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Orientation mechanisms for small solutes in the nematic liquid crystal 5CB- α , β - d_4

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Two principal mechanisms are shown to be important for the orientational order of small solute molecules in the nematic liquid crystal $4-(\alpha,\beta-d_4-n-\text{pentyl})-4'$ -cyanobiphenyl (5CB- $\alpha,\beta-d_4$). The interaction between the mean electric field gradient due to the liquid crystal and the molecular quadrupole moment of the solute is particularly important for small molecules such as hydrogen. For larger solutes, like 1,3,5-trichlorobenzene, the short-range interactions which are proportional to the size and shape of the solute are important. A model which takes both mechanisms into account is used to calculate solute molecular order parameters. Excellent agreement between the calculated parameters and those obtained from N.M.R. measurements is found.

1. Introduction

An understanding of the interactions responsible for molecular orientation in liquid-crystalline systems is highly desirable because of the importance of such systems in a variety of industrial applications and the fact that their biological analogues are found in the lipid membranes of many living systems. In general, these interactions are not well understood and the molecular orientation is often described in terms of a mean field theory in which the interaction potential is not specified [1, 2]. The main reason for this poor understanding is the complexity of the liquid crystal molecules. Their electronic properties are not well known and their flexibility makes calculation of the interaction potential extremely difficult. By comparison, small, rigid solute molecules whose size, shape, and concentration in the liquid crystal may be varied in a controlled manner are much easier to study. Nuclear magnetic resonance (N.M.R.) measurements are ideal for this purpose because the spectrum of the solute, which appears as sharp lines, can be easily distinguished from the broad liquid crystal spectrum [3–6]. In addition, partial deuteration of the liquid crystal permits examination of the effect of the solute on certain sites in the liquid crystal.

A mathematical description of the orientation of solutes in nematic liquid crystals has recently been proposed [7–9] and applied to solutes in the nematic solvents, Merck ZLI 1132, EBBA(N-(p-ethoxybenzylidene)-p'-n-butylaniline), and a 55 wt % 1132 mixture of the two. This description is based on two principal orientation mechanisms: (i) the interaction between the molecular quadrupole moment of the solute and the mean electric field gradient present in the liquid crystal [10–13] and (ii) the

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short-range repulsive interactions which are described in terms of a restoring force on the solute resulting from the perturbation of the liquid crystal by the solute. Both the mean electric field gradient and the force content describing the short-range interactions are properties of the liquid crystal, and are assumed to be the same for all solutes in a particular liquid crystal at a given temperature. The elements of the second-rank order parameter matrix [3] are calculated by combining the effects of these two mechanisms. Comparison of these order parameters with those obtained from N.M.R. measurements indicates the validity of the model.

N.M.R. spectra of nine solutes of different shapes and sizes, dissolved in the partially deuterated nematic liquid crystal 5CB- α , β - d_4 (4-(α , β - d_4 -n-pentyl)-4'cyanobiphenyl) were measured at various concentrations and temperatures. Molecular order parameters obtained from these spectra are compared with those calculated, and it is shown that the model is valid for this liquid crystal solvent. The dependence of both the external electric field gradient and the force constant on the quadrupolar splittings of the deuterons in the liquid crystal is also investigated. By taking into account changes in these quadrupolar splittings, the order parameters of the solutes can be predicted successfully for concentrations up to 10 mol % over the entire nematic range of the solutions. The interpretation of the results in terms of the orientational order of both solute and solvent using a mean field theory for mixtures of liquid crystals [2], dealt with in a previous publication [14], is compared with the current analysis.

