The structure of ethylbenzene as a solute in liquid crystalline solvents via analysis of proton NMR spectra

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Received 7th April 2000, Accepted 7th June 2000 Published on the Web 3rd July 2000

Previous attempts to analyze the proton spectrum of ethylbenzene as a solute in nematic liquid crystalline solvents failed, but a successful strategy has now been devised and is described here. The proton spectra of samples of ethylbenzene dissolved in four different liquid crystals have been analyzed to yield sets of the partially-averaged dipolar couplings, D_{ij} . The couplings are then used to test models for the structure and conformation of this molecule.

Introduction

The partially averaged dipolar couplings, D_{ij} , which can be obtained by analysing the spectra of samples dissolved in a liquid crystalline (LC) solvent, are related to the structure, orientational order and conformational distribution of the molecules. The challenge is to determine these molecular properties from the observed sets of D_{ij} . Perhaps the most intriguing aspect is that the data are for a molecule in a liquid phase, and the structure and conformational distribution may differ from those in either the gas or solid phases. For rigid molecules, which are moving rapidly compared with the magnitude of the dipolar couplings, the observed D_{ii} are averages over the molecular motion. The averaging is given by:

$$D_{ij} = \int D_{ij}(\beta, \gamma) P_{\rm LC}(\beta, \gamma) \sin \beta \, d\beta \, d\gamma \tag{1}$$

where $D_{i,i}(\beta,\gamma)$ is the value of the coupling when the molecule is at a fixed orientation with respect to the mesophase director specified by the polar angles β and γ , and $P_{LC}(\beta,\gamma)$ is the probability that the molecule is at this orientation. Eqn. (1) may be expressed in another way by introducing principal, orientational order parameters, S_{zz} and $S_{xx} - S_{yy}$, defined as:

$$S_{\alpha\alpha} = \int \frac{1}{2} (3 \cos^2 \theta_{\alpha} - 1) P_{\rm LC}(\beta, \gamma) \sin \beta \, d\beta \, d\gamma \tag{2}$$

to give:

$$D_{ij}/\text{Hz} = -\frac{\mu_0 \gamma_i \gamma_j h}{32\pi^3 r_{ij}^3} \left[S_{zz} (3 \cos^2 \theta_{ijz} - 1) + (S_{xx} - S_{yy}) (\cos^2 \theta_{ijx} - \cos^2 \theta_{ijy}) \right]$$
(3)

The $\theta_{ij\alpha}$ are the angles between the internuclear vector \mathbf{r}_{ij} and the molecule-fixed, principal axes.

For rigid molecules it is possible to obtain the relative positions of the interacting nuclei in the molecular frame, provided the value of r_{ij} for one pair of nuclei is assumed. It is also possible to allow for the effects of vibrational motion, so that accurate comparisons can be made between the structures of

DOI: 10.1039/b002803g

rigid molecules in the liquid crystalline and solid and gaseous phases.1,2

There are two intrinsic reasons why it is much more difficult to make such a comparison for molecules that we term 'flexible', that is they exhibit some large amplitude, internal motion, such as rotations about bonds. The first reason is that the proton spectra of flexible molecules can be very difficult to analyse. In the case of ethylbenzene, whose structure is shown in Fig. 1, the proton spectra of samples dissolved in liquid crystalline solvents are extremely complex, as demonstrated by the spectrum shown in Fig. 2, and previous attempts to analyse such spectra have failed. The second problem is that the orientational order and the conformational distribution of molecules in liquid crystalline phases are interdependent, so that eqn. (1), for a molecule like ethylbenzene with two bond



Fig. 1 Structure and atomic labelling for ethylbenzene.

3405 Phys. Chem. Chem. Phys., 2000, 2, 3405-3413

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Fig. 2 Comparison of the 300 MHz 1 H spectrum of a sample of ethylbenzene dissolved in the nematic solvent I35 (bottom) with that calculated with the parameters given in Table 2, column F (top).

rotational motions, becomes:³

$$D_{ij} = \int D_{ij}(\beta, \gamma, \psi, \phi) P_{\rm LC}(\beta, \gamma, \psi, \phi) \sin \beta \, d\beta \, d\gamma \, d\psi \, d\phi \qquad (4)$$

Here $D_{ij}(\beta,\gamma,\psi,\phi)$ and $P_{\rm LC}(\beta,\gamma,\psi,\phi)$ refer to a molecule in a fixed conformation, specified by ϕ and ψ , and orientation in the liquid crystalline phase, given by β and γ . In order to relate the sets of D_{ii} obtained from a successful analysis of a proton spectrum of a flexible molecule dissolved in liquid crystalline phase to its structure, orientational order and conformational state, it is necessary to develop a model for how the orientational order depends on the conformational state of the molecule. This requires modelling $P_{\rm LC}(\beta,\gamma,\psi,\phi)$. Mean field models of $P_{\rm LC}(\beta, \gamma, \psi, \phi)$ have been proposed and shown to produce reasonable results for several flexible molecules. Having obtained $P_{LC}(\beta,\gamma,\psi,\phi)$ it is then possible to derive $P_{\rm LC}(\psi,\phi)$, the probability that the molecule is in a conformation specified by ϕ and ψ independently of the orientation of the molecule in the phase. In one of the mean field models, known as the additive potential (AP) model, it is also possible to relate $P_{\rm LC}(\psi,\phi)$ to $V(\psi,\phi)$, the rotational potential when the molecule is in the same solvent, at the same temperature, but in an isotropic phase.³

As noted already an attempt to study the rotational potential of ethylbenzene (EB) in this way failed because it was not possible to analyse the proton spectrum. It was possible, however, to analyse the proton spectrum of 4-chloroethyl-[β-¹³C]benzene (CEB) in nematic solvents, and hence to obtain $V(\psi,\phi)$ for this *para*-substituted derivative of ethylbenzene.⁴ It was found that $V(\psi,\phi)$ obtained for CEB is very different from the potential determined by a combined microwave spectroscopy (MW) and molecular orbital (MO) calculation on ethylbenzene.⁵ This could be a real phenomenon, since the LC NMR data refer to a condensed, liquid phase, whilst the MW and MO results refer to an isolated molecule. It is also possible that the AP model is flawed and is producing a misleading result, and of course there is the simple interpretation that substitution by chlorine into the ring is changing $V(\psi,\phi)$. It would clearly be an advantage if the proton spectrum of ethylbenzene itself could be analysed to see if the LC NMR method still produces a result which is very different from that of the same, but isolated molecule.

