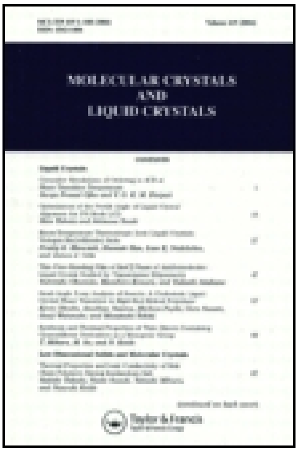

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^{2}H-NMR Study of Orientational Order in Binary Mixtures: A Nematic Phase of Biaxial Molecules

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^{2}H-NMR Study of Orientational Order in Binary Mixtures: A Nematic Phase of Biaxial Molecules

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Deuteron Magnetic Resonance (^{2}H-NMR) spectra have been obtained from a binary mixture of 2-fluorenyl-4′-tetradecyloxy benzoate-d_9 (FLOC$_{14}$) and *para*-Xylene-d_{10} (p-Xy), as a function of temperature. The liquid crystal, FLOC$_{14}$, is selectively deuterated on the rigid fluorene moiety while the p-Xy is perdeuterated. The quadrupolar splittings, ν_Q^k, allow the unambiguous determination of the temperature dependence of the orientational order parameters, S_{izz} and $(S_{ixx} - S_{iyy})$, of both species, $i = 1, 2$. These results are the first to provide information on the degree and asymmetry of orientational order, of both biaxial molecules, in the uniaxial nematic phase of a binary mixture. A new approach was adopted for analyzing the experimental data which uses a least squares fit of the quadrupolar splittings, ν_Q^k, to provide the four component order parameters, S_{1zz}, $(S_{1xx} - S_{1yy})$, S_{2zz} and $(S_{2xx} - S_{2yy})$.

The experimental results are interpreted using a recently proposed mean field theory of binary mixtures of biaxial molecules.[1] In the geometric mean approximation all particles couple to an identical mean field and the parameters of the theory are the ratios of intermolecular interaction strengths of the pure materials. There is good agreement between the predictions of theory and the four component order parameters determined from ^{2}H-NMR experiments, over the entire temperature range studied. Thus this description is capable of predicting the temperature dependence and interrelation of the nematic orientational order parameters for both components of the mixture. Analogous calculations on data from pure FLOC$_{14}$[2] gives a ratio of interaction strengths consistent with that obtained from the binary mixture.

INTRODUCTION

There continues to be considerable interest and attention focused on trying to understand and describe orientational order in liquid crystals. Obtaining a general, self consistent interpretation of results from different physical techniques is obviously an important and non-trivial task.[3] Part of this difficulty is a consequence

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of the fact that many spectroscopic methods use probe molecules, rather than monitoring the liquid crystal molecules directly, and thus are studying binary mixtures. The necessary, but simplistic, assumption that any probe faithfully reflects the behaviour of the liquid crystal molecules is clearly inadequate. The obvious advantage of probes is that they are small, rigid molecules of known symmetry whereas liquid crystals are large, flexible and exist in many different conformations of low symmetry. If significant advances are to be made it is crucial to understand molecular interactions in mixtures and thus delineate the explicit manner in which different probes report on their liquid crystalline environments. Anisotropic intermolecular potentials play a key role in the physics of liquid crystals and binary mixtures and thus must be explicitly included in any realistic theoretical description.

In the absence of external fields, all macroscopic properties of thermotropic nematic liquid crystal are uniaxial. Thus, despite the fact that the molecules are biaxial the phases are cylindrically symmetric. Biaxial phases have been observed in lyotropics,[4] in long chain polymers with nematogenic groups[5-8] and, more recently, in low molecular weight thermotropics.[9-11] However, there remains considerable speculation and controversy regarding the nature and origin of the phase biaxiality. Whether it is a consequence of molecular biaxiality or a result of statistical mechanical averaging over all possible molecular conformations is unclear.

This paper discusses and uses a new mean field theory that has recently been proposed for binary mixtures of biaxial molecules, forming either uniaxial or biaxial nematic phases.[1] This is more general and appropriate to real liquid crystals because, unlike previous treatments, it makes no simplifying assumptions about the symmetry of the phase, specific interactions, properties or relative concentrations of the two species. In binary mixtures the orientation of each biaxial particle is specified by two orientational order tensors, $S_{i\alpha\beta}$ and $T_{i\alpha\beta}$, which are simultaneously diagonalizable in a principal axis system. The theoretical variables are coupling constants which measure the strength of interactions between instantaneous orientation of the three distinguishable axes of particles i and j. If the geometric mean assumption is invoked then all particles interact with an identical nematic mean field, $\Lambda_{\alpha\beta}$, with coupling constants U_{ij}, V_{ij}, and W_{ij}.[1] The pseudopotentials give equations for the component order parameters which must be solved self-consistently to describe the general behaviour of binary mixtures of liquid crystals. For the, experimentally observed, uniaxial nematic phase the theory makes explicit predictions for the orientational order parameters of uniaxial and biaxial particles. In the case of cylindrically symmetric molecules the simplified description is equivalent to the existing mean field theory of binary mixtures[12] which has proved valuable in predicting and interpreting orientational order parameters obtained from ^{2}H-NMR experimental results in a variety of mixtures of liquid crystals over a wide range of temperatures and concentrations.[13,14] The two order parameters, S_{1zz} and S_{2zz}, describing the orientation of the long molecular axes, are related by temperature and concentration independent universal curves which are determined by the parameter r_1.[12] In the case of biaxial molecules there are unique relationships between all four order parameters, S_{1zz}, S_{2zz}, $(S_{1xx} - S_{1yy})$ and $(S_{2xx} - S_{2yy})$. These correlations are determined by ratios of the anisotropic interaction strengths, r_1, r_2 and r_3.[1] This paper reports the application of this formalism to a binary mixture of biaxial molecules, $FLOC_{14}$ and p-Xy. The theoretical parameters, r_i's, have been derived from non linear least squares fitting of the temperature dependent orientational order parameters derived from ^{2}H-NMR measurements.[15] In a comparable analysis on published data for pure $FLOC_{14}$[2] the value obtained for the only relevant parameter r_2, is consistent with that derived from the mixture. This is encouraging because it is essentially a molecular property and thus indicates the appropriateness of this description of component orientational order in binary mixtures of biaxial particles.