2. Experimental

The liquid crystal 5CB- α , β - d_4



was prepared in high purity [14, 15] and degassed under vacuum, via several freeze, pump, thaw cycles. The solutes were obtained from various suppliers and used without further purification. A sufficient amount of each of the solute gases (${}^{13}C_2$ acetylene, allene and propyne) to produce a concentration of ~ 10 mol % if all of the gas dissolved was condensed into samples of 5CB- α , β - d_4 at 77 K. The tubes were then sealed, and allowed to come to room temperature. Solid and liquid solutes (benzene; 1,3,5-trichlorobenzene; 1,3,5-tribromobenzene; 2-butyne; and 2,4-hexadiyne) were added to the liquid crystal and mixed thoroughly to give ~ 1 mol % solutions. Solutions of 9–10 mol % of 1,3,5-trichlorobenzene and 2,4-hexadiyne were also prepared. D₂ was condensed into a 9 mm o.d. pyrex glass tube containing 5CB- α , β - d_4 at 4 K to give a sample with a final pressure of approximately 15 atm. A similar sample containing a mixture of H₂, HD and D₂ yielded insufficient deuteron signal from the solutes to be useful.

Proton N.M.R. spectra of the solutes were obtained at 400 MHz, and deuteron spectra of the liquid crystal at 61.4 MHz, using a Bruker WH400 spectrometer. Spectra of the samples containing 1,3,5-trichlorobenzene and 2,4-hexadiyne at both concentrations (1 mol % and 9–10 mol %) were measured at 1–5 K intervals as the samples were cooled from the isotropic phase to the freezing point of the solution. Spectra of the samples containing other solutes were measured at 294 K, except benzene, which was measured at 296 K. For each sample the proton signal was measured through the observe channel of a 5 mm proton probe and the deuteron signal was measured through the lock channel without removing the sample from the probe, thus ensuring that both spectra were obtained at identical temperatures. The

spectra of D_2 were measured using a 10 mm broad-band probe with the deuteron spectrum being measure through the observe channel and the proton spectrum through the decouple channel. The temperature was controlled by means of a variable temperature gas flow unit.

Direct dipole-dipole coupling constants for the solutes were obtained from a least squares fit to the spectral line positions using the program LEQUOR [16]. ${}^{13}C_2$ acetylene was used so that the sign of the measured dipolar couplings could be related to the sign of ${}^{1}J_{CH}$ which is known to be positive. This is useful for acetylene because it is known to have a negative order parameter in at least one liquid crystal (EBBA) [17]. Indirect spin-spin coupling constants were obtained from the literature [18]. Molecular order parameters were calculated from the dipolar couplings as indicated in [8]. The error in order parameters is estimated to be ± 3 per cent.

The spectra of the solutes in 5CB- α , β - d_4 were generally more difficult to measure than those in other nematic liquid crystal solvents. Problems were encountered with low signal-to-noise ratios and the line widths of the peaks generally increased with increasing distance from the centre of the spectrum. Such effects are indicative of temperature and concentration gradients in the samples.

3. Results and discussion

It has been shown previously [7, 10, 11, 13] that most of the orientation of molecular hydrogen can be explained in terms of the interaction between the quadrupole moment of the hydrogen molecule and the mean electric field gradient of the liquid crystal and that this mechanism is also important in the orientation of other solute molecules. Of particular interest is the nematic liquid crystal made up of a 55 wt % 1132/EBBA mixture. In this liquid crystal the deuterons in D_2 experience no external field gradient. The order parameter of D_2 , however, is not zero in this mixture and other solutes have order parameters intermediate between those in the component liquid crystals indicating the importance of other orienting mechanisms. It has been found [7-9] that the orientation of solutes in this mixture can be described quite successfully by considering the short-range repulsive interactions between the solute and solvent. The interaction energy is calculated in terms of a model in which the liquid crystal is described as an elastic tube, which deforms to accommodate solute molecules. It then exerts a force on the solute as it attempts to regain the unperturbed minimum energy configuration. This force is characterized by a force constant, k, which is the same for all solutes in a given liquid crystal at a given temperature. The magnitude of the force itself depends on the size and shape of the solute molecule, which is modelled as a group of van der Waals spheres. The value of k is determined by a least squares fit of the calculated order parameters to the experimental values. For the 55 wt % 1132/EBBA mixture at 301.4 K it was found to be $5 \cdot 0$ dyne cm⁻¹.