We will demonstrate here that it is indeed now possible to analyse the proton spectra of ethylbenzene dissolved in nematic liquid crystalline solvents. This has been achieved by combining multiple quantum techniques^{6,7} with the well tested deuterium substitution method in order to obtain good starting parameters for the analysis of the fully protonated species. The spectra of ethylbenzene in four different liquid crystalline solvents have been analysed. Each spectrum analysis is described in detail because it has proved elusive to have a single protocol for unravelling these complex spectra, and each spectrum presented particular difficulties. The derivation of a conformational distribution for each of these samples also allows us to investigate whether this is affected appreciably by the nature of the liquid crystalline solvent.

Experimental

The following isotopomers were used: fully deuteriated ethylbenzene (I) (EB-d₁₀), which was purchased from Cambridge I sotope Lab. Inc., $(\beta,\beta,\beta-d_3]$ ethylbenzene (II) (EB-d₃), $[\alpha,\alpha-d_2]$ ethylbenzene (III) (EB-d₂) and ethylbenzene (IV) (EB), obtained from Sigma-Aldrich. The compounds II and III were synthesized according to the following procedure.

Synthesis of isotopically labelled samples

 $[\beta,\beta,\beta-d_3]$ Ethylbenzene (II). Deuteriation of acetophenone in the methyl group was achieved by refluxing with D₂O (99.9%) containing potassium carbonate until its isotopic purity was determined by NMR to be higher than 98%.

Aluminium chloride (82.87 mmol) in dry Et_2O (30 ml) was added, under N_2 , to a stirred mixture of $LiAlH_4$ (1.57 g, 41.37 mmol) in dry Et_2O (30 ml). The mixture was stirred for 15 min, after which acetophenone-d₃ (2.5 g, 20.29 mmol) in chloroform (60 ml) was added slowly, and the mixture was heated at reflux for 18 h. The excess of reducing agent was destroyed by careful addition of 40 ml H_2SO_4 solution (15% by weight), and the product was extracted into Et_2O (4 × 7 ml) and dried with sodium sulfate. Removal of the solvent left the crude product, which was distilled to yield EB-d₃ (1.69 g, 15.5 mmol, 76.4% yield, D = 98%).

 $[\alpha,\alpha-d_2]$ Ethylbenzene (III). EB-d₂ was obtained via the same method by replacing LiAlH₄ with LiAlD₄ (from Sigma-Aldrich, D = 98%).

Solvents and solutions

Samples in four nematic liquid crystalline solvents were studied:

A. I35 (Merck) with $R_1 = C_3H_7$ and $R_2 = C_5H_{11}$



B. ZLI 1132 (Merck) mixture of compounds with $R_{1}=C_{3}H_{7}, C_{5}H_{11}$ and $C_{7}H_{15}$

C. 152 same as I35 but with $R_1 = C_5 H_{11}$ and $R_2 = C_2 H_5$ D. EBBA



The following solutions were made:

Solvent	Isotopomers	Concentration (wt.%)
A. (I35)	I + IV equimolar II III	11.6 10.8 18.3
B. (ZLI 1132)	I + IV II III IV	16.7 16.5 16.4 16.7
C. (I52)	I + IV equimolar I + III equimolar	11.8 11.8
D. (EBBA)	I + IV equimolar	13.9

NMR spectra

All the spectra were recorded on a Bruker AC 300 at 300 K with the samples contained in 5 mm tubes. The following types of experiments were performed in addition to the ordinary, repeated single pulse method to obtain single quantum spectra.

Spin-echo spectra. The proton spectra of the partially deuteriated samples are simpler than those of ethylbenzene, as illustrated in Fig. 3(a), which shows the ¹H spectrum of EB-d₃ in I35. This spectrum depends upon both interproton and proton-deuterium dipolar couplings, and a simpler spectrum could be obtained by removing the couplings to deuterium. This can be achieved in principle by deuterium decoupling, but this was not possible on the spectrometer available. An alternative is to use spin-echo refocussing.⁸ The pulse sequence is shown in Fig. 4. The 180° pulse leads to a refocussing of both the chemical shifts and the spin couplings to all non-resonant nuclei at the time $2t_1$. Repeating the sequence with incremented values of t_1 whilst recording the whole of the free induction decay (FID) in t_2 leads to a 2D spectrum after Fourier transformation with respect to t_1 and t_2 . The projection on to the F_1 axis produces a spin-echo spectrum which is free from the effects of chemical shifts and the D_{ii} (HD). Fig. 3(b) shows such an echo spectrum for EB-d₃ in 135

Multiple quantum spectra. Two types of $N^{I}Q$ spectrum were obtained for samples of ethylbenzene, where N^{I} is the order of the multiple quantum coherence generated for the resonant spins. If the pulse sequence shown in Fig. 5(a) is used, the $N^{I}Q$ spectrum obtained as the skyline projection in the F_{1} domain is affected by all the spin interactions. An example of a 9Q is



Fig. 3 The 300 MHz ¹H spectra of a sample of $[\beta,\beta,\beta,-d_3]$ ethylbenzene dissolved in the nematic solvent I35: (a) normal spectrum and (b) a spin-echo spectrum.

shown in Fig. 6(a) for EB in I35. It is an advantage for the partially deuteriated samples also to record an $N^{I}Q$ spectrum with the pulse sequence shown in Fig. 5(b). The 180° pulse in the centre of the t_1 period should lead to a refocussing of both the chemical shifts and the dipolar couplings between the protons and deuterons, and produces an $N^{I}QR$ spectrum, if



Fig. 5 The multiple quantum experiments: (a) without and (b) with refocussing of the chemical shifts and coupling to non-resonant nuclei.



Fig. 6 The 300 MHz ¹H multiple quantum spectra of samples dissolved in the nematic solvent I35 of (a) ethylbenzene and (b) $[\beta,\beta,\beta,d_3]$ ethylbenzene. Spectrum (a) is a 9Q obtained with the sequence (a) of Fig. 5, and spectrum (b) is a 6QR obtained with sequence (b) in Fig. 5.

the spin system is first-order. An example with $N^{I} = 6$ is shown in Fig. 6(b) for EB-d₃ dissolved in I35. An attempt to obtain a similar $N^{I}QR$ spectrum for samples of EB-d₂ did not produce the required spectral simplification. This is probably because the D–D dipolar coupling in EB-d₂ is much larger than in EB-d₃.