EXPERIMENTAL

(i) Synthesis

The $FLOC_{14}$-d_9 was synthesized by the Organic Synthesis and Purification Group at the Liquid Crystal Institute of Kent State University (N. S. F. grant 881-8561). A detailed description of the chemical synthesis has been published.[2] The *para*-Xylene-d_{10} was obtained from MSD Isotopes and used without purification. A homogeneous mixture was obtained by micro-pipetting the p-Xylene-d_{10} into the isotropic phase of $FLOC_{14}$ and homogenizing with a vortex mixer. The molecular structures of $FLOC_{14}$ and p-Xylene are shown in Figure 1. Assuming 100% deuteration, the integrated intensity of the lines of a ^{2}H-NMR spectrum gives the actual concentration of the mixture as 11 mole%. The sealed sample was left in a regulated oven, at 413K, when not in use.

(ii) NMR Instrumentation

Deuteron NMR spectra were obtained at 32.8 MHz on a home built spectrometer in which the sample coil is in an oven. Helium gas is circulated between the coil and oven wall to maintain good thermal contact and low humidity. The temperature of the oven is controlled by a circulating oil bath (NESLAB EX-250-HT) which could be set and regulated to ±100 mK. The thermal gradient over the 5 mm sample tube had been previously determined, to be ±300 mK.[2] For consistent results, to avoid hysteresis and to ensure reproducible magnetic alignment, the sample was always taken into the isotropic phase at the start of a run and cooled slowly to the appropriate temperatures, where it was equilibrated for 45 minutes prior to data acquisition. Spectra were collected every 0.5K within 10K of the transition, $T_{NI}^{+} = 408.77K$, and every 3K for the next 42K.

All ^{2}H-NMR signals were recorded using an echo sequence, $(90_x - \tau - 90_y)$, to refocus the second rank quadrupolar interaction, $\hat{\mathcal{H}}_Q$. Fourier transformation from the top of the echo provides the frequency spectra from which the splittings, ν_Q^k, are measured. The relevant experimental parameters are as follows: 90 pulse length was 4.5 μs, echo delay $\tau = 100$ μs, dwell time = 5 μs (SW = ±100 kHz), recycle time of 1s, phase alternation of the second pulse, signal averaging for 2,500 scans and the digitized signal comprised of 2K complex points.

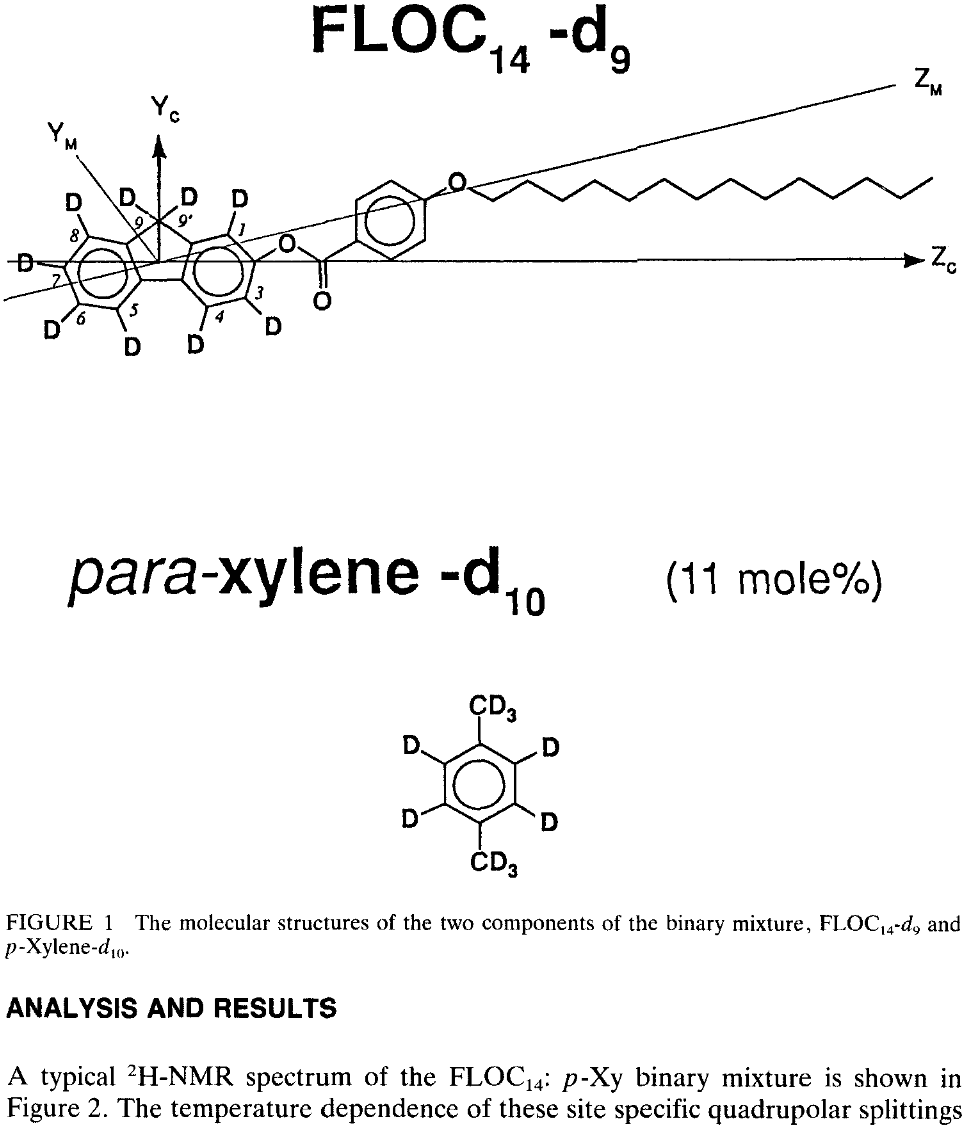

FIGURE 1 The molecular structures of the two components of the binary mixture, $FLOC_{14}$-d_9 and p-Xylene-d_{10}.

