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Zero electric field gradient mixtures for the elucidation of orientational mechanisms

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A novel zero electric field gradient nematic liquid crystal made up from two nematic liquid crystal components is employed as a solvent for a series of molecules ranging from small molecules to mesogens themselves. Nuclear magnetic resonance is used to determine the degree of order of the solute and solvent molecules. Results are compared to those obtained for two completely different zero electric field gradient nematic mixtures. The comparison strongly indicates that for a variety of molecules largely differing in size, shape and flexibility their degree of order can be described by a single orientation mechanism. This mechanism can be adequately modelled by a simple phenomenological mean field model based on the size and shape anisotropy of the dissolved species. The use of zero electric field gradient mixtures in combination with this mean field model allows the prediction of solute order parameters at approximately the 10 per cent level.

1. Introduction

In the presence of a strong magnetic field, as is commonly used in NMR experiments, a nematic liquid crystal can be uniformly aligned, resulting in a uniaxial, cylindrically symmetric liquid medium possessing an infinitesimal rotational symmetry axis and in which in the opposite directions along this axis, the director is indistinguishable. Solutes dissolved in an oriented liquid crystal also acquire a partial orientational ordering. For the past 30 years NMR has proved to be a powerful means of probing the orientational behaviour of both solvent and solute molecules in this anisotropic mesophase. The study of a large number of solutes and liquid crystalline materials has yielded a wealth of information about molecular properties [1–4]—for example relative geometries, quadrupolar coupling constants, indirect coupling tensors, nuclear shielding tensors—and has provided some insight into the orienting mechanisms responsible [5–7].

In spite of its simplicity, the theory of Maier and Saupe [8] remains one of the most successful descriptions of orientational ordering in nematics. The intermolecular forces acting on a given molecule are essentially approximated by a single-molecule potential function. Thus, each molecule is viewed as if it is moving in a field generated via its interaction with all molecules surrounding it and it is assumed that the field experienced by a particular molecule is independent of the degrees of freedom of every molecule except the one being considered. To obtain such a single-molecule potential representing the interaction of a molecule with its surroundings we average the

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potential for the intermolecular forces over all degrees of freedom of the other molecules in the nematic environment, as well as over the translational motion of the given molecule, neglecting short range orientational effects [9, 10]. In addition, Maier and Saupe neglect the internal degrees of freedom by taking the molecule to be a rigid rod, although this assumption can be generalized to rigid non-cylindrically symmetric molecules [11]. The most salient feature of the mean field description of Maier and Saupe and its extensions, however, is the use of a mean field approximation to obtain an expression for the form of the single-molecule potential with a particular dependence on the molecular orientation leading to the long range order characteristic of nematics. This interaction potential can of course be written as a series expansion in terms of an appropriate complete basis. In the case of Maier and Saupe the form of the potential is restricted to the first term (of rank two) of this expansion which transforms according to the uniaxial symmetry of the nematic phase [9–11]. However, the actual physical nature of the interactions responsible for the long range orientational order of the constituent molecules in nematic liquid crystalline materials remains a long-standing and intriguing problem.

In recent years the use of small, spectroscopically well-characterized solute molecules such as hydrogen [5, 12, 13] and methane [5, 14–16] as probe molecules for the orienting potential in nematic solvents has been a promising approach. Experiments using molecular hydrogen and its deuteriated analogues have demonstrated the presence of a mean electric field gradient (efg) in nematic liquid crystals [17, 18]. This average efg, a (temperature and concentration dependent) property of the solvent, can have a positive or negative sign depending on the particular liquid crystal chosen. Moreover, in the case of molecular hydrogen, the interaction between the anisotropic average efg and the molecular quadrupole moment explains the sign and most of the magnitude of its orientation parameter in a variety of nematic solvents.

A real breakthrough in experimental methods which can be used to obtain information about orienting mechanisms has been achieved by mixing liquid crystals possessing opposite average efgs. The average efg of the resulting nematic solvent—and hence its interaction with a solute's quadrupole moment leading to orientation—can thus be adjusted in a controlled way. By mixing the component liquid crystal materials in appropriate amounts, zero-efg mixtures can be formed.

The liquid crystal mixture made up of 55 wt% of Merck ZLI 1132 in EBBA (*N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline) at 301·4 K has been very useful, as this mixture essentially shows zero average external efg at the deuterons of molecular deuterium [18]. For molecular hydrogen, the orienting interaction with the molecular quadrupole moment accounts for most of the orientation and can be removed selectively in this 'magic' mixture, resulting in a small remaining orientation. However, for solutes other than molecular hydrogen, assuming that in this mixture they experience this same zero-efg, at least one additional interaction must be considered to explain their non-vanishing orientation. In fact, it has been found that the general orientation of solutes in this mixture can be described quite successfully by modelling the short range repulsive interactions between solute and solvent [19, 20]. In a simple phenomenological mean field model, the interaction potential is assumed to depend on the dimensions and shape anisotropy of the solute and on a force constant, a single adjustable parameter describing the liquid crystal environment in the spirit of Hooke's law, taken to be the same for all solutes at a given temperature. The solute molecules are represented by a rigid collection of van der Waals spheres that disturb the liquid crystal, modelled as an elastic tube with semi-rigid walls, by stretching the tube in a direction perpendicular to the director, when it accommodates the solute molecule. These repulsive interactions account for the observed orientation of a variety of small solutes in the zero-efg 1132/EBBA mixture quite accurately [19, 20]. Moreover, a study of the orientation of two larger (perdeuteriated) molecules, non-mesomorphic 4-methyl-4′-cyanobiphenyl (1CB-d_{11}) and the liquid crystal 4-*n*-pentyl-4′-cyanobiphenyl (5CB-d_{19}), used as solutes in this mixture, resulted in good agreement between theory and experiment [21]. More recent work has shown that extensions to this model give even better agreement [22–24]. The best fit to 46 small solutes of varying symmetry is a simulation that adds to the above potential a short range anisotropic interaction between the solute surface and the liquid crystal mean field [24]. Thus, for a variety of probe molecules, ranging in size from molecular hydrogen to the large, flexible liquid crystal molecules themselves, the orientation in this 'magic' mixture mainly depends on the size and shape of the molecule dissolved and in fact can be predicted with reasonable accuracy using a simple phenomenological mean field description.

In nematic solvents where an estimate of the mean external efg is available from NMR of dissolved molecular deuterium, calculations of the order parameters based on the combination of two principal mean field orientation mechanisms: (i) the interaction between the molecular quadrupole moment of the solute and the external efg present in the liquid crystal; and (ii) the short range repulsive interactions, have shown good agreement with measured order parameters for a range of small solutes [19, 20, 25]. This supports the validity of the assumption that other solutes experience the same mean external efg as molecular deuterium dissolved in a nematic liquid crystal under the same conditions.

The 55 wt% 1132/EBBA mixture at 301·4 K has been the only zero-efg solvent used to study orientational behaviour in nematic liquid crystals to date. Although the 5CB molecule has been the subject of a lot of research, an important property of the liquid crystal 5CB which has hitherto remained unexplored, is its potential to form a zero-efg nematic mixture together with for example, EBBA. Obviously experiments on small solutes similar to those carried out with the 55 wt% 1132/EBBA mixture can be performed with such a novel mixture. This allows for an interesting comparison of the orientational behaviour of solutes in quite different zero-efg nematic solvents. In this way the experimental evidence for the orienting mechanisms postulated above may be extended and could lead to confirmation of the present ideas about orienting interactions operative in liquid crystals. Since the average orientation of solutes depends on the degree of ordering of the solvent, a sensible comparison between different solutes can only be made if studied under identical circumstances. Care is taken in this study to dissolve the solutes studied as far as possible in the same solution at the same reduced temperature. The use of low concentrations of solutes is preferred to ensure: (i) that the solvent is not too strongly perturbed; (ii) that the solute acts as a useful probe molecule for the orientational forces operative in the anisotropic solvent; and (iii) that solute–solute interactions can be ignored. The use of selectively deuteriated liquid crystal molecules can provide information under the same experimental conditions about the orientational behaviour of these large molecules which, in contrast to the small solutes studied, exist in a large number of different conformations.