Analysis of the NMR spectra

We have succeeded in analysing the single quantum spectra of ethylbenzene in each of the four liquid crystalline solvents. The strategy used for the samples dissolved in I35 and ZLI 1132 was to start by analysing the ¹H spectra of the two partially deuteriated samples. This was achieved in the following stages.

The spin-echo spectrum given by EB-d₃ dissolved in I35 is dependent on 10 values of $D_{\rm HH}$ and its direct analysis is a challenging task. It was decided to approach this problem by first recording $N^{I}QR$ spectra with $N^{I} = 6$, 5 and 4. These were analysed by a procedure described by Castiglione et al.⁷ This is based on the method developed by Celebre et al.⁶ for the automatic analysis of the spectra of rigid molecules. The first step was to analyse the 6QR spectrum. If the molecule were rigid, this could be achieved in general using the permutative approach in which the variables are the order parameters $S_{\alpha\beta}$ appropriate for the symmetry of the molecule. The analysis starts by setting all the $S_{\alpha\beta}$ to zero, fixing the J_{ij} at estimates from similar compounds, or obtained from an analysis of the sample in an isotropic solvent, calculating the $q N^{I}QR$ spectra frequencies, and then trying iterative analysis with each of the p possible assignments to the k observed lines. This procedure has to be modified for a flexible molecule like ethylbenzene. In the case of EB-d₃ the variables are S_{zz}^{R} and $S_{xx}^{R} - S_{yy}^{R}$, which are local principal order parameters for the benzene ring, and the interproton $D_{\rm HH}$ between the ethyl group and the ring, and within the ethyl group, *i.e.* $D_{9, 14}$, $D_{10, 14}$, $D_{11, 14}$ and $D_{14, 15}$. In general the number of variables, n_p , is larger than k/2, which is the number of independent observed frequencies (the factor of $\frac{1}{2}$ occurs because the N^IQR spectra are symmetrical about their centre). Even when k/2 is larger than n_p it is frequently found that the parameters do not form an independent set, that is the spectral frequencies depend on linear combinations of the parameters rather than on each parameter individually.

To overcome both these problems Castiglione et al.7 introduced the principal component regression, PCR, method into the analysis. This determines sets of independent linear combinations of the parameters, and ranks these according to their influence on the calculated frequencies. In this way it is possible to identify those combinations which have the smallest effect on the calculation, and these can be removed from the variable parameter list until $n_p \leq k/2$. The permutative approach is then applied with the reduced set of variables. The next step is to add automatically lines from the $N^{I}QR$ spectrum with $N^{I} = 5$, which will contain some lines whose frequency is a linear combination of the frequencies in the multiple quantum spectrum with $N^{I} = 6$, but there will be additional lines. The parameter set chosen by PCR can be enlarged, and after the permutative analysis the process is repeated automatically with the next NQR spectrum of lower order $(N^{I} = 4)$. In this way it is possible to determine the best parameters that fit the set of $N^{I}QR$ spectra, and these are given in column A of Table 1. This set of dipolar couplings was then used as starting parameters in a conventional analysis of the spin-echo spectrum of the sample, and the result is given in column B of Table 1.

The next step was to analyse the normal proton spectrum of EB-d₃ in I35 with the values of column B, Table 1, as starting parameters, plus estimates for couplings not obtained from the spin-echo spectrum. Thus, the sum of the H–D couplings could be estimated from the heptuplets of intensity 1: 3: 6: 7: 6: 3: 1 which are easily recognized in the spectrum shown in Fig. 3(a). Estimates of the individual H–D couplings were then obtained by partitioning this sum in the same ratio as the H–H couplings obtained previously⁴ for CEB. The results are given in column B of Table 2.

The proton spectrum of the sample of EB-d_2 dissolved in I35 was then analysed by the conventional method using the values in column B of Table 2 as starting parameters, plus an estimate for $D_{16, 17}$ from the approximate relationship:⁹

$$D_{16,17} = -\Delta v_{16} / 7.4 \tag{5}$$

which is an average of the values measured for the two different methyl groups in 1,2,3-trimethoxybenzene, and Δv_{16} is the measured value of the quadrupolar splitting for the methyl deuterons in EB-d₃. The results are given in column A of Table 2. To obtain starting parameters for the analysis of the proton spectrum of EB in I35, the $D_{\rm HD}$ values obtained from

Table 1 Starting (column A) and final (column B) dipolar couplings D_{ij} , for ¹H spin-echo spectrum of EB-d3 in I35

	D_{ij}/Hz		
ij	A	В	
9,10	-1933.40	-1937.12 ± 1.41	
9,11	-272.98	-268.88 ± 1.43	
9,12	-49.00	-42.86 ± 0.77	
9,13	22.80	27.68 ± 1.03	
9,14	- 577.78	-626.48 ± 1.86	
10,11	-392.52	-367.73 ± 0.75	
10,12	22.80	27.68 ± 1.03	
10,14	-218.13	-268.88 ± 1.43	
11,14	-115.94	-136.41 ± 0.35	
14,15	2313.37	2337.84 ± 2.22	

Table 2 Chemical shifts, Δv_i , and dipolar coupling, D_{ij} , obtained from the analysis of ¹H single quantum spectra in I35 of the samples: IIIA_H (column A), IIA_H (column B) and IVA_H (column F). In columns C and D are reported the D_{ij} values of columns A and B with the D_{HD} scaled to the relative D_{HH} values. In column E are reported the averaged values of columns C and D used as starting parameters for the analysis of IVA_H