ANALYSIS AND RESULTS

A typical ^{2}H-NMR spectrum of the $FLOC_{14}$: p-Xy binary mixture is shown in Figure 2. The temperature dependence of these site specific quadrupolar splittings are given in the Table I and plotted in Figure 3. The objective is to analyze these quadrupolar splittings to provide the temperature dependence of the orientational order parameters of both molecules in the mixture. An analytical expression, relating the splittings of each site as a function of molecular geometry and orientation, is required.[15] Each deuteron experiences and interacts with the local electric field gradient (EFG) tensor and the Euler angles describing the rotation from this bond principle axis system into the laboratory frame determine the values of the observed quadrupolar splittings.

Attributing spectral lines to specific deuteron sites and determining the relative signs of the quadrupole couplings are non-trivial processes. For pure $FLOC_{14}$-d_9 this was done by Wu, Ziemneka and Doane[2] and this paper assumes an identical assignment. For convenience, the transformation from the bond principal axis system to the laboratory axis frame is performed in four steps.[15] The approach adopted here has fewer assumptions than the previous method[2] and a more detailed discussion of this analysis will be presented elsewhere.[15] The first transformation describes the relative orientation of the principal axes of the electric field gradient tensor of each deuterated site, j, and the rigid fluorene core. The Rose convention Euler angles describing this rotation, $(\alpha_1^j, \beta_1^j, \gamma_1^j)$, are obtained from X-ray data.[16] Next the rigid fluorene core is rotated into the FLOC$_{14}$ molecular axes and this transformation is described by the Euler angles, $(\alpha_2, \beta_2, \gamma_2)$, which reflect the thermal averaging over all conformations of the tail. The third transformation rotates the FLOC$_{14}$ molecular order tensor into the director frame. These Euler angles, $(\alpha_3, \beta_3, \gamma_3)$, are used to define the orientational order parameters of FLOC$_{14}$,

$$S_{1zz} = \left\langle \frac{3}{2}\cos^2(\beta_3) - \frac{1}{2} \right\rangle \text{ and } (S_{1xx} - S_{1yy}) = \left\langle \frac{3}{2}\sin^2(\beta_3)\cos(2\alpha_3) \right\rangle.$$

Finally the liquid crystal director must be rotated so that it is aligned with the laboratory frame z-axis, $(\alpha_4, \beta_4, \gamma_4)$. In NMR experiments the nematic phase is magnetically oriented and hence this transformation is irrelevant.

For the FLOC$_{14}$, $i = 1$, the site specific quadrupolar splittings, ν_Q^j, of positions $j = 1$–9 must be used to determine the order parameters, S_{1zz} and $(S_{1xx} - S_{1yy})$, of the rigid core of the liquid crystal molecule. The problem is clearly overdetermined and results from all positions must be self consistent. Although asymmetry parameters for aromatic deuterons are finite $(\eta \leq 0.04)$, they will be assumed to be zero in this analysis. This introduces negligible error provided the principal axis of the deuteron EFG tensor is not close to the magic angle. Predictably, this approximation appears to be the main source of error in the calculations, particularly for the smaller splittings. The effect of including a finite asymmetry parameter, $\eta \neq 0$, on the splittings and derived order parameters will be considered in a subsequent publication.[15] Ignoring η, the following expressions are derived for the splittings of deuterons at aromatic sites on the fluorene core, sites $j = 1$–8.

$$\begin{aligned}\nu_Q^j = \frac{3}{8}\,\tilde{\nu}_Q^j\{S_{1zz}[&\{3\cos^2(\beta_2) - 1\}\{3\cos^2(\beta_1^j) - 1\} \\ &- 3\sin(2\beta_2)\sin(\alpha_2)\sin(2\beta_1^j) - 3\sin^2(\beta_2)\cos(2\alpha_2)\sin^2(\beta_1^j)] \\ &+ (S_{1xx} - S_{1yy})[\sin^2(\beta_1^j)\cos(2\alpha_2)\{1 + \cos^2(\beta_2)\} \\ &- \sin(2\beta_1^j)\sin(\alpha_2)\sin(2\beta_2) + \{3\cos^2(\beta_1^j) - 1\}\sin^2(\beta_2)]\}\end{aligned} \tag{1}$$

where; β_2 and α_2 describe the rotation from core to molecular order tensor frame and $\tilde{\nu}_Q^j = [e^2q^jQ_D/h]$ is the quadrupolar coupling constant of the jth site. For the aromatic deuterons of the fluorene ring, $j = 1–8$, the intrinsic value is taken to be $\bar{\nu}^j_Q = \bar{\nu}^{AR}_Q = 182$ kHz while for $j = 9$ it is $\bar{\nu}^9_Q = 169$ kHz. The splitting for the aliphatic carbon on the $j = 9$ site is

$$\nu^9_Q = \frac{3}{8}\bar{\nu}^9_Q\{S_{1zz}[\{1 - 3\cos^2(\beta_2)\} + 3\cos(2\alpha_2 + 2\gamma_1)\sin^2(\beta_2)] + (S_{1xx} - S_{1yy})[\sin^2(\beta_2) - \{1 + \cos^2(\beta_2)\}\cos(2\alpha_2 + 2\gamma_1)]\}. \quad (2)$$

A nonlinear least squares fit routine was employed to determine the parameters S_{1zz}, $(S_{1xx} - S_{1yy})$, β_2, and α_2. This analysis revealed that α_2 was consistently close to $(-\pi/2)$ proving that there is no twist of the rigid segment with respect to the molecular order matrix axis.[15] The routine minimized the function

$$\chi^2 = \sum_j \left[\frac{\nu^{j,\text{exp}}_Q - \nu^{j,\text{the}}_Q(\beta^j_1;\, S_{1zz},\, (S_{1xx} - S_{1yy}),\, \beta_2)}{\sigma_j}\right]^2. \quad (3)$$

By adjusting the three parameters S_{1zz}, $(S_{1xx} - S_{1yy})$, and β_2 the best fit to all the experimental data was obtained.[15] The function $\nu^{j,\text{the}}_Q$ is calculated from the analytical expression given in Equation (2) using the fitted values of the three parameters. The temperature dependence of the order parameters is given in Table II and shown in Figure 4 (i).