The results presented here are obtained using a novel zero-efg nematic mixture of 5CB and EBBA and show that the orientation of both solute and solvent molecules studied in different zero-efg mixtures at the same reduced temperature are virtually identical apart from a scaling factor. This indicates that for a range of small solutes and the solvent molecules themselves, the orientation in both zero-efg mixtures can generally be described by a single orienting interaction. These results provide strong support for a general description of the orienting mechanisms operative in non-zero efg nematic solvents in terms of two major interactions: (i) an interaction responsible for the orientation in zero-efg mixtures; (ii) an interaction between the molecular quadrupole moment of the solute and the external efg present in the liquid crystal.

In addition, the orienting interaction of solutes in the zero-efg mixtures studied will be shown to be adequately described by a simple phenomenological mean field model based on solute size and shape anisotropy. With this approach orientation parameters can be predicted at approximately the 10 per cent level.

2. Experimental

The liquid crystals used were

1132:	Merck ZLI 1132 (see [3] for composition)
5CB:	4-*n*-pentyl-4′-cyanobiphenyl, obtained from BDH Ltd, as well as the (partially) deuteriated nematogens, synthesized by G. S. Bates, U.B.C.
EBBA-d_2:	*N*-(4-ethoxybenzylidene)-2,6-dideutero-4′-*n*-butylaniline (synthesized as described in [20])
5CB-α,β-d_4:	4-(α,β-d_4-*n*-pentyl)-4′-cyanobiphenyl (synthesized as indicated in [26]).

These liquid crystals, as well as the compounds dissolved in the two liquid crystal mixtures described in the present study (see table 1 for their composition), were used without further purification. The solutes used in this study were: benzene, 1,3,5-trifluorobenzene, 1,3,5-trichlorobenzene, 1,3,5-tribromobenzene, molecular deuterium, 1,2-^{13}C-acetylene, propyne, allene (1,2-propadiene), 2-butyne, 2,4-hexadiyne, 1,4-dichlorobenzene, 1,4-dibromobenzene and 5CB-d_{19} (perdeuteriated 5CB, synthesized as described in [21]). Samples were prepared in either standard 5 mm o.d. NMR tubes or 9 mm o.d. Pyrex glass tubes (for samples containing molecular deuterium) by dissolving amounts of several solutes sufficient to produce a reasonable signal. Care was taken to avoid too high a total concentration of solutes, the total amount of compounds dissolved being approximately 3·5 mol% for the samples measured. For the samples containing compounds which are gaseous at room temperature, the liquid crystal was first thoroughly degassed by several pump-freeze-thaw cycles and cooled to either liquid nitrogen or liquid helium temperature (for molecular deuterium) to condense a sufficient volume of gas into the sample tube which was then sealed and tested in an oven at about 400 K. Several isotopically substituted methanes were also condensed into the sample tubes containing molecular deuterium. The methane spectra will not be analysed here.

^{1}H and ^{2}H free induction decays were measured on a Bruker WH400 spectrometer operating at 9·4 T (400·1 MHz for protons, 61·4 MHz for deuterons). For the samples in 5 mm tubes, the proton signal was measured through the observe channel of a 5 mm proton probe and the deuteron signal was observed through the lock channel. The spectra of the samples containing molecular deuterium were obtained using a 10 mm broadband probe, the ^{2}H spectra being measured through the observe channel and the ^{1}H spectra through the decouple channel. Thus ^{1}H and ^{2}H spectra were obtained without removing the sample from the probe, ensuring that these spectra were recorded under the same experimental conditions. All experiments were performed with sample

Table 1. Experimental quadrupolar coupling constant B, dipolar coupling constant D and order parameter S_{zz} for molecular deuterium together with the calculated estimate for the mean electric field gradient F_{ZZ} present in each liquid crystal mixture used in the experiments reported.

Solvent composition	T/K	T_{red} (*a*)	B/Hz	D/Hz	S_{zz} (*b*)	B/D	$F_{ZZ}/10^9$ esu (*c*)
30·0 wt% EBBA-d_2 + 70·0 wt% 5CB-α,β-d_4	316	0·969	−84·92 (2)	3·46 (1)	$-5{\cdot}07\times10^{-4}$	−24·58 (8)	0·2 (1·6)
30·0 wt% EBBA-d_2	316	0·988	−73·28 (2)	2·96 (1)	$-4{\cdot}35\times10^{-4}$	−24·76 (8)	3·3 (1·1)
+ 70·0 wt% 5CB-α,β-d_4 (*d*)	317	0·991	−76·18 (4)	3·10 (1)	$-4{\cdot}55\times10^{-4}$	−24·57 (11)	−0·4 (2·1)
56·5 wt% 1132 + 43·5 wt% EBBA-d_2	322	0·953	−101·01 (1)	4·10 (1)	$-6{\cdot}03\times10^{-4}$	−24·62 (8)	1·1 (0·2)

(*a*) T_{red} is the ratio of the temperature T and the temperature at which the nematic to (all) isotropic phase transition for the particular sample starts to take place.

(*b*) The experimental order parameter S_{zz}, describing the average orientation of the internuclear axis z of the deuterium molecule with respect to the space fixed Z axis along the magnetic field direction, is obtained from the experimental dipolar coupling D using the relationship [2]

$$D = -h\frac{\gamma_{\mathrm{DD}}^2}{4\pi^2}\langle r_{\mathrm{DD}}^{-3}\rangle S_{zz},$$

with the internuclear distance r_{DD} for deuterium averaged over vibrations and centrifugal distortion (see [12]).

(*c*) The estimate for the extra-molecular mean electric field gradient in the solvent is obtained from the quadrupolar coupling constant as discussed in [17].

$$\mathrm{esu} = \mathrm{statvolt\,cm^{-2}} = 2{\cdot}998\times10^{6}\,\mathrm{V\,m^{-2}}.$$

(*d*) The solvent for this sample, as well as for the samples appearing in the other tables, was actually taken from a single batch mixture of 1·0070 g 5CB-α,β-d_4, 6·153 g 5CB and 3·113 g EBBA-d_2.

Table 2. (*a*) Spectral parameter (Hz) for solutes and deuteron quadrupolar line splittings $\Delta\nu$ (Hz) for deuteriated component liquid crystals in 56·5 wt% 1132/EBBA-d_2 at 322 K. The reduced temperature for the samples is also given.

		56·5 wt% 1132/EBBA-d_2 at 322 K			
Molecule	Parameter (*a*)	Sample 1	Sample 2	Sample 3	Sample 4
Benzene	D_{ortho}			−550·22 (7)	
	D_{meta}			−106·44 (5)	
	D_{para}			−69·36 (7)	
1,3,5-Trifluorobenzene	$D_{\mathrm{HF}\,ortho}$				−582·0 (4)
	$D_{\mathrm{HF}\,para}$				−73·4 (3)
	D_{HH}				−135·4 (3)
1,3,5-Trichlorobenzene	D_{HH}	−141·78 (1)	−149·82 (7)	−141·50 (5)	−148·75 (2)
1,3,5-Tribromobenzene	D_{HH}		−146·21 (3)		
Deuterium	D_{DD}	4·10 (1)			
	B_{D}	−101·01 (1)			
Acetylene	D_{HH}	−259·55 (10)			
Propyne	$D_{geminal}$				1268·66 (31)
	$D_{\mathrm{HH'}}$				−178·68 (25)
	$\Delta\sigma$/ppm				0·9835 (34)
Allene	D_{cis}				971·58 (11)
	D_{trans}				−177·51 (9)
2-Butyne	$D_{geminal}$			1541·78 (24)	
	$D_{\mathrm{HH'}}$			−122·68 (5)	
	$J_{\mathrm{HH'}}$			2·87 (9)	