		D _{ij} /Hz					
ij	$J_{ij}{}^{a}/\mathrm{Hz}$	A	В	С	D	Ε	F
1,2 1,3 1,4 1,5 1,6 1.8 2,3 2,4 2,6 2,8	8.00 2.00 2.00 0.00 0.00 6.00 2.00 0.00 0	$\begin{array}{c} -2111.84 \pm 0.06 \\ -292.63 \pm 0.16 \\ -48.15 \pm 0.07 \\ 35.10 \pm 0.06 \\ -102.60 \pm 0.08 \\ -418.11 \pm 0.09 \\ -386.36 \pm 0.17 \\ 35.10 \pm 0.06 \\ -28.66 \pm 0.10 \\ -152.33 \pm 0.10 \end{array}$	$\begin{array}{c} -1925.37 \pm 0.04 \\ -267.23 \pm 0.06 \\ -45.52 \pm 0.05 \\ 28.21 \pm 0.04 \\ -611.80 \pm 0.07 \\ -58.97 \pm 0.03 \\ -366.76 \pm 0.07 \\ 28.21 \pm 0.04 \\ -170.05 \pm 0.07 \\ -21.49 \pm 0.04 \end{array}$	$\begin{array}{r} -2111.84\\ -292.63\\ -48.15\\ 35.10\\ -667.93\\ -418.11\\ -386.36\\ 35.10\\ -186.58\\ -152.33\end{array}$	$\begin{array}{r} -1925.37\\ -267.23\\ -45.52\\ 2821\\ -611.80\\ -383.89\\ -366.76\\ 28.21\\ -170.05\\ -139.90\end{array}$	$\begin{array}{r} -2018.60\\ -279.93\\ -46.83\\ 31.65\\ -639.86\\ -401.00\\ -376.56\\ 31.65\\ -178.31\\ -146.11\end{array}$	$\begin{array}{c} -2033.39 \pm 0.04 \\ -282.00 \pm 0.07 \\ -46.88 \pm 0.04 \\ 32.49 \pm 0.10 \\ -644.48 \pm 0.06 \\ -405.19 \pm 0.04 \\ -378.54 \pm 0.08 \\ 31.63 \pm 0.10 \\ -179.51 \pm 0.06 \\ -147.09 \pm 0.04 \end{array}$
2,8 3,6 3,8 6,7 6,8 8,9	0.00 0.00 0.00 7.60 0.00	$-21.98 \pm 0.08 \\ -121.31 \pm 0.09 \\ 67.41 \pm 0.07 \\ -222.22 \pm 0.05 \\ \Delta v_{ij}/\text{Hz}$	$\begin{array}{c} -130.93 \pm 0.04 \\ -16.66 \pm 0.08 \\ 2324.74 \pm 0.04 \\ 61.29 \pm 0.02 \end{array}$	-143.09 -121.31 438.84 -222.22	-130.93 -108.46 2324.74 398.99	$-137.01 \\ -114.88 \\ 2324.74 \\ 418.91 \\ -222.22$	$\begin{array}{c} -138.56 \pm 0.04 \\ -138.56 \pm 0.04 \\ -116.53 \pm 0.04 \\ 2454.42 \pm 0.05 \\ 414.18 \pm 0.03 \\ -207.78 \pm 0.03 \end{array}$
1,3 2,3 6,3 8,3 ^a Take fr	rom Brugel ¹⁵ a	$ \frac{-162.19 \pm 0.06}{-91.55 \pm 0.06} \\ -1705.68 \pm 0.07 $ and kept fixed.	$\begin{array}{c} -147.31 \pm 0.11 \\ -79.83 \pm 0.13 \\ -1223.56 \pm 0.10 \end{array}$				$\begin{array}{c} -156.02 \pm 0.09 \\ -87.52 \pm 0.10 \\ -1211.14 \pm 0.07 \\ -1702.12 \pm 0.07 \end{array}$

the EB-d₃ and -d₂ isotopomers were multiplied by $\gamma_{\rm H}/\gamma_{\rm D}$ to give values for the appropriate $D_{\rm HH}$. This produced the data in columns C and D of Table 2, which were then averaged to yield (column E) the starting values for the dipolar couplings with which to analyse the proton spectrum of EB in I35 by the conventional method. Before commencing this analysis a 9Q spectrum of EB in I35 was obtained and used to obtain the chemical shifts, keeping the coupling constants fixed in the iterations. The final results are shown in column F of Table 2. Note the closeness of the $D_{\rm HH}$ values in columns E and F. Without achieving such a good set of starting values it was not possible to analysis the complex proton spectrum. A similar procedure was followed for samples of EB-d₃,

EB-d₂ and EB dissolved in ZLI 1132, with the results shown

in Table 3. More care was taken to have the same concentrations of the samples of the three isotopomers in ZLI 1132, since it was realized from the experience with I35 as solvent that this would lead to a better set of starting values (column E) for the analysis of the fully protonated sample.

The solvents I52 and I35 are very similar and so it was expected that the ordering of ethylbenzene would also be very similar in these two solvents. To analyse the spectrum of ethylbenzene in I52, therefore, it was not necessary to record the full range of spectra on the isotopomers I–IV. The experiences of analysing the spectra in I35 and ZLI 1132 emphasized the importance of recording spectra on the different isotopomers in the same solvent as near as possible at an identical concentration. For I52, therefore, all the samples used contained EB-

Table 3 Chemical shifts, Δv_i , and dipolar coupling, D_{ij} , obtained from the analysis of ¹H single quantum spectra in ZLI 1132 of the samples: IIB_H (column A), IIB_H (column B) and IVB (column F). In columns C and D are reported the D_{ij} values of columns A and B with the D_{HD} scaled to the relative D_{HH} values, and in column E the averaged values used are starting parameters for the analysis of IVB_H

		D _{ij} /Hz					
ij	$J_{ij}{}^a/{ m Hz}$	A	В	С	D	E	F
1,2	8.00	-1452.56 ± 0.16	-1458.22 ± 0.04	-1452.56	-1458.22	-1455.39	-1474.92 ± 0.04
1,3	2.00	-209.35 ± 0.31	-211.45 ± 0.06	-209.35	-211.45	-210.40	-213.84 ± 0.06
1,4	2.00	-51.25 ± 0.14	-51.59 ± 0.04	-51.25	- 51.59	-51.42	-51.90 ± 0.04
1,5	0.00	-12.89 ± 0.48	-12.87 ± 0.09	-12.89	-12.87	-12.88	-12.67 ± 0.08
1,6	0.00	-75.49 ± 0.22	-493.60 ± 0.06	-491.77	-493.60	-492.68	-499.11 ± 0.05
1,8	0.00	-287.53 ± 0.19	-44.85 ± 0.04	-287.53	-292.16	-289.84	-293.10 ± 0.04
2,3	6.00	-405.07 ± 0.34	-406.50 ± 0.07	-405.07	-406.50	-405.78	-409.50 ± 0.06
2,4	2.00	-12.61 ± 0.46	-13.34 ± 0.09	-12.61	-13.34	-12.97	-12.90 ± 0.08
2,6	0.00	-20.00 ± 0.23	-131.99 ± 0.06	-130.33	-131.99	-13114.	-133.49 ± 0.06
2,8	0.00	-106.71 ± 0.24	-16.37 ± 0.03	-106.71	-106.65	-106.68	-108.00 ± 0.04
3,6	0.00	-16.29 ± 0.19	-99.77 ± 0.03	-106.15	-99.77	-102.96	-100.84 ± 0.04
3,8	0.00	-83.68 ± 0.16	-12.69 ± 0.03	-83.68	-82.70	-83.19	-84.61 ± 0.04
6,7	0.00		1538.57 ± 0.05		1538.57	1538.57	1549.01 ± 0.06
6,8	7.60	54.47 ± 0.08	54.27 ± 0.03	354.83	353.53	354.18	353.84 ± 0.02
8,9	0.00	-271.93 ± 0.09		-271.93		-271.93	-264.37 ± 0.02
		$\Delta v_{ij}/{ m Hz}$					
1,3		-104.84 ± 0.42	-107.33 ± 0.06				-108.29 ± 0.08
2,3		-50.04 ± 0.43	-48.52 ± 0.07				-50.48 ± 0.09
6,3			-1248.05 ± 0.06				-1240.99 ± 0.07
8,3		-1715.04 ± 0.28					-1707.83 ± 0.06
' Taken	from Brugel15	⁵ and kept fixed.					