For the small rigid p-Xylene-d_{10}, $i = 2$, the analysis is relatively straightforward since the order parameters, S_{2zz} and $(S_{2xx} - S_{2yy})$, are obtained from two simultaneous equations for the splittings, ν^{AR}_Q and ν^{Me}_Q. Again it is assumed that the angle between the principal axis of the EFG tensor and the static magnetic field is not near the magic angle so that terms containing the asymmetry parameter, η, can be ignored. The methyl group is rapidly rotating and it's splitting is given by

$$\nu^{Me}_Q = \frac{3}{4} S_{2zz}\, \bar{\nu}^{Me}_Q\, [3\cos^2(\xi) - 1] \quad (4)$$

and for the aromatic sites,

$$\nu^{AR}_Q = \frac{3}{4}\bar{\nu}^{AR}_Q\{S_{2zz}[3\cos^2(\zeta) - 1] + (S_{2xx} - S_{2yy})\sin^2(\zeta)\} \quad (5)$$

with $\xi = 70.5°$, $\zeta = 60°$, $\bar{\nu}^{Me}_Q = 169$ kHz and $\bar{\nu}^{AR}_Q = 182$ kHz. The two equations are solved to yield the order parameters of p-Xylene, S_{2zz} and $(S_{2xx} - S_{2yy})$. For the aromatic deuterons the uncertainties in the splittings are taken to be the same as those used for FLOC$_{14}$ and simple error propagation is employed to estimate errors in the order parameters. The temperature dependence of the orientational order parameters of p-Xylene, S_{2zz} and $(S_{2xx} - S_{2yy})$, is presented in Figure 4 (ii).

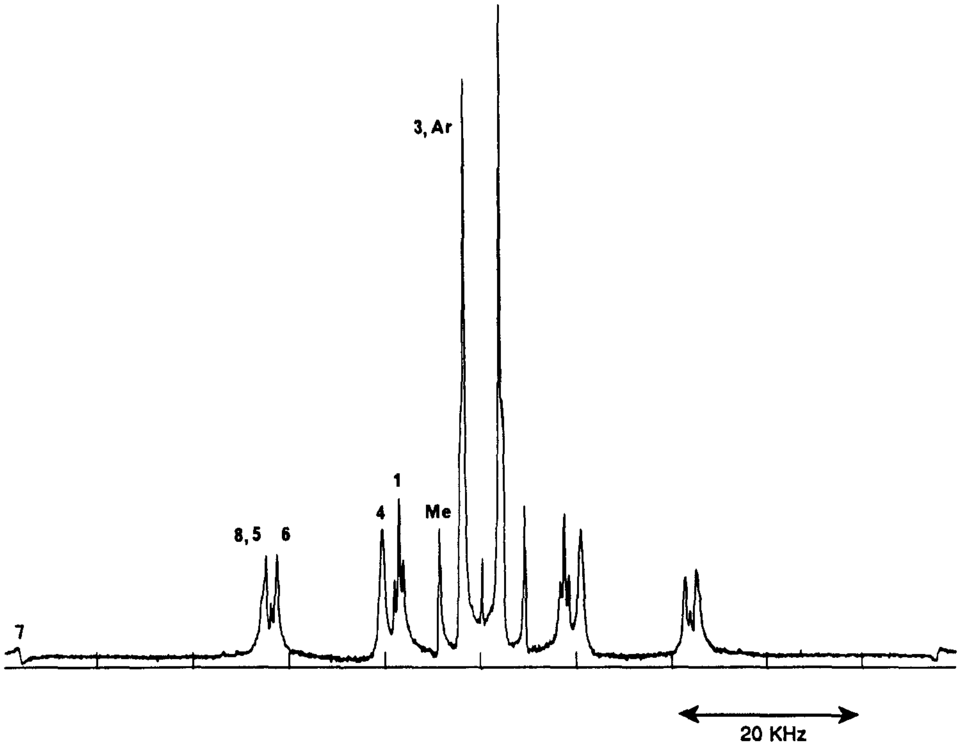

FIGURE 2 ^{2}H-NMR Spectrum of the binary mixture of FLOC$_{14}$-d_9: p-Xylene-d_{10}, at a temperature of $T = 366.99$ K.

DISCUSSION AND CONCLUSIONS

It has been demonstrated that ^{2}H-NMR experimental results are capable of providing the temperature dependence of the order parameters in uniaxial nematic phases of binary mixtures. A recently proposed theory[1] has been successful in interpreting the results. This provides an appropriate description of the orientation of biaxial molecules in binary mixtures and has predictive capabilities over a wide range of temperature and composition.[1] It is applicable to both uniaxial and biaxial nematic phases and since concentration is explicitly included it does not require one component to be infinitely dilute.[17]

The four order parameters of the FLOC$_{14}$: p-Xy mixture have been fitted (nonlinear least squares) to universal curves. The results, shown in Figure 5, correspond to the following parameters:

$$\begin{aligned} r_1 &= 0.251 \pm 0.008 \\ r_2 &= -0.16 \pm 0.01 \\ r_3 &= 0.084 \pm 0.004. \end{aligned} \tag{6}$$