2,4-Hexadiyne	$D_{geminal}$		3514 (116)		
	$D_{HH'}$		−83·91 (4)		
	$J_{HH'}$		1·23 (7)		
1,4-Dichlorobenzene	D_{ortho}	−1873·05 (43)	−2004·0 (3)	−1881·4 (5)	−1984·1 (13)
	D_{meta}	75·97 (25)	85·7 (3)	78·0 (5)	83·2 (13)
	D_{para}	−22·83 (40)	−23·5 (5)	−22·5 (15)	−23·2 (13)
1,4-Dibromobenzene	D_{ortho}		−2214·3 (13)		
	D_{meta}		116·0 (10)		
	D_{para}		−13·0 (11)		
EBBA-d_2	$\Delta\nu_Q$ (*b*)	$14·01 \times 10^3$	$14·95 \times 10^3$	$14·19 \times 10^3$	$14·83 \times 10^3$
5CB-α,β-d_4	$\Delta\nu_\alpha$ (*c*)	$51·42 \times 10^3$			
	$\Delta\nu_\beta$ (*c*)	$34·40 \times 10^3$			
5CB-d_{19}	$\Delta\nu_\gamma$ (*c*)	$36·56 \times 10^3$			
	$\Delta\nu_\delta$ (*c*)	$23·63 \times 10^3$			
	$\Delta\nu_{methyl}$ (*c*)	$17·2 \times 10^3$			
	$\Delta\nu_{ar(CN)}$ (*d*)	$10·03 \times 10^3$			
	T_{red} (*e*)	0·953	0·942	0·944	0·953

(*a*) The dipolar couplings for benzene, 1,3,5-trifluorobenzene, propyne and allene depend on the same *J* couplings cited in [19].

(*b*) Quadrupolar line splitting for deuterons *ortho* to the nitrogen of the butylaniline ring of EBBA-d_2.

(*c*) Quadrupolar line splitting for deuterons in the pentyl chain of deuteriated 5CB. Greek letters indicate the position starting at the phenyl ring.

(*d*) Quadrupolar line splitting for aromatic deuterons in the cyanophenyl ring of 5CB-d_{19}.

(*e*) T_{red} is the ratio of the temperature T and the temperature at which the nematic to (all) isotropic phase transition for the particular sample starts to take place.

Table 2. (*b*) Spectral parameters (Hz) for solutes and deuteron quadrupolar line splittings $\Delta\nu$ (Hz) for deuteriated component liquid crystals in 30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K. The reduced temperature for the samples is also given.

		30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K						
Molecule	Parameter (*a*)	Sample 1	Sample 2	Sample 3 (*b*)	Sample 4	Sample 5	Sample 6	Sample 7
Benzene	D_{ortho}					−500·41 (14)		
	D_{meta}					−96·86 (15)		
	D_{para}					−63·12 (20)		
1,3,5-Trifluorobenzene	$D_{\mathrm{HF}\,ortho}$							−447·40 (30)
	$D_{\mathrm{HF}\,para}$							−56·34 (29)
	D_{HH}							−104·45 (34)
1,3,5-Trichlorobenzene	D_{HH}		−127·86 (3)	−124·38 (4)	−130·77 (2)	−128·24 (20)	−135·26 (5)	−113·11 (17)
1,3,5-Tribromobenzene	D_{HH}				−127·01 (7)			
Deuterium	D_{DD}	3·46 (1)	2·96 (1)	3·10 (1)				
	B_{D}	−84·92 (2)	−73·29 (2)	−76·18 (4)				
Acetylene	D_{HH}		−263·75 (50)	−252·95 (33)				
Propyne	$D_{geminal}$					938 (62)		1030 (342)
	$D_{\mathrm{HH'}}$					−157·99 (24)		−137·16 (84)
	$\Delta\sigma$/ppm					0·8214 (15)		0·6777 (63)
Allene	D_{cis}							Not assigned
	D_{trans}							

2-Butyne	$D_{geminal}$					1353·7 (89)		
	$D_{HH'}$					−107·11 (3)		
	$J_{HH'}$					2·73 (6)		
2,4-Hexadiyne	$D_{geminal}$				3018 (90)			
	$D_{HH'}$				−75·45 (3)			
	$J_{HH'}$				1·29 (6)			
1,4-Dichlorobenzene	D_{ortho}		−1718·65 (50)	−1669·46 (56)	−1772 (3)	−1722 (3)	−1826·4 (8)	−1515 (50)
	D_{meta}		72·12 (37)	69·89 (70)	80 (2)	72·4 (20)	77·0 (10)	
	D_{para}		−19·76 (10)	−19·57 (70)	−33 (2)	−21 (2)	−20·9 (5)	
1,4-Dibromobenzene	D_{ortho}				−1976 (2)			
	D_{meta}				116·3 (15)			
	D_{para}				15 (2)			
EBBA-d_2	$\Delta\nu_Q$ (*c*)	$14·40 \times 10^3$	$13·82 \times 10^3$	$13·58 \times 10^3$	$14·32 \times 10^3$	$14·11 \times 10^3$	$14·89 \times 10^3$	$12·54 \times 10^3$
5CB-α,β-d_4	$\Delta\nu_\alpha$ (*d*)	$50·48 \times 10^3$	$48·48 \times 10^3$	$47·63 \times 10^3$	$50·22 \times 10^3$	$49·48 \times 10^3$	$51·71 \times 10^3$	$44·14 \times 10^3$
	$\Delta\nu_\beta$ (*d*)	$33·62 \times 10^3$	$32·03 \times 10^3$	$31·44 \times 10^3$	$33·46 \times 10^3$	$32·78 \times 10^3$	$34·67 \times 10^3$	$28·84 \times 10^3$
5CB-d_{19}	$\Delta\nu_\delta$ (*d*)						$23·40 \times 10^3$	$19·40 \times 10^3$
	$\Delta\nu_{ar(CN)}$ (*e*)						$10·48 \times 10^3$	$8·5 \times 10^3$
	T_{red} (*f*)	0·969	0·988	0·991	0·980	0·978	0·977	0·988

(*a*) The dipolar couplings for benzene, 1,3,5-trifluorobenzene, propyne and allene depend on the same J couplings cited in [19].

(*b*) Identical to sample 2 but measured at 317 K.

(*c*) Quadrupolar line splitting for deuterons *ortho* to the nitrogen of the butylaniline ring of EBBA-d_2.

(*d*) Quadrupolar line splitting for deuterons in the pentyl chain of deuteriated 5CB. Greek letters indicate deuteron position starting at the phenyl ring.

(*e*) Quadrupolar line splitting for aromatic deuterons in the cyanophenyl ring of 5CB-d_{19}.

(*f*) T_{red} is the ratio of the temperature T and the temperature at which the nematic to (all) isotropic phase transition for the particular sample starts to take place.

tubes spinning around an axis parallel to the external magnetic field. The temperature was controlled by means of a variable temperature gas flow unit. All samples were heated to the isotropic phase and mixed thoroughly before being placed into the probe and left to equilibrate for at least half an hour before the NMR spectra were recorded.

3. Results and discussion

The mean efg present in a nematic solvent can be derived from the NMR spectrum of molecular deuterium as discussed by Patey *et al.* [17] and Barker *et al.* [18]. Weaver *et al.* [25] have determined this efg at several temperatures for the liquid crystal 5CB-α,β-d_4 and it is found to have the same sign as 1132. Therefore, when mixed in the correct proportion, together with a solvent such as EBBA (possessing an efg of opposite sign [17]), these two liquid crystals can in principle form a nematic solvent possessing a mean zero-efg. For molecular deuterium dissolved in such a mixture, the ratio of the quadrupolar coupling constant B and the dipolar coupling constant D determined from the NMR spectrum is equal to the gas phase value ($-24{\cdot}58$ at 320 K for D_2 [12, 17]).

In table 1 values for the measured ratio B/D of molecular deuterium are presented in a novel 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture at 316 K. For comparison, a mixture made up of 56·5 wt% 1132 in EBBA-d_2 at 322 K was also employed. This represents a zero-efg mixture very similar in composition to the 'magic mixture' used previously [18, 19], the only difference being that its reduced temperature is slightly closer to that of the EBBA/5CB mixture. It should be pointed out that the estimates for the mean efg (F_{ZZ}) in table 1 for both mixtures are two orders of magnitude smaller than the values obtained for the pure, component liquid crystals [17, 25].