In order to analyse our results for the solutes in 5CB- α , β - d_4 in terms of the above model, the effect of the average field gradient, F_{ZZ} , must be taken into account. This mean electric field gradient may be calculated from the N.M.R. spectrum of D₂ dissolved in 5CB- α , β - d_4 in the same manner as in [10] and [11]. Values of F_{ZZ} for 5CB- α , β - d_4 at various temperatures are presented in table 1 with the measured dipolar and quadrupolar coupling constants of D₂ and the quadrupolar splittings of the α and β deuterons of the 5CB- α , β - d_4 . The temperature T_r is defined as T/T_{N-1} where T_{N-1} is the nematic to isotropic phase transition temperature of the solution. The values of

T/K	T _r	<i>B</i> /Hz†	D/Hz†	$F_{ZZ} 10^{11}$ e.s.u.	$\Delta v_{\alpha}/kHz$	$\Delta v_{\beta}/\mathrm{kHz}$
275	0.8929	901.41 + 0.18	-38.92 + 0.13	3.60 + 0.13	67.21	50.78
285	0.9253	709.19 + 0.33	-30.43 ± 0.15	2.52 ± 0.24	62.65	45.70
295	0.9578	524.85 + 0.23	-22.80 ± 0.10	2.30 ± 0.16	56.25	39.33
300	0.9740	424.93 ± 0.18	-18.64 ± 0.08	2.15 ± 0.13	51.09	34.91
305	0.9903	299.37 ± 0.20	-13.00 ± 0.08	1.30 ± 0.13	42.39	28.05
307	0.9968	219.45 ± 0.20	-9.70 ± 0.09	1.23 ± 0.14	34.23	22.27

Table 1. D_2 in 5CB.

 $\dagger B$ and D are the quadrupolar and dipolar coupling constants as defined in [7].

$$B = 3/4 \langle eqQ/h \rangle S,$$

$$D_{ij} = -(h\gamma_i\gamma_j/4\pi^2) \langle r_{ij}^{-3} \rangle S$$

where S is the order parameter of the symmetry axis of the D_2 molecule.

	Solute	S(exp)	S(calc)‡	S(calc)§	$\Delta v_{\alpha}/kHz$	$\Delta v_{\beta}/kHz$
(a)	1,3,5-Tribromobenzene	-0.2160	-0.2124	-0.2170	50.05	34.21
(b)	1,3,5-Trichlorobenzene	-0.2139	-0.1920	-0.2116	53.61	37.21
(c)	Benzene	-0.1352	- 0.1353	-0.1158	44.03	29.50
(d)	Hydrogen	0.0033	0.0175	0.0206	56.25	39.33
(e)	Propyne	0.1668	0.1475	0.1618	53.17	36.62
(f)	Acetylene	0.1686	0.1429	0.1712	58.11	41.18
(g)	2-Butyne	0.1624	0.1774	0.1738	48.04	32.61
(\widetilde{h})	2.4-Hexadiyne	0.3545	0.3684	0.4445	55.68	39.03
(i)	Allene	0.1160	0.1105	0.1209	52.20	36.43

Table 2. Order parameters of solutes in 5CB at 294 K[†].

[†]All samples were measured at T = 294 K except benzene which was measured at T = 296 K.

 $\ddagger k = 4.22 \text{ dyne cm}^{-1}, F_{ZZ} = 2.30 \times 10^{11} \text{ e.s.u. for all solutes.}$

k and F_{ZZ} for each solute scaled using Δv_x (see text). $k_0 = -1.26$ dyne cm⁻¹ and k_i for the D₂ sample at 294 K = 5.15 dyne cm⁻¹.

 F_{ZZ} are about 30 per cent as large as those observed in EBBA and 1132 [10] and are of the same sign as in 1132.

In table 2 we show measured order parameters for nine solutes [18] with $C_3 v$ or higher symmetry dissolved in 5CB- α , β - d_4 along with the quadrupolar splittings of the liquid crystal deuterons. These experimental order parameters may then be predicted in a similar manner as in [8], taking into account the interaction between the electric field gradient given in table 1 and the molecular quadrupole moments [18] of the solutes. We have used the electric field gradient as measured using the D₂ in 5CB- α , β - d_4 sample at 295 K and have fitted the value of the force constant by a least squares procedure. The value obtained for the force constant is 4.22 dyne cm⁻¹. The results of the fit are shown in column 2 of table 2 and plotted in figure 1. Excellent agreement between the calculated and experimental values is obtained.