TABLE I

The experimental data of quadrupolar splittings, ν_Q^i (kHz), for the binary mixture FLOC$_{14}$: *p*-Xy

T (°C)	ν_Q^1	ν_Q^3	ν_Q^4	ν_Q^5	ν_Q^6	ν_Q^7	ν_Q^8	ν_Q^{AR}	ν_Q^{Me}
93.82	−34.08	7.47	−40.97	−88.77	84.13	191.84	−88.77	7.47	17.33
96.60	−33.59	7.52	−40.23	−87.60	83.35	188.87	−87.60	7.52	17.38
99.53	−32.81	7.57	−39.55	−86.13	82.52	187.06	−86.13	7.57	17.19
102.46	−31.98	7.62	−38.63	−84.77	81.54	183.98	−84.77	7.62	17.09
105.30	−31.01	7.44	−37.65	−83.01	80.37	181.30	−83.00	7.44	16.89
108.13	−29.93	7.67	−36.43	−81.10	78.61	177.00	−81.10	7.67	16.60
111.05	−28.17	7.62	−34.67	−76.56	76.56	173.09	−76.56	7.62	15.92
114.02	−28.86	7.52	−32.81	−73.88	73.88	164.46	−73.88	7.18	15.87
117.00	−20.75	7.72	−26.03	−61.57	63.10	143.26	−61.57	6.69	13.53
118.22	−19.82	7.67	−24.61	−59.10	60.84	137.74	−59.10	6.49	12.89
118.63	−19.87	7.59	−24.37	−58.06	59.96	135.25	−58.06	6.40	12.79
119.05	−19.14	7.57	−23.58	−56.99	58.84	133.40	−56.99	6.35	12.60
119.57	−18.75	7.52	−22.80	−56.20	57.81	132.37	−56.20	6.20	12.31
120.00	−18.46	7.47	−22.31	−54.83	56.98	129.78	−54.83	6.15	11.95
120.44	−17.92	7.37	−21.93	−53.27	55.67	127.69	−53.27	6.00	11.94
120.97	−17.14	7.23	−20.50	−51.45	54.25	124.51	−51.47	5.90	11.04
121.52	−16.41	7.08	−19.43	−49.71	52.78	121.97	−49.71	5.67	11.33
121.97	−16.98	6.98	−18.26	−47.75	51.86	119.19	−47.75	5.66	10.25
122.50	−15.67	6.79	−16.99	−45.51	50.34	115.87	−45.51	5.47	9.86
122.99	−14.68	6.59	−16.44	−42.99	48.49	113.28	−42.99	5.23	8.74
123.47	−13.08	6.49	−15.77	−40.58	47.56	110.30	−40.58	5.13	7.39
123.97	−12.79	6.40	−14.99	−41.16	45.31	105.02	−41.16	5.33	7.66

This description is useful because it provides a physical interpretation of these parameters as ratios of anisotropic interaction potentials.[1] The r_1 parameter is defined to be the ratio of the anisotropic interaction strength coupling the long axes of each molecule to the uniaxial order parameters, and thus determines the relative values of S_{1zz} and S_{2zz}.

$$r_1 = \left[\frac{U_{22}}{U_{11}}\right]^{1/2} \tag{7}$$

For the case of uniaxial molecules[12] this parameter is defined as

$$r_1 = \left[\frac{T_{NI,1}\,\rho_2}{T_{NI,2}\,\rho_1}\right]^{1/2} \tag{8}$$

where; T_{NI} is Nematic-Isotropic transition temperature of species i and ρ_i its num-