The interactions responsible for the orientation of compounds dissolved in these zero-efg solvents can now be compared at quite similar (though not identical) reduced temperatures. It should be noted in table 1 that the orientation of deuterium is described by small, but non-vanishing values for S_{zz}. This indicates that, although the orientation of deuterium is dominated by the interaction between its molecular quadrupole moment and the mean efg, it is not the only orienting mechanism [13]. This is again similar to the situation found for deuterium in the 55 wt% 1132/EBBA mixture [18, 19].

In tables 2 (*a*) and (*b*) measured ^{1}H and ^{2}H NMR spectral parameters are presented for twelve compounds dissolved in our two zero-efg mixtures. In all but one sample tube, both 1,3,5-trichlorobenzene and 1,4-dichlorobenzene are present, whereas the other solutes have been distributed amongst the samples. The quadrupolar line splittings for the deuterons of the component solvent molecules EBBA-d_2 and 5CB-α,β-d_4 are also given, as well as the observed line splittings for 5CB-d_{19} in the samples that were doped with a minute amount of this liquid crystal material used as a solute. The less trivial NMR spectra were analysed with the aid of the Bruker PANIC programme to obtain the dipolar couplings.

The average orientation of a solute can be described in terms of an order parameter tensor defined as

$$S_{\alpha\beta}=\langle\tfrac{3}{2}\cos\vartheta_\alpha\cos\vartheta_\beta-\tfrac{1}{2}\delta_{\alpha\beta}\rangle,$$

where ϑ_α is the angle between the molecule fixed α axis and the space fixed Z axis along the magnetic field direction. In tables 3 (*a*) and (*b*), the order parameters evaluated from the experimental dipolar couplings in tables 2 (*a*) and (*b*) are presented. Ten of the solutes studied possess a three-fold or higher symmetry axis and, by selecting this axis as the molecule fixed z axis, S_{zz} is the only order parameter required to specify their orientation. Both 1,4-dichlorobenzene and 1,4-dibromobenzene have D_{2d} symmetry. Choosing the x, y and z axes in the symmetry planes gives S_{zz} and $S_{xx}-S_{yy}$ as the only independent order parameters for these molecules. The order parameters have been derived assuming that there is no correlation between the degree of order and the intramolecular motions for the compounds studied. This assumption may be questionable for tetrahedral molecules such as methane [5, 14, 15], but is reasonable in other cases. The order parameters were calculated using the molecular structures used in a previous study of these molecules in the 55 wt% 1132/EBBA-d_2 mixture [19, 20]. Moreover, with the exception of molecular deuterium, the solutes are assumed rigid, and internal motions are neglected. A rigorous treatment of internal motion effects would require detailed knowledge of the harmonic and anharmonic force field for every molecule. The error in the values obtained for the molecular order parameters introduced by our simplified approach is estimated to be less than 5 per cent.

In principle, the observed quadrupolar couplings for the deuteriated component liquid crystals provide detailed information on the C–^{2}H bond order parameters of each specific site of these large, flexible molecules that can exist in many conformations. An intriguing objective is to see to what extent the ideas developed for the orientation of small solutes can indeed be transferred to the description of the liquid crystal molecules themselves. In order to relate the experimental quadrupolar couplings rigorously to the orientational order, the alkyl chain flexibility must be modelled. Such an approach has been taken by Hoatson *et al.* who indeed successfully explained the quadrupolar line splittings for 5CB-d_{19} in the zero-efg mixture made up of 55 wt% 1132 in EBBA [21]. However, in the present study these quadrupole couplings themselves are used as a measure of the nematic environment felt at these sites and a more quantitative analysis is not pursued.

For a rigorous comparison of the interactions responsible for the observed orientational order of both solute and solvent molecules, a number of severe demands should be met. First, the observed molecular order must be obtained correctly from the observed quantities. Infinitely diluted samples should be used to avoid solute–solute interactions as well as perturbations of the anisotropic environment. Also, to ensure that the observed order results from orienting forces of the same magnitude, the experiments should be performed at the same (reduced) temperature. Finally, as the orienting forces are reflected only indirectly in the observed properties, molecules of low symmetry probably probe the anisotropic environment in a more distinctive way. These criteria are not strictly met for the experiments reported here. Differences among the samples are apparent in the variations of the values given in tables 2 and 3. However, for a particular molecule that is present (possibly together with other compounds, all at low concentration) in several samples of the same nematic solvent at quite similar temperatures, small differences in orientational order probably result from slightly different magnitudes of the orienting interactions. Under these circumstances, such small differences in ordering will, to a first approximation, correlate linearly with changes in the orienting forces. As can be seen from table 3, the values of S_{zz} for 1,3,5-trichlorobenzene and 1,4-dichlorobenzene show an identical variation (within ~1 per cent) among the samples made up with both our zero-efg mixtures. The same behaviour can be noticed for the quadrupolar line splittings of the component liquid crystal EBBA-d_2 in both solvents. This implies that in a zero-efg mixture, differences among the samples for a single solvent can be taken into account by scaling to an orientation parameter of a particular reference compound. Both the solutes 1,3,5-trichlorobenzene and 1,4-dichlorobenzene, as well as EBBA-d_2, are therefore appropriate choices to monitor sample differences.

In contrast, scaling to a reference compound is inappropriate for solutes in a pure nematic phase such as EBBA-d_2 in which more than one orienting mechanism is prevalent. For example, consider the data by Kok *et al.* [20], where samples containing ten solutes with a three-fold or higher symmetry axis were studied using both pure EBBA-d_2 at $T_{\mathrm{red}}=0{\cdot}8611$ and the 55 wt% 1132/EBBA-d_2 mixture at $T_{\mathrm{red}}=0{\cdot}8787$. In these experiments, the quadrupolar line splittings for the deuterons of EBBA-d_2 show only minor variations (within ~ 1·5 per cent) for the samples made up in either solvent. Thus, the experimental conditions did not change significantly among the samples. However, there is a large variation in the relative change with liquid crystal solvent of the order parameters S_{zz} for the solutes themselves. This is a common observation for molecules studied in different nematic solvents where several orienting interactions contribute significantly to the observed order. This variation is shown in figure 1, where ratios for the molecular order parameter S_{zz} for solutes in several pure liquid crystal solvents with respect to the order in the 56·5 wt% 1132/EBBA-d_2 mixture measured in this study are shown. To account for small differences among the samples, the order parameters used in figure 1 are scaled by S_{zz} for 1,3,5-trichlorobenzene in the same solvent. Quadrupolar liquid crystal deuteron line splittings are included as well. Note

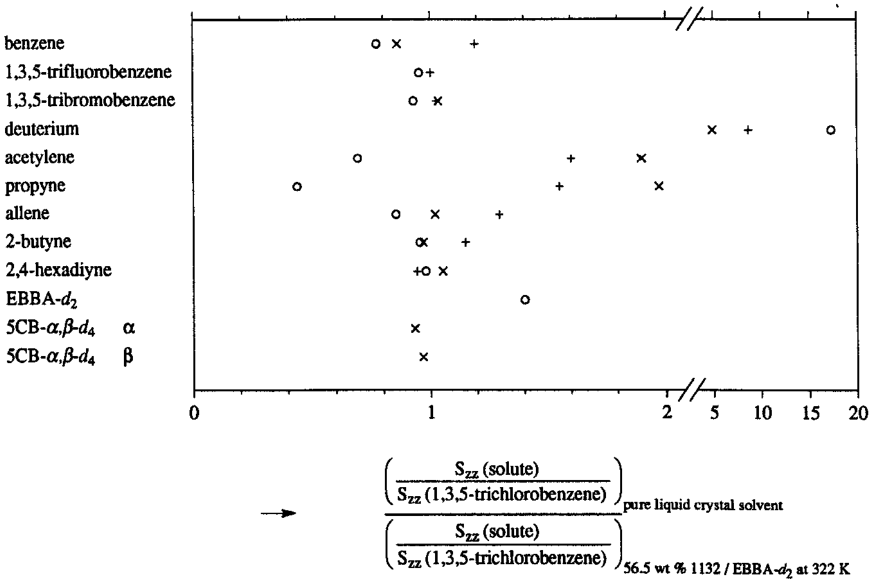


Figure 1. Ratio of the experimental molecular order parameter S_{zz} for sets of solutes in pure liquid crystal solvents: EBBA-d_2 (○, at 301·4 K, data taken from [20]), 1132 (+, at 301·4 K, data taken from [20]) and 5CB-α,β-d_4 (×, at 294 K—benzene at 296 K; —, data taken from [25]) and in 56·5 wt% 1132 in EBBA-d_2 at 322 K both scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents. If available, the ratio using the experimental quadrupole line splittings $\Delta\nu$ (instead of S_{zz} of the solute) for deuterons of the deuteriated liquid crystals, scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene in these solvents is also shown. For deuterium in both pure 1132 and 5CB-α,β-d_4 and acetylene in EBBA-d_2 the absolute ratios are shown as these solutes possess an order parameter S_{zz} of opposite sign in these solvents compared to the 56·5 wt% 1132/EBBA-d_2 mixture.