3409

Table 4 Chemical shifts, Δv_i , and dipolar couplings, D_{ij} , obtained from the analysis of the ¹H single quantum spectra in 152 of the samples: EB-d₂ (column A, starting parameters; and column B, final parameters) and EB (column C)

		$D_{ij}/{ m Hz}$		
ij	$J^a_{ij}/{ m Hz}$	A	В	С
9,10	8.00	-1938.00	-1890.67 ± 0.07	-1900.87 ± 0.04
9,11	2.00	-257.00	-256.12 ± 0.14	-258.06 ± 0.05
9,12	2.00	-40.00	-32.61 ± 0.11	-32.87 ± 0.04
9,13		34.00	52.56 ± 0.18	52.68 ± 0.07
9,14		-72.00	-88.10 ± 0.08	-579.93 ± 0.06
9,16		-369.00	-376.98 ± 0.10	-381.53 ± 0.04
10,11	6.00	-309.00	-269.05 ± 0.15	-268.65 ± 0.07
10,12	2.00	34.00	52.00 ± 0.23	51.86 ± 0.07
10,14		-47.00	-26.01 ± 0.14	-165.37 ± 0.07
10,16		-134.00	-137.15 ± 0.11	-137.79 ± 0.04
11,14		-19.00	-19.11 ± 0.06	-128.99 ± 0.04
11,16		-113.00	-109.28 ± 0.06	-110.13 ± 0.04
14,15				2448.37 ± 0.05
14,16	7.60	66.00	54.93 ± 0.04	350.76 ± 0.03
16,17		-105.00	-112.15 ± 0.05	-104.70 ± 0.02
		$\Delta v_{ij}/{ m Hz}$		
9,11			-155.02 ± 0.20	-153.74 ± 0.08
10,11			-86.99 ± 0.26	-87.39 ± 0.08
14,11				-1232.31 ± 0.07
16,11			-1729.73 ± 0.13	-1723.29 ± 0.07
^a Fixed.				

d₁₀, and the concentrations were adjusted so that the deuterium quadrupolar splittings in the separate samples were equal. This ensures that the orientational order is the same, and hence that the proton spectra should yield very similar dipolar couplings. The first step was to analyse the proton spectrum of EB-d₂ in I52. The deuterium quadrupolar splittings were used to calculate the values of S_{zz}^{R} and $S_{xx}^{R} - S_{yy}^{R}$ from:

$$\Delta v_i = \frac{3}{4} q_{\text{CD}i} \{ S_{zz}^{\text{R}} [(3 \cos^2 \theta_{\text{CD}i} - 1) + \eta_i \sin^2 \theta_{\text{CD}i}] + (S_{xx}^{\text{R}} - S_{yy}^{\text{R}}) [\sin^2 \theta_{\text{CD}i} + \frac{1}{3} \eta_i (\cos^2 \theta_{\text{CD}i} + 1)] \}$$
(6)

where θ_{CDi} is the angle between the *i*th C–D bond and the z axis. The deuterium quadrupolar coupling constant, q_{CDi} , was taken to be 185 kHz for the aromatic sites and the asymmetry parameter, η_i , was set to zero. The dipolar couplings between

Table 5 Chemical shifts Δv_i , and dipolar couplings, D_{ij} , obtained from the analysis of the ¹H single quantum spectra of EB in EBBA

ij	$J_{ij}{}^a/{ m Hz}$	D _{ij} /Hz
9,10	8.00	-1120.37 ± 0.09
9,11	2.00	-149.21 ± 0.14
9,12	2.00	-14.41 ± 0.09
9,13		40.58 ± 0.09
9,14		-327.04 ± 0.15
9,16		-231.69 ± 0.12
10,11	6.00	-119.61 ± 0.15
10,12	2.00	40.58 ± 0.09
10,14		-95.39 ± 0.16
10,16		-83.32 ± 0.13
11.14		-75.49 ± 0.08
11,16		-66.47 ± 0.10
14,15		1580.71 ± 0.11
14,16	7.60	174.08 ± 0.09
16,17		34.34 ± 0.14
		$\Delta v_{ij}/{ m Hz}$
9,11		-92.63 ± 0.20
10,11		-38.19 ± 0.20
14,11		-1291.33 ± 0.15
16,11		-1758.03 ± 0.18
^a Fixed.		

protons in the ring were then calculated from eqn. (3) with a regular hexagonal geometry for the ring. The deuterium spectrum shows a triplet line shape for the deuterons at positions 6 and 7, from which it was possible to obtain $D_{14, 15}^{\text{DD}}$, and hence to calculate the interproton coupling $D_{14,15}$. The proton coupling within the methyl group, $D_{16,17}$, was obtained from eqn. (5) and the observed value of Δv_{16} . It remained to estimate values for $D_{9, 16}$, $D_{10, 16}$ and $D_{11, 16}$ and this was done by scaling the values obtained for EB in I35 by the factor 0.94, which is the ratio of the total widths of the two spectra. The values of $D_{\rm HD}$ were estimated from the quintets of intensity 1:2:3:2:1 which are observed in the proton spectrum. The starting parameters used, and the final values obtained by analysis of the proton spectrum of EB-d₂ in I52, are given in columns A and B of Table 4. Scaling the values of $D_{\rm HD}$ in column B to give the corresponding $D_{\rm HH}$ produced a set of starting parameters from which it was possible to analyse the proton spectrum of EB in I52, with the result shown in column C of Table 4.