Three assumptions have been made in calculating the solute order parameters using our model: (i) solute-solute interactions can be ignored, (ii) the solute does not perturb the liquid crystal, and (iii) all solutes experience exactly the same average environment. These three assumptions will only be valid for infinitely dilute samples at precisely the same temperature. Our experiments do not satisfy these criteria.



Figure 1. Orientation of solutes in 5CB- α , β - d_4 : experimental versus calculated order parameters in 5CB- α , β - d_4 . The calculated order parameters have been obtained using a model based on the short-range interactions and the interaction between the mean electric field gradient due to the liquid crystal and the molecular quadrupole moment of the solute [2]. The points are labelled in the same manner as in table 2. The force constant describing the short-range interactions has been obtained from a least squares fit to the solid line of slope 1. T = 294 K; k = 4.22 dyne cm⁻¹; $F_{ZZ} = 2.305 \times 10^{11}$ e.s.u.; correlation coefficient = 0.997.

Difference among samples are apparent in the variation of liquid crystal splittings (Δv_{a} and Δv_{β} in columns 4 and 5 of table 2). However, for all spectra run on samples reported in this paper, a plot of Δv_{α} versus Δv_{β} gives, to an excellent approximation, a single universal curve. It is only for higher solute concentrations, for example 15 mol % 1,3,5-trichlorobenzene, that deviations from this curve are significant. Thus for the samples reported here, the solutes have little effect on the conformational averaging or on the value of $(S_{xx} - S_{yy})/S_{zz}$ of the liquid crystal. Hence either the α or β splitting of the liquid crystal can be used to monitor the state of the liquid crystal molecule. We shall use the α splitting to make small corrections to the values of F_{ZZ} and k for each sample. In this study we shall use the liquid crystal quadrupole splittings as an internal control and not as a measure of the orientational order of the liquid crystal. The correlation between the order parameters of solute and liquid crystal are the subject of a separate paper [14]. For the purpose of making small corrections for the effects of finite dilution and temperature differences among samples we shall assume (i) that F_{ZZ} for a sample with a given liquid crystal quadrupolar splitting is the same as in the sample containing D_2 with the same liquid crystal quadrupolar splitting, and (ii) that k for a sample with a given liquid crystal quadrupolar splitting is the same as for the sample containing 1,3,5-trichlorobenzene with the same liquid crystal quadrupolar splitting.

A plot of the calculated field gradient (table 1) versus the measured quadrupolar splitting of the α deuterons of the 5CB- α , β - d_4 (figure 2) shows a roughly linear correlation. The best straight line through the points has slope 6.62×10^9 e.s.u. kHz⁻¹ and intercept -1.28×10^{11} e.s.u. (A similar curve for the β deuterons has slope 7.82×10^9 e.s.u. kHz⁻¹ and intercept -0.70×10^{11} e.s.u.) There is considerable scatter in the results, primarily from the fact that the dipolar and quadrupolar splittings



Figure 2. Electric field gradients in 5CB- α , β - d_4 : the measured electric field gradient versus the quadrupolar splitting of the α deuterons of the 5CB- α , β - d_4 . The electric field gradient is measured from the spectrum of D₂ dissolved in the 5CB- α , β - d_4 . The variation in both quantities is obtained by varying the temperature. The slope and intercept of the best straight line through the points are 6.64 × 10⁹ e.s.u. kHz⁻¹ and -1.28 × 10¹¹ e.s.u.; correlation coefficient = 0.941.

of the D_2 cannot be measured accurately enough to give very accurate values for F_{ZZ} . This graph, however, can be used as a calibration curve for F_{ZZ} .

