole moment of 1CB at 294 K, the order matrix of 1CB at other temperatures throughout the nematic range is calculated by the model to give values of S_{zz} and $S_{yy} - S_{xx}$ as reported in table 4. A comparison of calculated and experimental values of S_{zz} is presented in figure 4(*a*), which gives S_{zz} as a function of reduced temperature. The model gives a very good fit to the experimental results.

Figure 4 (*b*) compares experimental and calculated values of the asymmetry in the order matrix by plotting $S_{yy} - S_{xx}$ versus S_{zz}. In this plot $S_{yy} - S_{xx}$ values predicted by the model lie in a curve coincidental with the experimental results. Also shown are the values calculated if only the short range mechanism is considered. The single mechanism can only account for a part of the observed asymmetry in the order matrix, giving a curve well below and centred to the right of the experimental results. A fit of **Q** with just the long range mechanism gives asymmetries close in magnitude to the experimental results, but the curve lies to the left of the experimental one in agreement with [21]; in addition, unrealistically large values of $Q_{zz} = +16{\cdot}9 \times 10^{-5}\,C\,m^{-2}$ and $Q_{yy} - Q_{xx} = 8{\cdot}1 \times 10^{-5}\,C\,m^{-2}$ are required. It is apparent that neither mechanism alone can explain the temperature dependence of the orientation of 1CB in 5CB. Fitting the model with both mechanisms at a single temperature gives

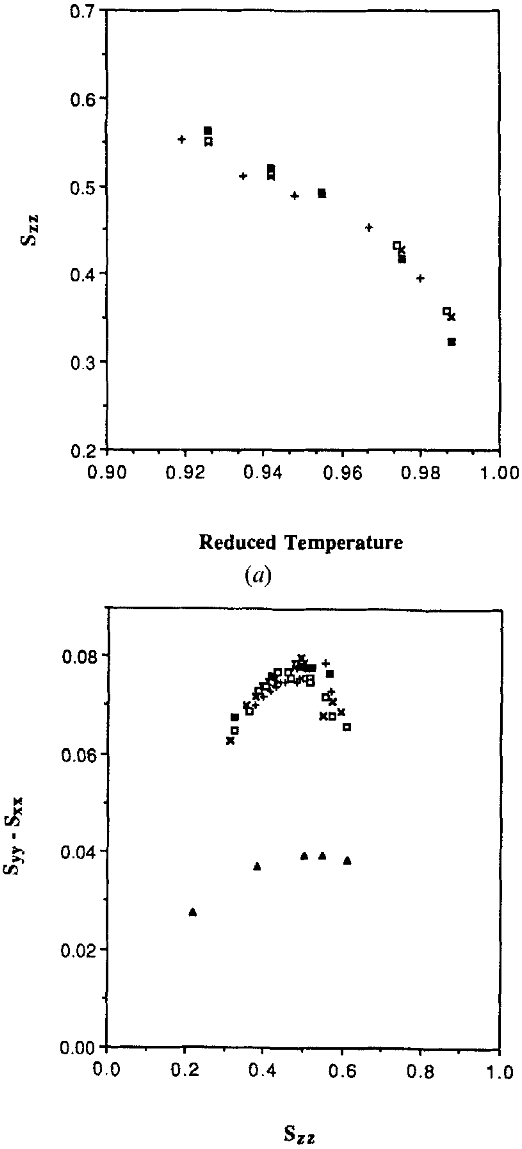

Figure 4. (*a*) Plot of the experimental and calculated values of S_{zz} of 1CB-d$_{11}$ against reduced temperature (T/T_{NI-}): experimental values for x, 3 mol % 1CB-d$_{11}$; □, 10 mol % 1CB-d$_{11}$; +, 25 mol % 1CB-d$_{11}$; calculated values are shown as ■. (*b*) Plot of the asymmetry of the order matrix of 1CB, $S_{yy} - S_{xx}$, against S_{zz}: experimental values for x, 3 mol % 1CB-d$_{11}$; □, 10 mol % 1CB-d$_{11}$; +, 25 mol % 1CB-d$_{11}$; ■, calculated values using the two-mechanism model; ▲, values of the best fit when only the short range mechanism is considered.

sensible values of k and **Q** for 1CB, which in turn predict the order matrix at other temperatures in very good agreement with experimental results.

Considering the simplicity of our description of the short range interaction, the two mechanism model predicts the orientational behaviour of 1CB in 5CB extremely well. Modelling the liquid crystal as an elastic continuum is an immense simplification of the actual hard body interactions which occur between the solute and the medium.

The estimation of the molecular quadrupole moment of 1CB is derived from quadrupole moments of other solutes, the values of which vary greatly in the literature. In addition, the value of the predicted quadrupole moment tensor of 1CB is very sensitive to small changes in the geometry of 1CB and to the value of k chosen for the model.

4. Conclusions

We have studied mixtures of 1CB and 5CB in order to investigate the mechanisms of molecular orientation in nematic phases. Although 1CB is non-mesogenic, it is structurally similar to the nematic liquid crystal 5CB, differing only in the length of the alkyl chain. Because of this similarity, 1CB is a useful probe for studying the intermolecular interactions responsible for orientational order. The concentration of 1CB dissolved in 5CB has no effect on the ^{2}H-N.M.R. spectra of either the 1CB or the 5CB in samples observed at equivalent reduced temperatures. However, the relatively high symmetry and rigidity of 1CB makes interpretation of the spectral results much simpler than is the case with flexible, asymmetric liquid crystal molecules.

The results are consistent with a model which describes the intermolecular interactions with two terms. The first is the interaction between the mean electric field gradient of the medium with the molecular quadrupole moment of the solute. The second is a simple model for the short range repulsive forces, which treats the liquid crystal as an elastic medium.

Using the model we obtain an estimate for the molecular quadrupole moment tensor of 1CB, and this in turn is used to predict the temperature dependence of the order matrix of 1CB in 5CB. The model, previously shown to be adequate for small solutes, is shown here to be very successful in predicting the orientation of larger molecules. This is an important step toward developing a successful model for flexible, asymmetric liquid crystal molecules.

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