It is important to note the following points. (i) Attempts to analyse the proton spectrum of EB in I52 starting with the parameters in column A of Table 4 were not successful. This means that it was essential to analyse the proton spectrum of $EB-d_2$ before that of EB in I52. (ii) Attempts to analyse the proton spectrum of EB-d₂ without using the knowledge gained by the work on the spectra in I35 and ZLI 1132 were also unsuccessful.

Finally we analysed the proton spectrum of EB dissolved in EBBA by starting from dipolar couplings estimated wholly from the quadrupolar splittings obtained from EB-d₁₀ dissolved in the same sample, and the data obtained on the samples in the other three solvents. This proved to be possible, but probably would not have been successful if the data on the other three samples had not been available. The results are shown in Table 5.

Conformational analysis

The potential governing rotation of the methyl group in ethylbenzene is expected to be approximately 3-fold in character, and to have a barrier height of $> 12 \text{ kJ mol}^{-1}$. In this case it is reasonable to assume that the protons spend all their time in the three minimum energy positions, and the averaging of the D_{ij} over ϕ reduces to being $\frac{1}{3}[D_{ij}(\psi,0^\circ) + D_{ij}(\psi,120^\circ) + D_{ij}(\psi,240^\circ)]$. The barrier for rotation about the ring-C bond was obtained by Caminati *et al.*,⁵ to be of the form:

$$V(\psi) = V_2(1 + \cos 2\psi) + V_4(1 - \cos 4\psi)$$
(7)

with $V_2 = 3.08 \text{ kJ mol}^{-1}$ and $V_4 = 0.45 \text{ kJ mol}^{-1}$. Caminati et al., also allowed for some geometry relaxation by making the angle α in Fig. 1 depend on ψ :

$$\alpha(\psi) = \alpha_0 + \frac{1}{2}\Delta\alpha_0\{[1 - \cos 2(90^\circ - \psi)] + 0.05[1 - \cos 4(90^\circ - \psi)]\}$$
(8)

They obtained values of $\alpha_0 = 112.75^\circ$ and $\Delta \alpha = 3.49^\circ$. In order to relate the D_{ij} obtained for the ethylbenzene to $V(\psi)$ we will use the additive potential method^{3,10} for modelling $P_{\rm LC}(\beta,\gamma,\psi)$. We first define a mean potential $U(\beta,\gamma,\psi)$ as:

$$U(\beta,\gamma,\psi)/RT = -\ln[P_{\rm LC}(\beta,\gamma,\psi)] - \ln Z \tag{9}$$

where

$$Z = \int \exp[-U(\beta,\gamma,\psi)/RT] \sin \beta \, d\beta \, d\gamma \, d\psi \qquad (10)$$

The total mean potential can be divided conveniently as

$$U(\beta,\gamma,\psi) = U_{\text{ext}}(\beta,\gamma,\psi) + U_{\text{int}}(\psi)$$
(11)

where $U_{\text{ext}}(\beta,\gamma,\psi)$ is a potential of mean torque, that is, the totally anisotropic part of $U(\beta, \gamma, \psi)$ which vanishes in the iso-

Table6Thedifference $\Delta D_{ij}(\%) = \{[D_{ij}(\text{observed}) - D_{ij}(\text{calculated})]/D_{ij}(\text{observed})\} \times 100$ for ethylbenzene dissolved in135, ZLI 1132, I52 and EBBA

	$\Delta D_{ij}(\%)$			
ij	135	ZLI 1132	152	EBBA
9,10	-0.7	0.9	-0.4	-0.1
9,11	-0.9	-1.3	-0.6	-0.1
9,12	-1.1	-1.7	-1.1	-0.3
9,13	-2.7	-1.6	-0.7	0.7
9,14	0.8	2.0	0.2	0.5
9,16	0.8	-7.7	-0.4	-1.7
10,11	0.0	0.4	0.1	0.9
10,12	1.3	3.2	0.8	0.7
10,14	1.4	1.4	1.6	2.4
10,16	-5.5	-7.2	-4.8	-5.4
11,14	1.3	1.1	1.7	2.0
11,16	-5.4	-7.2	-5.2	-5.4
14,15	0.7	-1.7	-03	0.4
14,16	2.1	2.1	2.3	-0.6
16,17	-2.4	-0.1	4.9	-5.5

tropic phase, whilst $U_{int}(\psi)$ is finite in all phases and is the rotational potential for the molecule in an isotropic environment. We will identify $U_{int}(\psi)$ with $V(\psi)$ for the rotation about the ring-C bond for a molecule in the isotropic phase of the mesogenic solvent molecules.

In the AP model $U_{\text{ext}}(\beta,\gamma,\psi)$ is written as

$$U_{\text{ext}}(\beta, \gamma, \psi) = -\varepsilon_{2,0}(\psi)C_{2,0}(\beta) - 2\varepsilon_{2,2}(\psi)C_{2,2}(B, \gamma) \quad (12)$$

where the $C_{2, m}(\beta, \gamma)$ are modified spherical harmonics. The conformation dependence of the interaction coefficients is modelled by expressing them as sums of contributions, $\varepsilon_{2, n}(j)$, from each of the *j* rigid subunits in the molecule:

$$\varepsilon_{2,m}(\psi) = \sum_{j} \sum_{n} \varepsilon_{2,n}(j) D_{n,m}^2(\Omega_j)$$
(13)

 $D_{n,m}^2(\Omega_j)$ is the Wigner function describing the orientation of the *j*th fragment in reference axes fixed in some rigid fragment, for example the benzene ring in ethylbenzene. The rigid fragments in ethylbenzene are the aromatic ring and the alkyl group. The ring has C_{2v} symmetry and requires $\varepsilon_{2,0}^R$ and $\varepsilon_{2,2}^R$. The alkyl group is sub-divided into a C–C bond and five equivalent C–H bonds. These bonds have axial symmetry and require just $\varepsilon_{2,0}^{CC}$ or $\varepsilon_{2,0}^{CH}$. It has been found in studies on many similar compounds that setting $\varepsilon_{2,0}^{CH} = 0$ does not affect the precision with which observed and calculated dipolar couplings can be brought into agreement, and the same situation is found to hold for ethylbenzene.