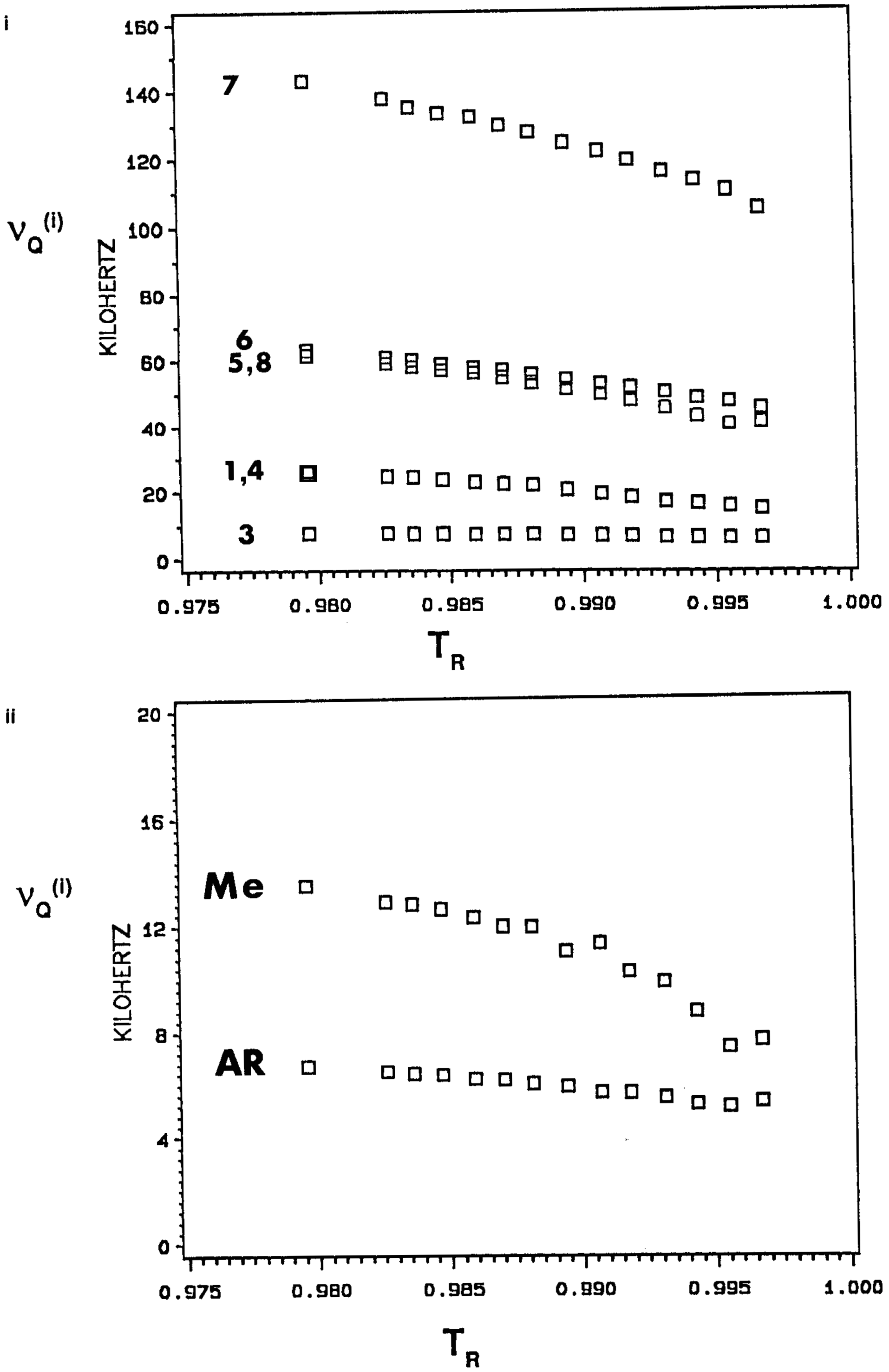

FIGURE 3 The site specific quadrupolar splittings, $\nu_Q^{(i)}$, as a function of reduced temperature, T_R. (i) FLOC$_{14}$-d_9 and (ii) p-Xylene-d_{10}.

TABLE II

Results of nonlinear least squares fits of the parameters for $FLOC_{14}$ [S_{1zz}, (S_{1xx} − S_{1yy}), β_2] and *p*-Xy [S_{2zz}, (S_{2xx} − S_{2yy})]

T(°C)	χ^2	S_{1zz} [a]	$(S_{1xx}-S_{1yy})$ [b]	β_2 [c]	S_{2zz} [d]	$(S_{2xx}-S_{2yy})$ [e]
93.82	0.1802	0.81	−0.057	6.901	0.205	0.141
96.60	0.4399	0.80	−0.058	6.930	0.206	0.142
99.53	0.2355	0.79	−0.060	6.924	0.203	0.142
102.46	0.3981	0.78	−0.061	6.946	0.202	0.142
105.30	0.1543	0.77	−0.062	6.960	0.200	0.140
108.13	0.3701	0.75	−0.063	6.964	0.197	0.140
111.05	0.1768	0.73	−0.071	6.909	0.189	0.137
114.02	0.1394	0.69	−0.068	7.011	0.188	0.133
117.00	0.8430	0.60	−0.074	6.889	0.160	0.119
118.22	0.9017	0.58	−0.073	6.897	0.152	0.114
118.63	0.5614	0.57	−0.072	6.901	0.152	0.113
119.05	1.0292	0.56	−0.073	6.895	0.149	0.112
119.57	2.1360	0.55	−0.074	6.874	0.145	0.109
120.00	1.6554	0.54	−0.074	6.875	0.142	0.107
120.44	1.9613	0.53	−0.074	6.821	0.141	0.105
120.97	2.9376	0.52	−0.076	6.837	0.131	0.101
121.52	4.3038	0.51	−0.077	6.834	0.134	0.100
121.97	4.8322	0.49	−0.080	6.857	0.121	0.096
122.50	6.1790	0.48	−0.083	6.874	0.117	0.092
122.99	8.6532	0.47	−0.084	6.775	0.104	0.086
123.47	9.1134	0.45	−0.087	6.756	0.088	0.079
123.97	5.9930	0.43	−0.076	6.834	0.091	0.082

[a] $\delta S_{1zz} = \pm 0.01$.

[b] $\delta (S_{1xx} - S_{1yy}) = \pm 0.014$.

[c] $\delta \beta_2 = \pm 0.005$.

[d] $\delta S_{2zz} = \pm 0.018$.

[e] $\delta (S_{2xx} - S_{2yy}) = \pm 0.021$.

ber density. For biaxial particles the corresponding theoretical parameter, r_1, exists but can no longer be rigorously defined by equation (8). However, a crude approximation for the virtual transition temperature of *p*-Xylene can be made (assuming the same molar volumes). Since $T_{NI,1}$ = 409.61K (136.45°C) for pure $FLOC_{14}$-d_9 this gives a $T^*_{NI,2}$ = 26.42K (−246.73°C) for *p*-Xylene, which is well below the crystallization temperature, as required for a non-mesogenic molecule.[18]

The parameter governing the coupling of the instantaneous orientation of the short axes with the biaxial order parameters is given by

$$r_2 = \left[\frac{W_{11}}{U_{11}}\right]^{1/2} \tag{9}$$

Since these interaction potentials are single particle properties they can, in principle, be derived from the behaviour of the pure materials. r_2 is equivalent to the parameter δ in the theory of molecular biaxiality proposed by Beregersen, Palffy-Muhoray and Dunmur.[19] An identical analysis of the pure FLOC_{14} data[2] gave a value of $r_2 = -0.13 \pm 0.01$, which although not quite within experimental error is at least consistent with that obtained from the mixture.

The third parameter determines the ratio of anisotropic interaction potentials of coupling of the short and long axes of unlike species,

$$r_3 = \left[\frac{W_{22}}{U_{11}}\right]^{1/2} \tag{10}$$

This is unique to this treatment of binary mixtures of biaxial particles and it should again be stressed that there is a lack of reciprocity in these couplings.[1] Hence it is incorrect to ignore this effect and assume a single interaction strength, even in the infinite dilution limit.[17] Like the treatment of Emsley *et al.*[17] the parameter r_2 (corresponding to λ) is a molecular property and thus explicitly temperature independent.[17]

CONCLUSIONS

NMR is distinguished by its ability to provide information on molecular orientation at specific sites of both molecules in binary mixtures and thus has the potential to make a significant contribution to the understanding of liquid crystal systems. This paper reports ^{2}H-NMR experimental results which have been used to determine the four component order parameters in a nematic binary mixture of biaxial molecules. The temperature dependence of the order parameters, which is readily obtained from the spectra, contains information on the order, asymmetry, flexibility and motion of the liquid crystal molecules.