We obtain a similar curve for the force constant by assuming that the value of k corresponding to a given liquid crystal splitting, Δv_{α} , is the same for all solutes. We then approximate the force constant k_i for a given sample *i* by the linear equation

$$k_i = k_0 + \Delta v'_{\alpha} (dk/d\Delta v_{\alpha}), \qquad (1)$$

where Δv_{α}^{i} is the quadrupolar splitting due to the α deuterons in the 5CB- α , β - d_{4} . The linear form of equation (1) is adequate for making the small corrections among samples.

In order to obtain $dk/d\Delta v_{\alpha}$ and k_0 we choose one solute and calculate the values of k_i needed to explain its experimental order parameters for several values of Δv_{α}^i as

T _r	S(exp)	$\Delta v_{\alpha}/kHz$	$\Delta v_{\beta}/kHz$	Concentration/ mol %
0.9803	- 0.1859	47.46	32.13	1†
0.9639	-0.2139	53.61	37.21	1
0.9475	-0.2336	57.86	40.94	1
0.9311	-0.2496	61.18	44.24	1
0.9148	-0.2629	63.82	46.97	1
0.8984	-0.2748	66.02	49.51	1
0.9930	-0.1474	39.84	26.61	9‡
0.9895	-0.1578	43.15	29.01	9
0.9861	-0.1690	44.84	30.40	9
0.9826	-0.1778	46.31	31.74	9
0.9791	-0.1828	47.57	32.80	9
0.9617	-0.2068	53.87	38.09	9
0.9443	-0.2255	57.98	41.87	9
0.9268	- 0.2402	61.36	45.17	9

Table 3. 1,3,5-Trichlorobenzene in 5CB.

 $\dagger T_{N-1} = 305 \text{ K.} \ddagger T_{N-1} = 287 \text{ K.}$



Figure 3. Force constant in 5CB- α , β - d_4 : the force constant describing the short-range interactions between solvent and solute versus the quadrupolar splitting of the α deuterons of the 5CB- α , β - d_4 . The value of the force constant is that needed to explain the orientation of 1,3,5-trichlorobenzene; $dk/d\Delta v_a = 0.1141$ dyne cm⁻¹ kHz⁻¹; $k_0 = -1.26$ dyne cm⁻¹; correlation coefficient = 0.992.

obtained at several different temperatures. For this purpose we have chosen 1,3,5trichlorobenzene. In table 3 we present experimental order parameters and liquid crystal quadrupolar splittings for a variety of temperatures and two concentrations of the solute. From these results and values of the field gradient obtained from figure 2 we can use our model to obtain the force constant, k_i , for 1,3,5-trichlorobenzene as a function of the splitting of the α deuterons of the 5CB- α , β - d_4 . The results of this calculation are presented in figure 3. From this plot we obtain a value of 0·1141 dyne cm⁻¹ kHz⁻¹ for $dk/d\Delta v_{\alpha}$ and -1.26 dyne cm⁻¹ for k_0 . (A similar curve using β deuterons gives $dk/d\Delta v_{\beta} = 0.1329$ dyne cm⁻¹ kHz⁻¹ and $k_0 = -0.19$ dyne cm⁻¹.) As is evident from figure 3, our assumption that the variation of k with Δv_{α} is linear is valid over the range of the experimental results.

Order parameters for the other solutes may now be calculated. We use the liquid crystal splitting for each sample, Δv_{α}^{i} , to obtain the field gradient and force constant for the sample from figures 2 and 3. The order parameters obtained from this calculation are shown in column 3 of table 2 and are plotted against the experimental values in figure 4. Again an excellent agreement with the experimental results is obtained. However, it is important to point out that unlike the order parameters presented in figure 1, only the calculated value for 1,3,5-trichlorobenzene has been fitted to the experimental value. The excellent agreement for the other solutes indicates very clearly that the force constant and electric field gradient may be transferred from one solute to another provided that the variation in experimental conditions between samples is taken into account. The value of k_i calculated for the D₂ solution at 295 K is then 5.15 dyne cm⁻¹. The order parameters calculated using the β deuteron splittings to scale F_{ZZ} and k differ from those reported in column 3 of table 2 by at most 3.1 per cent, and the value of k_i obtained for the D₂ solution at 295 K is 0.12 dyne cm⁻¹ less than obtained using the α splittings. Hence the calculated order parameters do not depend on which quadrupolar splitting is used to calculate F_{ZZ} and k.