Note that in the calculations it is easier to use equivalent Cartesian forms of these tensor components. Thus, $\varepsilon_{2,0}^{R}$ is replaced by $(2/3)^{1/2}\varepsilon_{zz}^{R}$, $\varepsilon_{2,2}^{R}$ by $\frac{1}{2}(\varepsilon_{xx}^{R} - \varepsilon_{yy}^{R})$, and $\varepsilon_{2,0}^{CC}$ by $(2/3)^{1/2}\varepsilon_{CC}$, where the CC represents the direction of the C_7 - C_8 bond.

The data for 4-chloroethylbenzene was fitted to the observed D_{ii} by varying these three interaction coefficients, and some or all of the parameters defining the bond rotational potential. Thus, it was found that fixing V_2 , V_4 , α_0 , $\Delta\alpha_0$ and the bond lengths and angles at the values determined by Caminati et al.⁵, and varying the three interaction coefficients, did not give a good fit to the NMR data, that is, the rms error, $R = \sum_{ij} \{ [D_{ij}(\text{observed}) - D_{ij}(\text{calculated})]^2 / F \}^{1/2}, \text{ is unaccept-}$ ably large. A good fit to 14 of the D_{ij} could be obtained by introducing a similar dependence of the angle β on ψ as that in eqn. (9) for α , and varying all nine variables (the seven above plus β_0 and $\Delta\beta$, but the values obtained for α_0 and $\Delta\alpha_0$ are very different from those calculated by Caminati et al., and were judged to be unlikely. Moreover, the shape obtained for $V(\psi)$ is quite different in character from that calculated, having minima at 0° and 90° with a maximum at about 45° .

This shape results because $V_4 \gg V_2$ whereas Caminati *et al.* calculated the reverse relative magnitudes, which produces a minimum at 90° and a maximum at 0°. Fixing $V_4 = 0$ and varying the other eight variables gave a higher, but acceptable, rms value, and $V(\psi)$ now has essentially the same shape as calculated by Caminati *et al.*, but still with unreasonable values for the angular distortion parameters.

When the fitting procedures used for 4-chloroethylbenzene were repeated for the new data on ethylbenzene, the same kind of unacceptable results were obtained. Quite clearly, therefore, the NMR data are not consistent with the results from the molecular orbital calculations. The most probable reason for this disagreement is that the geometry calculated by the molecular orbital method is for an isolated molecule, which is not undergoing vibrational motion, whereas the D_{ii} are averages over these modes, and are for a molecule which is in a liquid phase, and hence may be affected by intermolecular forces. A method for averaging the D_{ij} over vibrational modes when all these are of small amplitude, and intermolecular effects are ignored, has been developed, but is not applicable to a molecule like ethylbenzene which has bond rotational motion. The magnitudes of the changes produced by vibrational averaging on interproton couplings in more rigid, simpler molecules have been found to be of the order of about 0-5%, and so we have explored the possibility of finding a structure for ethylbenzene which will fit the observed couplings within this kind of error on the individual couplings. To do this it was simpler to assume that the molecule rotates as a rigid entity, that is with fixed values of the angles α and β . The data on the solution in I35 were fitted first.

The first step was to determine the relative positions of the protons in the aromatic ring which fit the inter-ring D_{ij} exactly. This can be done by using eqn. (3) with the $S_{\alpha\beta}$ replaced by local order parameters,³ $S^R_{\alpha\beta}$. To do this it is necessary to fix one of the interproton distances, and the choice was made of $r_{9,10} = r_{12,13} = 2.48$ Å. The six independent inter-ring proton couplings were then used to obtain the two order parameters, S^R_{zz} and $S^R_{xx} - S^R_{yy}$, and the coordinates x_9, z_9, x_{10}, z_{10} , with $x_{11} = z_{11} = 0$. The bond lengths and angles in the aromatic ring were then adjusted to give these proton coordinates, and the resulting structure is shown in Fig. 1.

The second step was to explore the effect of changing the structure of the ethyl group so as to produce an acceptable rms error by varying the values of the $\varepsilon_{2,n}(j)$ and the coefficients defining the rotational potential $V(\psi)$. This was done by determining the sensitivity of the fit to changes in the bond lengths and angles. This led to an acceptable fit being obtained by changing the C-H bond lengths in the methyl and methylene groups to 1.1 Å, and increasing the angle HCH in the methylene group from 109.5 to 113.5°.

The potential describing rotation about the C_1 - C_7 bond was simplified to

$$V(\psi) = V_2 \cos 2\psi + V_4 \cos 4\psi \tag{14}$$

The effect was explored too of raising the restriction that rotation of the methyl group about the C_7 - C_8 bond can be approximated as jumps between just three, equivalent positions. To do this the potential was described as

$$V(\phi) = V_3 \cos 3\phi \tag{15}$$

with a value of -6 kJ mol^{-1} for V_3 ($\phi = 0^\circ$ corresponds to the C₈-H₁₆ bond being in the *xz* plane as shown in Fig. 1). Doing this has only a small effect on the fit obtained. In fact, with $V_3 = -6 \text{ kJ mol}^{-1}$ it was found that the full effects on the D_{ij} of methyl rotation could be obtained by allowing the protons to oscillate through $\pm 30^\circ$ about their minimum energy positions.

This structural and dynamic model for ethylbenzene was used to fit the D_{ij} obtained for all four data sets and the results are summarized in Table 6, which gives the percentage

Table 7 The interaction parameters $\varepsilon_{aa}(kJ \text{ mol}^{-1})$ and the potential coefficients V_2 and V_4 ($kJ \text{ mol}^{-1}$) for ethylbenzene as a solute in nematic solvents and obtained by fitting the observed dipolar couplings to those calculated by the additive potential method

	I35	ZLI 1132	152	EBBA
$egin{aligned} & \varepsilon_{xx}^{\mathbf{R}} \ & \varepsilon_{xx}^{\mathbf{R}} - \varepsilon_{yy}^{\mathbf{R}} \ & \varepsilon_{cc} \ & V_2 \ & V_4 \end{aligned}$	$\begin{array}{c} 3.462 \pm 0.001 \\ 4.736 \pm 0.017 \\ 1.040 \pm 0.001 \\ 1.73 \pm 0.14 \\ 0.19 \pm 0.41 \end{array}$	$\begin{array}{c} 2.508 \pm 0.001 \\ 3.843 \pm 0.021 \\ 0.713 \pm 0.001 \\ 1.87 \pm 0.40 \\ -0.19 \pm 0.94 \end{array}$	$\begin{array}{c} 3.157 \pm 0.001 \\ 3.675 \pm 0.011 \\ 1.035 \pm 0.001 \\ 1.70 \pm 0.09 \\ 0.06 \pm 0.28 \end{array}$	$\begin{array}{c} 1.849 \pm 0.001 \\ 1.656 \pm 0.001 \\ 0.699 \pm 0.001 \\ 1.76 \pm 0.08 \\ -0.19 \pm 0.24 \end{array}$