Table 3. (*a*) Molecular order parameters derived from the experimental dipolar couplings in table 2 (*a*) for solutes in 56·5 wt% 1132 in EBBA-d_2 at 322 K.

		56·5 wt% 1132/EBBA-d_2 at 322 K			
Molecule	Parameter (*a*)	Sample 1	Sample 2	Sample 3	Sample 4
Benzene	S_{zz}			−0·14026 (64)	
1,3,5-Trifluorobenzene	S_{zz}				−0·18019 (98)
1,3,5-Trichlorobenzene	S_{zz}	−0·19141 (1)	−0·20226 (9)	−0·19103 (7)	−0·20082 (3)
1,3,5-Tribromobenzene	S_{zz}		−0·19739 (4)		
Deuterium	S_{zz}	$-6{\cdot}02 \times 10^{-4}$			
Acetylene	S_{zz}	0·07941 (3)			
Propyne	S_{zz}				0·12419 (17) (*b*)
Allene	S_{zz}				0·1068 (28)
2-Butyne	S_{zz}			0·14960 (6) (*c*)	
2,4-Hexadiyne	S_{zz}		0·31842 (15) (*c*)		
1,4-Dichlorobenzene	S_{zz}	0·24551 (6)	0·26267 (4)	0·24660 (7)	0·26007 (12)
	$S_{xx}-S_{yy}$	0·14320 (39)	0·14726 (44)	0·14156 (61)	0·1480 (19)
	$S_{xx}-S_{yy}/S_{zz}$	0·5833 (15)	0·5605 (16)	0·5741 (26)	0·5692 (70)
1,4-Dibromobenzene	S_{zz}		0·28954 (17)		
	$S_{xx}-S_{yy}$		0·1316 (12)		
	$S_{xx}-S_{yy}/S_{zz}$		0·4545 (50)		

(*a*) For the molecules possessing a three-fold or higher symmetry axis, this axis is chosen to be the molecule fixed *z* axis. For, 1,4-dichlorobenzene and 1,4-dibromobenzene, the *z* axis pasess through both halogen atoms, the *y* axis is perpendicular to the benzene plane and the *x* axis is perpendicular to both the *y* and *z* axes. The molecular structures have been taken from the various references quoted in [19, 20].

(*b*) Order parameter S_{zz} derived from $D_{\mathrm{HH}'}$.

(*c*) Order parameter S_{zz} derived from $D_{\mathrm{HH}'}$ assuming unhindered methyl group rotation.

Table 3. (*b*) Molecular order parameters derived from the experimental dipolar couplings in table 2 (*b*) for solutes in 30·0 wt% EBBA-d_2 in 5CB-α,β-d_4 at 316 K.

		30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K						
Molecule	Parameter (*a*)	Sample 1	Sample 2	Sample 3 (*b*)	Sample 4	Sample 5	Sample 6	Sample 7
Benzene	S_{zz}					−0·12761 (63)		
1,3,5-Trifluorobenzene	S_{zz}							−0·13861 (36)
1,3,5-Trichlorobenzene	S_{zz}		−0·17261 (3)	−0·16791 (5)	−0·17654 (3)	−0·17313 (27)	−0·18260 (7)	−0·15270 (23)
1,3,5-Tribromobenzene	S_{zz}				−0·17147 (10)			
Deuterium	S_{zz}	$-5{\cdot}07\times10^{-4}$	$-4{\cdot}35\times10^{-4}$	$-4{\cdot}55\times10^{-4}$				
Acetylene	S_{zz}		0·08070 (15)	0·07739 (10)				
Propyne	S_{zz}					0·10980 (17) (*c*)		0·09533 (58) (*c*)
Allene	S_{zz}							Not assigned
2-Butyne	S_{zz}					0·13062 (4) (*d*)		
2,4-Hexadiyne	S_{zz}				0·28631 (11) (*d*)			
1,4-Dichlorobenzene	S_{zz}		0·22527 (5)	0·21882 (7)	0·23226 (39)	0·22571 (39)	0·23939 (10)	0·1986 (66)
	$S_{xx}-S_{yy}$		0·12815 (55)	0·1247 (10)	0·1245 (31)	0·1282 (31)	0·1358 (14)	—
	$S_{xx}-S_{yy}/S_{zz}$		0·5689 (23)	0·5699 (45)	0·536 (12)	0·568 (13)	0·5671 (57)	—
1,4-Dibromobenzene	S_{zz}				0·25838 (26)			
	$S_{xx}-S_{yy}$				0·1000 (23)			
	$S_{xx}-S_{yy}/S_{zz}$				0·3871 (85)			

(*a*) For the molecules possessing a three-fold or higher symmetry axis, this axis is chosen to be the molecule fixed *z* axis. For, 1,4-dichlorobenzene and 1,4-dibromobenzene the *z* axis passes through both halogen atoms, the *y* axis is perpendicular to the benzene plane and the *x* axis is perpendicular to both the *y* and *z* axes. The molecular structures have been taken from the various references quoted in [19, 20].

(*b*) Identical to sample 2 but measured at 317 K.

(*c*) Order parameter S_{zz} derived from $D_{HH'}$.

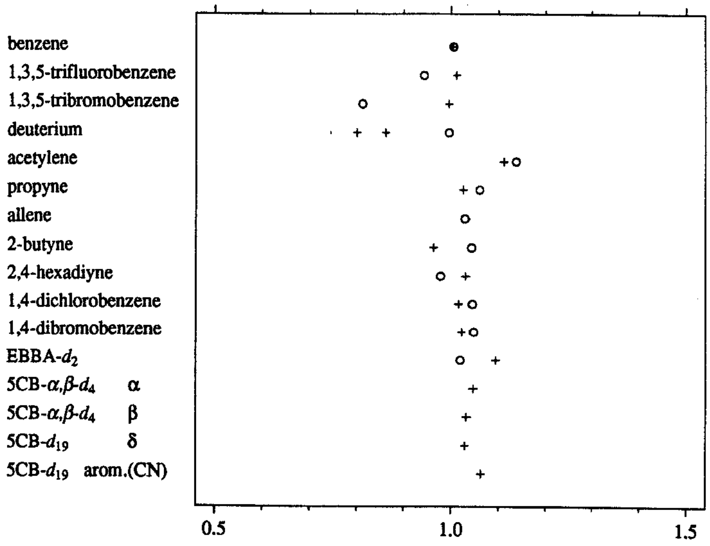
(*d*) Order parameter S_{zz} derived from $D_{HH'}$ assuming unhindered methyl group rotation.

the change of scale required to include molecular deuterium, and the fact that deuterium and acetylene have order parameters of opposite sign for some of the solvents. In figure 1 variations for both solvent and solute order exceeding 20 per cent are not uncommon.