The temperature dependence of k determined from the 1,3,5-trichlorobenzene samples can be used to compare the value of the force constant with that obtained for



Figure 4. Orientation of solutes in 5CB- α , β - d_4 : calculated versus experimental order parameters for solutes dissolved in 5CB- α , β - d_4 . The calculated order parameters have been obtained in the same manner as for figure 1 except that values of F_{ZZ} and k have been obtained from figures 2 and 3 using the quadrupolar splittings of the α deuterons of the 5CB- α , β - d_4 (see text). The labelling of the points refers to table 2. Correlation coefficient = 0.994.

another liquid crystal at the same reduced temperature. For the mixture 55 wt % 1132/EBBA at $T_r = 0.8787$, k is 5.0 dyne cm⁻¹ [8]. From our results at the same T_r , the value of k is 7.25 dyne cm⁻¹ in 5CB- α , β - d_4 . It is not clear a priori how the force constant should change with changes in the structure of the liquid crystal. The values are of similar magnitude, but the 5CB- α , β - d_4 value is larger than that for the 55 wt % 1132/EBBA mixture.

To further test the above scaling method we compare the experimental order parameters obtained for the two 2,4-hexadiyne samples at various temperatures [14] with those calculated using values of k_i from figure 3, and F_{ZZ} from figure 2. The results of this calculation are presented in figure 5 on the same scale as figures 1 and 4 to allow easy comparison between the plots. As can be seen, fairly good agreement is obtained between the calculated and experimental results. However, the results lie on a straight line whose slope is slightly different from 1. This could be because our assumptions that all solutes experience exactly the same average environment, and that the correlations in figures 2 and 3 are linear, are not entirely valid. None the less, for the purpose of making relatively small corrections to k and F_{ZZ} , our method would appear to be quite good. In addition, as can be seen from figure 5, the method predicts order parameters for both dilute and concentrated samples.

For the purpose of applying small corrections for differences in temperature and concentration among samples, the dependence of F_{ZZ} (figure 2) and k (figure 3) on the liquid crystal splittings has been taken to be linear. However, the straight lines in figures 2 and 3 do not go through the origin indicating that the linear approximation is not appropriate for a large range of liquid crystal splittings. This is of interest because a mean field theory for mixtures of liquid crystals predicts that a plot of the order parameter of one component of the mixture versus that of the second component will fall on a universal curve [2]. In a previous publication [14] the results reported here have been used to test this theory by treating



Figure 5. Orientation of 2,4-hexadiyne in $5CB-\alpha,\beta-d_4$: calculated versus experimental order parameters for 2,4-hexadiyne in $5CB-\alpha,\beta-d_4$. The calculated order parameters have been obtained in the same manner as for figure 1 except that values of F_{ZZ} and k have been obtained from figures 2 and 3 using the quadrupolar splittings of the α deuterons of the $5CB-\alpha,\beta-d_4$ (see text). Correlation coefficient = 0.991; \bullet , 1 mol %; \blacksquare , 9 mol %.

the solutes as molecules that would form a liquid crystal phase if they did not first crystallize.

Although figures 2 and 3 are not plots of order parameters, the variables involved $(F_{ZZ}, k \text{ and } \Delta v_x)$ are related to the solute and solvent order parameters. In the previous publication [14] we assumed that magnetic susceptibility measurements provide a reasonable estimate of a liquid crystal order parameter. Unfortunately, neither the magnetic susceptibility measurements, which emphasize the effect of the aromatic core, nor the liquid crystal α and β splittings are readily related to the molecular order parameter needed in the theory. A proper treatment must await a calculation that includes both the flexibility and asymmetry of the liquid crystal. However, the α and β splittings are a smooth function of the liquid crystal order parameter. From our model, the solute order parameter is also a smooth function of F_{ZZ} and k. Thus mean field theory predicts that the graphs in figures 2 and 3 should be smooth *curves*.