Table 8 The quadrupolar splittings $\Delta v(\pm 100)$ (Hz) obtained from the deuterium spectra of samples containing equimolar amounts of ethylbenzene and ethylbenzene-d₁₀ dissolved in I35, ZLI 1132, I52 and EBBA

	135	ZLI 1132	152	EBBA
$\Delta v_9 = \Delta v_{10}$ Δv_{11} Δv_{14} Δv_{16}	$ \begin{array}{r} 15161 \\ 69000 \\ -26935 \\ 1690 \end{array} $	16 780 54 931 - 18 713 2 055	$11165\\67587\\-26037\\846$	$5117 \\ 40800 \\ -16560 \\ \pm101$

difference between observed and calculated D_{ij} . The interaction parameters and potential coefficients obtained are given in Table 7. The errors on individual couplings are acceptable, bearing in mind the simplicity of the model, and the expected effect that vibrational averaging could be producing. Note that the potential function has a similar shape to that obtained by Caminati et al.⁵ The values obtained for V_2 are independent within the experimental error of the liquid crystalline solvent used, and V_4 is essentially zero. The average value of V_2 over the four solvents is 1.76 ± 0.6 kJ mol⁻¹ compared to the value of 3.08 kJ mol⁻¹ determined by Caminati et al. The difference may reflect a significant intermolecular contribution to the rotational potential which is favouring the conformation with $\psi = 0^\circ$. It is certainly safe to conclude from these results that the rotational potential $V(\psi)$ for ethylbenzene in a liquid phase is essentially 2-fold in character, but the bond lengths and angles given in Fig. 1 should be regarded as being reasonable approximations to ethylbenzene in an averaged, rigid structure in a liquid phase.

Deuterium quadrupolar coupling tensors

The splittings, Δv_i , in the deuterium spectra were used to ensure that the different samples had the same orientational order of the ethylbenzene molecules, and they were also used to obtain local order parameters, $S^{\rm R}_{\alpha\beta}$, for the ring, and hence estimates of the dipolar coupling constants between ring protons from eqn. (3). To do this required choosing values for $q_{\text{CD}i}$ and η_i . We can reverse this procedure to obtain experimental values of the quadrupole tensors from values of the ring order parameters determined from the measured dipolar couplings. For each sample it was assumed that the values of $q_{\rm CDi}$ and η_i are the same at ortho, meta and para positions. The deuterium spectra show that Δv_i are the same for *ortho* and meta positions, which is to be expected if the benzene ring is essentially an undistorted hexagonal shape. With this assumed geometry the values of $\Delta v_9(=\Delta v_{10})$ and Δv_{11} shown in Table 8 were used to derive $q_{\rm CD}$ and η for each sample, and these are reported in Table 9. Note that the values obtained in this way are subject to a systematic error caused by the assumption of the regular hexagonal geometry. This has been estimated by calculating the values of $q_{\rm CD}$ and η when $\theta_{\rm CD}$ in eqn. (6) for the *ortho* and *meta* positions is changed by $\pm 1^{\circ}$.

The most striking feature of the data in Table 9 is the variation of $q_{\rm CD}$ with the liquid crystalline solvent. A part of this variation may be attributed to the neglect of vibrational motion on the $D_{\rm HH}$, which will modify the values of the $S_{\alpha\alpha}^{\rm R}$ obtained. A similar source of error stems from our assumption that the ring geometry does not change on rotation of the ethyl group. Finally, there may also be a contribution to the observed splitting, which originates from a non-zero, averaged electric field gradient along the director of the liquid crystal. This could arise if the distribution around the director of the vectors connecting the solute and solvent centres has no higher than cylindrical symmetry.¹¹⁻¹⁴

Table 9 also gives values of $q_{\rm CD}$ for the CD₂ and CD₃ deuteriums derived from the values of Δv_{14} and Δv_{16} . These were obtained by using:

$$\Delta v = \frac{3}{2} q_{\rm CD} S_{\rm CD} \tag{16}$$

which assumes that $\eta = 0$ for these positions. The order parameter for the C–D bond, $S_{\rm CD}$, was calculated from $P_{\rm LC}(\beta,\gamma,\psi,\phi)$.

The values of q_{CD} for the aliphatic deuteriums again vary with the solvent. Note that it is not so easy to estimate the errors in these values, which will have a similar origin to those for the aromatic deuteriums with the addition of an error from the assumption of a zero asymmetry parameter.

Conclusion

We have demonstrated that the previously unanalysable proton spectra of ethylbenzene dissolved in liquid crystalline solvents can be analysed by a strategy which combines partial deuteriation, spin-echo and multiple quantum spectroscopy. We can reasonably expect that spin systems of similar complexity will also succumb to the same strategy, provided the deuteriated derivatives can be synthesized. This opens the way to investigating the structure, conformation and orientational ordering of complex flexible molecules dissolved in liquid crystalline solvents.

We have also shown that the dipolar couplings obtained for ethylbenzene as a solute in four liquid crystalline solvents are consistent with a reasonable geometry for the molecule, but one which has significant differences to that obtained by a molecular orbital calculation. The potential governing rotation about the ring-carbon bond is found to be essentially 2-fold in character, in agreement with the molecular orbital study.

Table 9 Values of the quadrupolar coupling constants q_{CD} (kHz) and the asymmetry parameter η for deuteriums in ethylbenzene-d₁₀ dissolved in I35, ZLI 1132, I52 and EBBA, derived from the data in Table 8

i		I35	ZLI 1132	152	EBBA
9,10,11 14	9 _{СР} η 9 _{СР}	175 ± 2 0.07 ± 0.03 172	192 ± 2 0.04 ± 0.03 180	184 ± 2 0.05 ± 0.03 169	189 ± 2 0.04 ± 0.03 169
16	$q_{\rm CD}$	173	161	175	_

Acknowledgement

This work was supported by the Ministero dell'Universitá e della Ricerca Scientifica e Tecnologica (*ex* 40% "Cristalli Liquidi" Programme 1997/1998).

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