The major difference between the pure liquid crystals in figure 1 and our 56·5 wt% 1132 in the EBBA-d_2 mixture is the absence of an average efg in the latter solvent. It can be shown that the orientation of molecular deuterium is dominated by the interaction of this efg with the molecular quadrupole moment, resulting in the large variations observed for deuterium in figure 1. The experiments reported in this paper are performed in two quite different, yet essentially zero-efg, nematic solvents. The effects of scaling and the differences in orientational order among three different zero-efg mixtures are demonstrated in figure 2. The ratios of observed order parameters S_{zz} for solutes and quadrupolar line splittings of solvent molecules, scaled by the order parameters S_{zz} for 1,3,5-trichlorobenzene (and 1,4-dichlorobenzene) to correct for small sample differences, are shown in figure 2 (*a*) (and (*b*)). It can be seen that molecular deuterium now shows a similar orientation in all three zero-efg mixtures, in contrast to figure 1. This is an intriguing result, as in these solvents the interaction between the molecular quadrupole moment and the efg (responsible for most of the orientation in the pure component liquid crystals) should yield a negligible contribution to the observed order for molecular deuterium. From figures 2 (*a*) and (*b*) it can be seen that the other solutes orient in the same way in these mixtures at comparable reduced temperatures and apparently experience no mean efg, just like molecular deuterium. This stresses the importance of using liquid crystals in which the orienting interactions can be varied in a controlled way, as differences among liquid crystal solvents are notably a result of a different mean efg. Because the ratios of the solute order parameters S_{zz} vary within a narrow range of about 10 per cent in the zero-efg solvents, these results indicate that to a remarkably good approximation the set of all solutes experience the same average environment. Apparently the observed order for the solutes can be attributed mainly to a single orienting interaction. If, for a solute, the orientation in one of these mixtures is measured together with an internal reference, for example, 1,3,5-trichlorobenzene, the orientation of the solute can be predicted with good accuracy in any of the other zero-efg mixtures from the orientation of that reference compound alone. This important result underlines the special role that zero-efg mixtures play in elucidating orienting mechanisms.

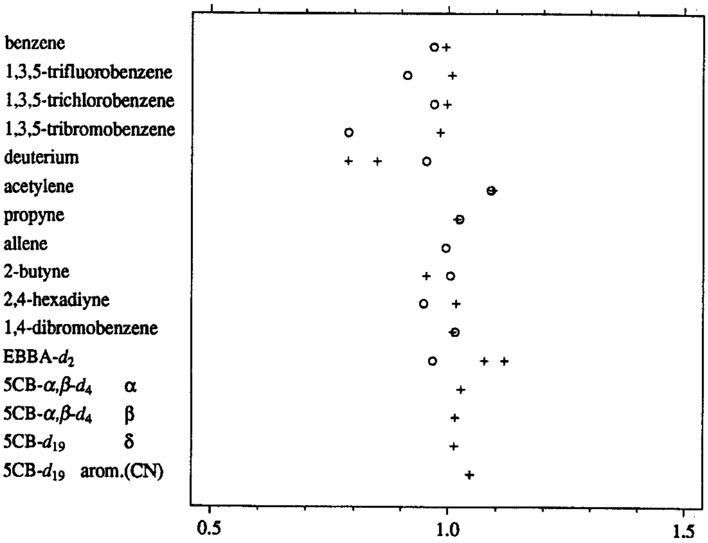
In figures 2 (*a*) and (*b*), the quadrupolar line splittings observed for several sites of the component liquid crystal molecules are included, scaled in the same way as S_{zz} for the solutes to account for small differences between the samples. These large, flexible solvent molecules behave in the same way as the smaller solutes studied and appear to experience the same average environment to a good approximation. This justifies the use of solute molecules as a good starting point for investigating the nature of the orienting mechanisms operative in nematic solvents.

For 1,4-dichlorobenzene and 1,4-dibromobenzene, any two of the three non-vanishing order parameters are independent and therefore provide additional information about the active orienting interactions. If the solutes experience the same average environment in different liquid crystal solvents, this should be reflected in the order parameter ratio $S_{xx}-S_{yy}/S_{zz}$, which should then be the same and essentially temperature independent [27]. Comparing these ratios for the zero-efg mixtures in tables 3 (*a*) and (*b*) with the values obtained for the 55 wt% 1132 in the EBBA-d_2 mixture for 1,4-dichlorobenzene (0·5477) and 1,4-dibromobenzene (0·4275), as evaluated from



$$\longrightarrow \quad \frac{\left(\dfrac{S_{zz}\,(\text{solute})}{S_{zz}\,(1{,}3{,}5\text{-trichlorobenzene})}\right)_{\text{zero electric field gradient mixture}}}{\left(\dfrac{S_{zz}\,(\text{solute})}{S_{zz}\,(1{,}3{,}5\text{-trichlorobenzene})}\right)_{56.5\ \text{wt}\ \%\ 1132\,/\,\text{EBBA-}d_2\ \text{at}\ 322\ \text{K}}}$$

(*a*)



$$\longrightarrow \quad \frac{\left(\dfrac{S_{zz}\,(\text{solute})}{S_{zz}\,(1{,}4\text{-dichlorobenzene})}\right)_{\text{zero electric field gradient mixture}}}{\left(\dfrac{S_{zz}\,(\text{solute})}{S_{zz}\,(1{,}4\text{-dichlorobenzene})}\right)_{56.5\ \text{wt}\ \%\ 1132\,/\,\text{EBBA-}d_2\ \text{at}\ 322\ \text{K}}}$$

(*b*)

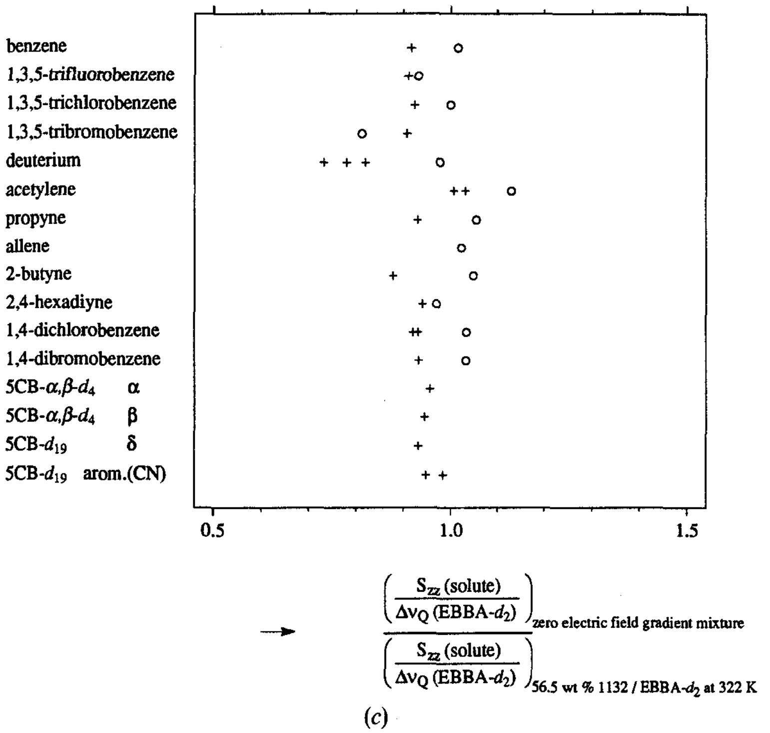


Figure 2. Ratio of the experimental molecular order parameter S_{zz} for sets of solutes in zero mean electric field gradient mixtures: 55 wt% 1132 in EBBA-d_2 (○, at 301·4 K, data taken from [20]), 30·0 wt% EBBA-d_2 in 5CB-α,β-d_4 (+, at 316 K) and in 56·5 wt% 1132 in EBBA-d_2 at 322 K both scaled by the corresponding value of S_{zz} for 1,3,5-trichlorobenzene (figure 2(*a*)) and S_{zz} for 1,4-dichlorobenzene (see figure 2(*b*)); the experimental quadrupole line splitting $\Delta\nu$ for the deuterons in EBBA-d_2 (see figure 2(*c*)) in these solvents. If available, the ratio using the experimental quadrupole line splittings $\Delta\nu$ (instead of S_{zz} of the solute) for deuterons of the deuteriated liquid crystals, scaled by the values mentioned above in these solvents is also shown.

the data in [20], shows that for 1,4-dichlorobenzene these values are in excellent agreement. This confirms again that 1,4-dichlorobenzene indeed experiences the same orienting forces in all three zero-efg solvents. For 1,4-dibromobenzene the values are less conclusive in this respect as $S_{xx}-S_{yy}/S_{zz}$ varies about 15 per cent. A study of additional lower symmetry solutes as for example, in [20], could provide useful additional information to see whether the orienting behaviour of 1,4-dichlorobenzene or of 1,4-dibromobenzene is more typical for solutes in zero-efg mixtures.