Further, the mean field theory for mixtures [14] predicts that the order parameter of one component is completely determined by that of the other, regardless of temperature or composition. This prediction gives credence to our scaling procedure where we calculate the values of F_{ZZ} and k for the sample of interest from those for another sample with exactly the same α deuteron quadrupolar splitting. This calculation obviates the need for performing all experiments on infinitely dilute samples at exactly the same temperature, and explains why we get good agreement between experiment and theory for solute concentrations up to 10 mol %.

4. Conclusions

We have shown that our model, based on the interaction between the electric field gradient due to the liquid crystal and the molecular quadrupole moment of the solute and the short range repulsive interactions, can describe the orientation of solutes in 5CB- α , β - d_4 very well. We have also shown that effects due to the variation in solute concentration and temperature among samples can be accounted for by scaling the force constant for small range interactions and the mean field gradient of the liquid crystal using the splittings of either the α or β deuterons of the liquid crystal. The current analysis is qualitatively consistent with a mean field theory for mixtures of liquid crystals [2] and gives insight into the specific form of the physical interactions involved. A more quantitative treatment is complicated by the fact that the interaction potential from our model for the short range interaction does not have the simple P_2 (cos θ) dependence of the Maier–Saupe [1] mean field theory.

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References

- [1] MAIER, W., and SAUPE, A., 1959, Z. Naturf. (a), 14, 882.
- [2] PALFFY-MUHORAY, P., DE BRUYN, J. R., and DUNMUR, D. A. 1985, Molec. Crystals liq. Crystals, 127, 301.
- [3] BUCKINGHAM, A. D., and MCLAUCHLAN, K. A., 1967, Prog. N.M.R. Spectrosc., 2, 63.
- [4] DIEHL, P., and KHETRAPAL, C. L., 1969, N.M.R. Basic Principles and Progress, Vol. 1 (Springer-Verlag), p. 1.
- [5] EMSLEY, J. W., and LINDON, J. C., 1975, N.M.R. Spectroscopy using Liquid Crystal Solvents (Pergamon Press).
- [6] KHETRAPAL, C. L., and KUNWAR, A. C., 1983, Adv. liq. Crystals, 6, 173.
- [7] BURNELL, E. E., VAN DER EST, A. J., PATEY, G. N., DE LANGE, C. A., and SNIJDERS, J. G., 1987, Bull. magn. Reson. (in the press).
- [8] VAN DER EST, A. J., KOK, M. Y., and BURNELL, E. E., 1986, Molec. Phys., 60, 397.
- [9] KOK, M. Y., VAN DER EST, A. J., and BURNELL, E. E., Liq. Crystals (submitted).
- [10] PATEY, G. N., BURNELL, E. E., SNIJDERS, J. G., and DE LANGE, C. A., 1983, Chem. Phys. Lett., 99, 271.
- [11] BARKER, P. B., VAN DER EST, A. J., BURNELL, E. E., PATEY, G. N., DE LANGE, C. A., and SNIJDERS, J. G., 1984, Chem. Phys. Lett., 107, 426.
- [12] SNIJDERS, J. G., DE LANGE, C. A., and BURNELL, E. E., 1983, J. chem. Phys., 79, 2964.
- [13] SNIJDERS, J. G., DE LANGE, C. A., and BURNELL, E. E., 1983, Israel J. Chem., 23, 269.
- [14] BATES, G. S., BURNELL, E. E., HOATSON, G. L., PALFFY-MUHORAY, P., and WEAVER, A., 1987, Chem. Phys. Lett., 134, 161.
- [15] BATES, G. S., BECKMANN, P. A., BURNELL, E. E., HOATSON, G. L., and PALFFY-MUHORAY, P., 1986, *Molec Phys.*, 57, 351.
- [16] DIEHL, P., KELLERHALS, H., and LUSTIG, E., 1972, NMR Basic Principles and Progress, Vol. 6 (Springer-Verlag), p. 1.
- [17] DIEHL, P., SÝKORA, S., NIEDERBERGER, W., and BURNELL, E. E., 1974, J. magn. Reson., 14, 260.
- [18] The references for the J couplings, molecular structures and molecular quadrupole moments are given in table 2 of [8].