It has been demonstrated that the recently proposed mean field theory of binary mixtures of biaxial molecules[1] is very successful in interpreting ^{2}H-NMR experimental data. Physical parameters can be extracted which provide unique and important information about the anisotropic intermolecular interactions between biaxial molecules in the nematic liquid crystalline mixtures. If the geometric mean assumption is made all particles couple to an identical mean field. The theory is consistent, in the limits of a uniaxial phase, molecular cylindrical symmetry and single component systems, in that it simplifies to previous descriptions.[12,19] It is the first to calculate the free energy explicitly, to include the concentration dependence and to allow for biaxial nematic phases.

There is an intimate relationship between theory and experiment and the development of realistic molecular theories of liquid crystals and binary mixtures requires results from physical techniques that are capable of probing molecular properties sensitive to orientation and dynamics. Obviously mixtures and pure

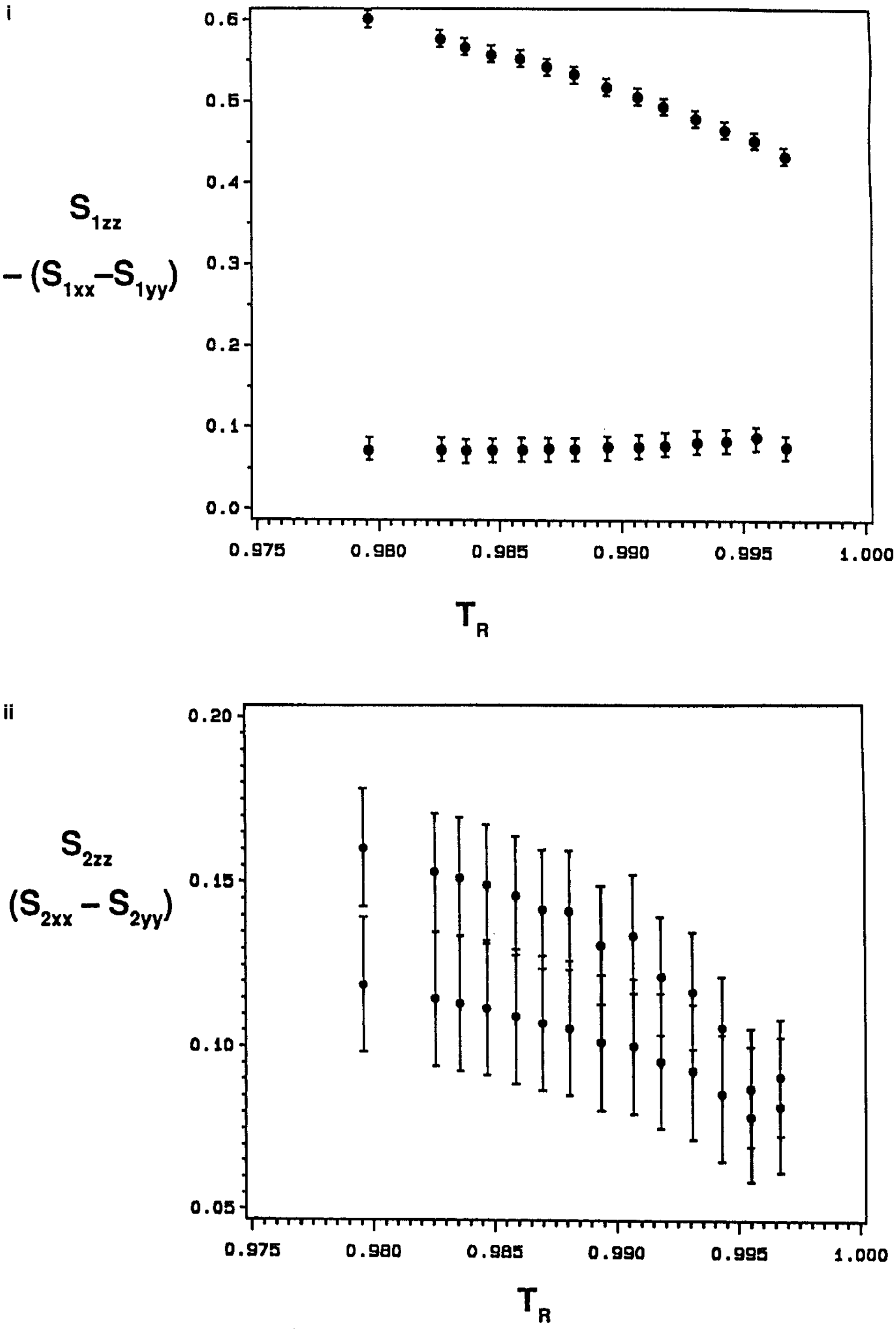

FIGURE 4 Molecular orientational order parameters of both components, S_{izz} and $(S_{ixx} - S_{iyy})$, as a function of reduced temperature, T_R. (i) $i = 1$, FLOC$_{14}$-d_9 and (ii) $i = 2$, p-Xylene-d_{10}.