In figure 2(*c*) the quadrupolar line splittings observed for the component liquid crystal EBBA-d_2 are used, instead of the order parameter S_{zz} of a reference solute as in figures 2(*a*) and (*b*), to scale the observed order parameter S_{zz} for solutes and quadrupolar line splittings for solvent deuteron sites to compare their orientation in the zero-efg mixtures. Although it is again confirmed that most compounds experience the same average environment within approximately 10 per cent, the values now show slightly more scatter. For all solutes except 1,3,5-tribromobenzene, the ratios for the 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture at 316 K are consistently about 9 per cent lower than those obtained for the 55 wt% 1132/EBBA-d_2 mixture at 301·4 K. From tables 2 and 3 it can also be noted that the ratio of the quadrupolar line splittings for both EBBA-d_2 and 5CB-α,β-d_4 to S_{zz} for either 1,3,5-trichlorobenzene or 1,4-dichlorobenzene tend to be smaller in the 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture. The differences are about 4 per cent for the deuteron sites of 5CB-α,β-d_4 and 9 per cent for EBBA-d_2. These differences might be caused by differences in the conformational averaging, but this is difficult to ascertain without further modelling of the flexibility of the alkyl chain.

The difference in figures 2 (*a*)–(*c*) is the choice of experimental splitting used for the purpose of scaling. This scaling is necessary to account for the small differences among the sample tubes which arise because of differences in temperature and solute concentration. All three methods should be equivalent if our assumption is correct that small differences in ordering will, to a first approximation, correlate linearly with changes in the orienting forces. If we are interested in qualitative comparisons of orientation parameters, as demonstrated by the results of figure 2, choosing splittings of an arbitrary solute for scaling purposes is acceptable. For a more quantitative comparison, scaling the potential itself would be preferable. Such a procedure would take care of the non-linear dependence of solute orientation parameters on the liquid crystal potential. Since the true anisotropic potential is not known, a reasonable approach is to multiply a simple $P_2(\cos\vartheta)$ Maier–Saupe potential by an appropriate scaling factor, so as to reproduce the order parameter of one chosen solute that is present in all sample tubes. We shall come back to this point later.

Although the results obtained here indicate that to a good approximation the compounds dissolved in different zero-efg mixtures experience the same average environment, the actual physical nature of the interaction responsible still remains unspecified. In this respect the simple phenomenological mean field description of the short range repulsive interaction between solute and solvent as developed by van der Est *et al.* [19, 20] is an attractive candidate. This potential has the form

$$U = \tfrac{1}{2}kC^2, \qquad (1)$$

where k is a Hooke's law force constant and C is the circumference of the van der Waals molecule projected onto a plane perpendicular to the director. This model, which depends on the dimensions and shape anisotropy of the solute, has been used successfully to describe the orientation of a large variety of solutes. We now apply this model to explain the order parameters in tables 3 (*a*) and (*b*) of the solutes in the two zero-efg mixtures studied here. The results are summarized in tables 4 (*a*) and (*b*). The single force constant k has been obtained by a least squares fit to the experimental order parameter S_{zz} for all the solutes in a particular sample under the assumption that all solutes indeed experience the same zero-efg. The molecular structures and van der Waals radii required to represent the solute as a rigid collection of van der Waals spheres are taken from the references quoted in [19, 20]. It can be seen from table 4 that the force constants k that describe the liquid crystal environment for all solutes in a sample are very similar for the two solvents. The force constants obtained for the samples of the 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture at 316 K are about 15 per cent lower than those for the mixture made up of 56·5 wt% 1132 in EBBA-d_2 at 322 K. The values compare reasonably well with the force constant of $5{\cdot}44 \times 10^{-3}\,\mathrm{N\,m^{-1}}$ that has been obtained from a least squares fit to the experimental order parameters for 46 solutes dissolved in 55 wt% 1132/EBBA-d_2 at 301·4 K [24]. It is obvious from table 4 that the order parameter of molecular deuterium obtained from the fit deviates greatly from experiment and even has the wrong sign, similar to observations made for the 55 wt% 1132/EBBA mixture [19]. A more detailed

Table 4. Experimental and calculated order parameters for solutes in the zero mean electric field gradient mixtures 56·5 wt% 1132/EBBA-d_2 at 322 K (table 4 (*a*)) and 30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K (table 4 (*b*)). The order parameters are calculated using a model (see equation (1)) based on the short range repulsive interactions which depend on the size and shape of the solute [19]. The force constant *k* governing the interaction has been obtained using a least squares fit of the order parameter S_{zz} for all solutes in a sample to the experimental value. The values for the order parameters S_{xx} and S_{yy} of 1,4-dichlorobenzene and 1,4-dibromobenzene have been calculated using the value of the force constant obtained in the fit for the sample.

4 (*a*)

56·5 wt% 1132/EBBA-d_2 at 322 K

	Molecule	Parameter (*a*)	Experimental	Calculated
Sample 1				
$k = 4{\cdot}93 \times 10^{-3}\,\mathrm{N\,m^{-1}}$	1,3,5-Trichlorobenzene	S_{zz}	−0·19141	−0·1831
	Deuterium	S_{zz}	−0·00060	0·0120
	Acetylene	S_{zz}	0·07941	0·0683
	1,4-Dichlorobenzene	S_{xx}	−0·05115	−0·0830
		S_{yy}	−0·19436	−0·1697
		S_{zz}	0·24551	0·2527
Sample 2				
$k = 4{\cdot}76 \times 10^{-3}\,\mathrm{N\,m^{-1}}$	1,3,5-Trichlorobenzene	S_{zz}	−0·20226	−0·1778
	1,3,5-Tribromobenzene	S_{zz}	−0·19739	−0·1911
	2,4-Hexadiyne	S_{zz}	0·31842	0·3455
	1,4-Dichlorobenzene	S_{xx}	−0·05771	−0·0794
		S_{yy}	−0·20496	−0·1641
		S_{zz}	0·26267	0·2435
	1,4-Dibromobenzene	S_{xx}	−0·07898	−0·1090
		S_{yy}	−0·21056	−0·1778
		S_{zz}	0·28954	0·2867
Sample 3				
$k = 4{\cdot}94 \times 10^{-3}\,\mathrm{N\,m^{-1}}$	Benzene	S_{zz}	−0·14026	−0·1038
	1,3,5-Trichlorobenzene	S_{zz}	−0·19103	−0·1834
	2-Butyne	S_{zz}	0·14960	0·1647
	1,4-Dichlorobenzene	S_{xx}	−0·05252	−0·0832
		S_{yy}	−0·19408	−0·1700
		S_{zz}	0·24660	0·2532
Sample 4				
$k = 5{\cdot}37 \times 10^{-3}\,\mathrm{N\,m^{-1}}$	1,3,5-Trifluorobenzene	S_{zz}	−0·18019	−0·1553
	1,3,5-Trichlorobenzene	S_{zz}	−0·20082	−0·1963
	Propyne	S_{zz}	0·12419	0·1185
	Allene	S_{zz}	0·10676	0·1076
	1,4-Dichlorobenzene	S_{xx}	−0·05602	−0·0925
		S_{yy}	−0·20405	−0·1837
		S_{zz}	0·26007	0·2762

(*a*) See table 3 (*a*) for choice of molecular axis system.