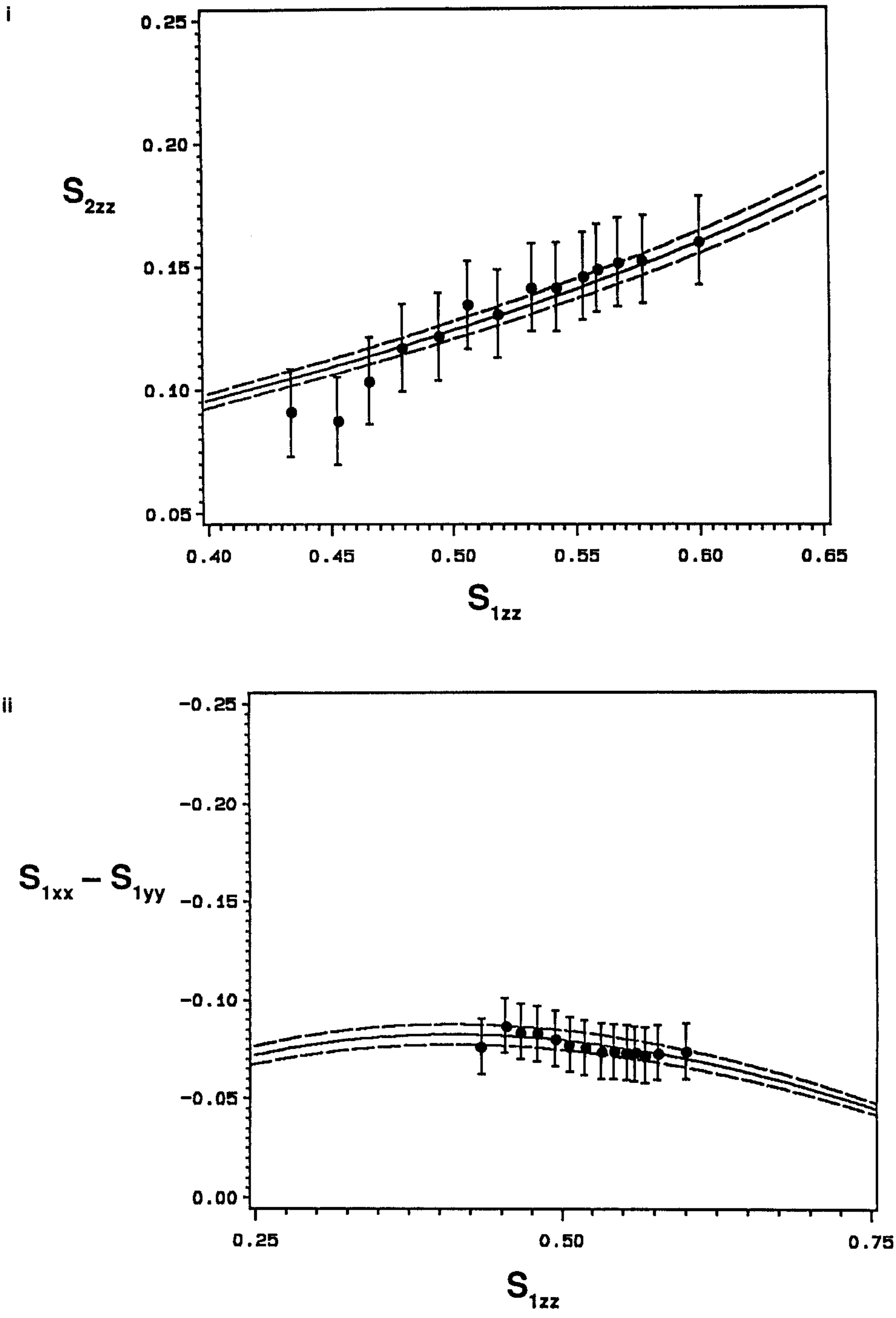

FIGURE 5 Interrelations of the orientational order parameters with the best non linear least squares fit[15] to the ratios of interaction potentials, r_i, given in the text. (i) S_{2zz} versus S_{1zz}, (ii) $(S_{1xx} - S_{1yy})$ versus S_{1zz} and (iii) $(S_{2xx} - S_{2yy})$ versus S_{1zz}.

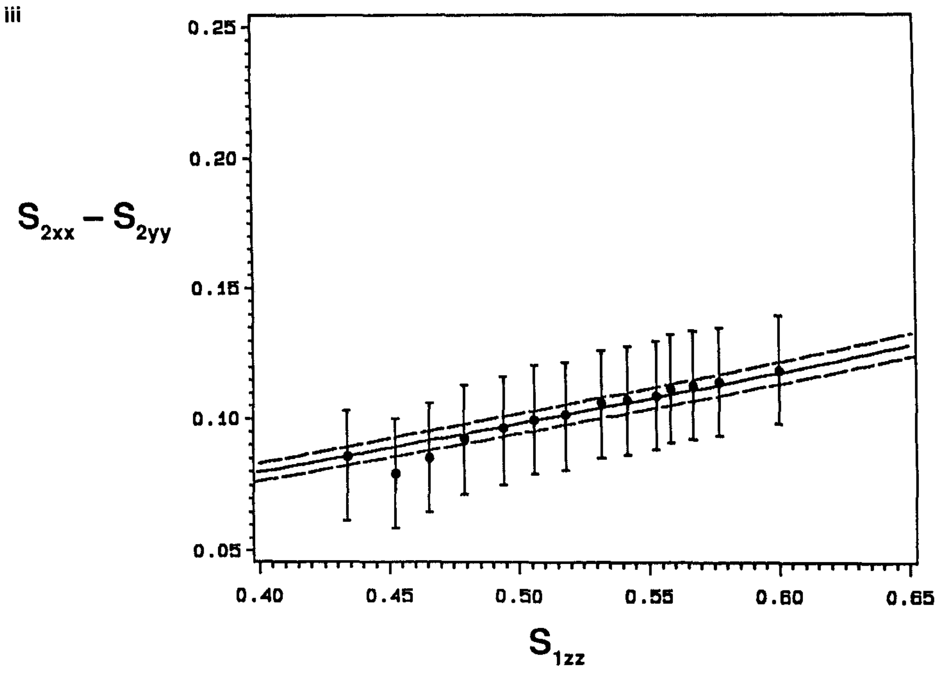

FIGURE 5—(*Continued*)

materials are fundamentally different and it is incorrect to assume that probe molecules are capable of monitoring their environment in an unbiased way.

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