4(*b*)

30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K

	Molecule	Parameter (*a*)	Experimental	Calculated
Sample 1 $k=-0\cdot20\times10^{-3}\,\mathrm{Nm}^{-1}$	Deuterium	S_{zz}	−0·00051	−0·00051
Sample 2 $k=4\cdot44\times10^{-3}\,\mathrm{Nm}^{-1}$	1,3,5-Trichlorobenzene	S_{zz}	−0·17261	−0·1705
	Deuterium	S_{zz}	−0·00043	0·0110
	Acetylene	S_{zz}	0·08070	0·0625
	1,4-Dichlorobenzene	S_{xx}	−0·04856	−0·0744
		S_{yy}	−0·17671	−0·1565
		S_{zz}	0·22527	0·2309
Sample 3 (*b*) $k=4\cdot32\times10^{-3}\,\mathrm{Nm}^{-1}$	1,3,5-Trichlorobenzene	S_{zz}	−0·16791	−0·1663
	Deuterium	S_{zz}	−0·00046	0·0106
	Acetylene	S_{zz}	0·07739	0·0606
	1,4-Dichlorobenzene	S_{xx}	−0·04706	−0·0717
		S_{yy}	−0·17176	−0·1521
		S_{zz}	0·21882	0·2238
Sample 4 $k=4\cdot17\times10^{-3}\,\mathrm{Nm}^{-1}$	1,3,5-Trichlorobenzene	S_{zz}	−0·17654	−0·1618
	1,3,5-Tribromobenzene	S_{zz}	−0·17147	−0·1742
	2,4-Hexadiyne	S_{zz}	0·28631	0·3049
	1,4-Dichlorobenzene	S_{xx}	−0·05388	−0·0688
		S_{yy}	−0·17838	−0·1475
		S_{zz}	0·23226	0·2162
	1,4-Dibromobenzene	S_{xx}	−0·07918	−0·0952
		S_{yy}	−0·17920	−0·1595
		S_{zz}	0·25838	0·2546
Sample 5 $k=4\cdot44\times10^{-3}\,\mathrm{Nm}^{-1}$	Benzene	S_{zz}	−0·12761	−0·0958
	1,3,5-Trichlorobenzene	S_{zz}	−0·17313	−0·1705
	Propyne	S_{zz}	0·10980	0·0984
	2-Butyne	S_{zz}	0·13062	0·1491
	1,4-Dichlorobenzene	S_{xx}	−0·04875	−0·0744
		S_{yy}	−0·17695	−0·1565
		S_{zz}	0·22571	0·2309
Sample 6 $k=4\cdot65\times10^{-3}\,\mathrm{Nm}^{-1}$	1,3,5-Trichlorobenzene	S_{zz}	−0·18260	−0·1773
	1,4-Dichlorobenzene	S_{xx}	−0·05181	−0·0790
		S_{yy}	−0·18758	−0·1635
		S_{zz}	0·23939	0·2425
Sample 7 $k=4\cdot01\times10^{-3}\,\mathrm{Nm}^{-1}$	1,3,5-Trifluorobenzene	S_{zz}	−0·13861	−0·1224
	1,3,5-Trichlorobenzene	S_{zz}	−0·15270	−0·1564
	Propyne	S_{zz}	0·09533	0·0883
	1,4-Dichlorobenzene	S_{xx}	—	−0·0654
		S_{yy}	—	−0·1420
		S_{zz}	0·1986	0·2075

(*a*) See table 3 (*b*) for choice of molecular axis system.

(*b*) Identical to sample 2 but measured at 317 K.

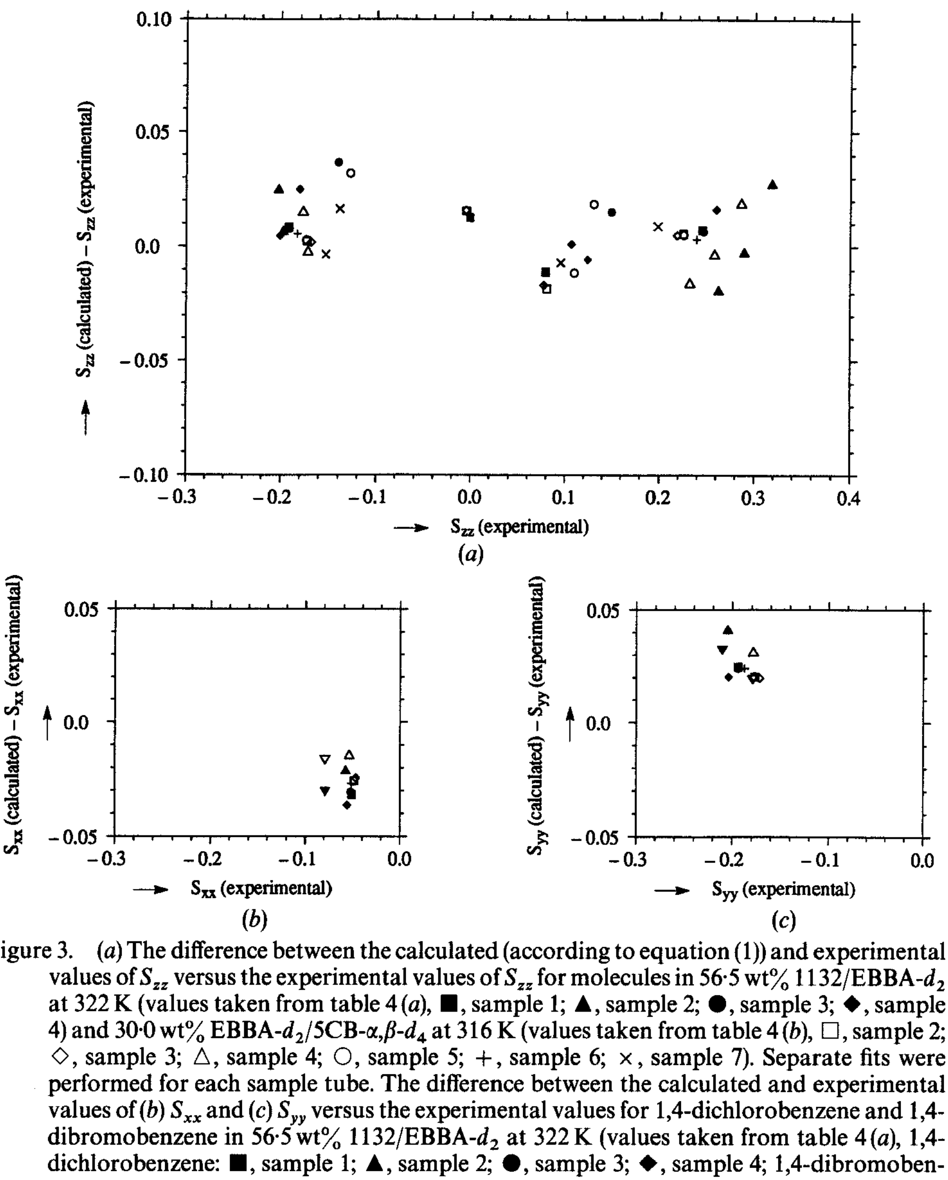


Figure 3. (*a*) The difference between the calculated (according to equation (1)) and experimental values of S_{zz} versus the experimental values of S_{zz} for molecules in 56·5 wt% 1132/EBBA-d_2 at 322 K (values taken from table 4 (*a*), ■, sample 1; ▲, sample 2; ●, sample 3; ◆, sample 4) and 30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K (values taken from table 4 (*b*), □, sample 2; ◇, sample 3; △, sample 4; ○, sample 5; +, sample 6; ×, sample 7). Separate fits were performed for each sample tube. The difference between the calculated and experimental values of (*b*) S_{xx} and (*c*) S_{yy} versus the experimental values for 1,4-dichlorobenzene and 1,4-dibromobenzene in 56·5 wt% 1132/EBBA-d_2 at 322 K (values taken from table 4 (*a*), 1,4-dichlorobenzene: ■, sample 1; ▲, sample 2; ●, sample 3; ◆, sample 4; 1,4-dibromobenzene: ▼, sample 2) and in 30·0 wt% EBBA-d_2/5CB-α,β-d_4 at 316 K (values taken from table 4 (*b*), 1,4-dichlorobenzene: □, sample 2; ◇, sample 3; △, sample 4; ○, sample 5; +, sample 6; 1,4-dibromobenzene: ▽, sample 4).

discussion of the order parameters of the various isotopomers of hydrogen in liquid crystal solvents possessing small efgs has been presented by van der Est *et al.* [13].

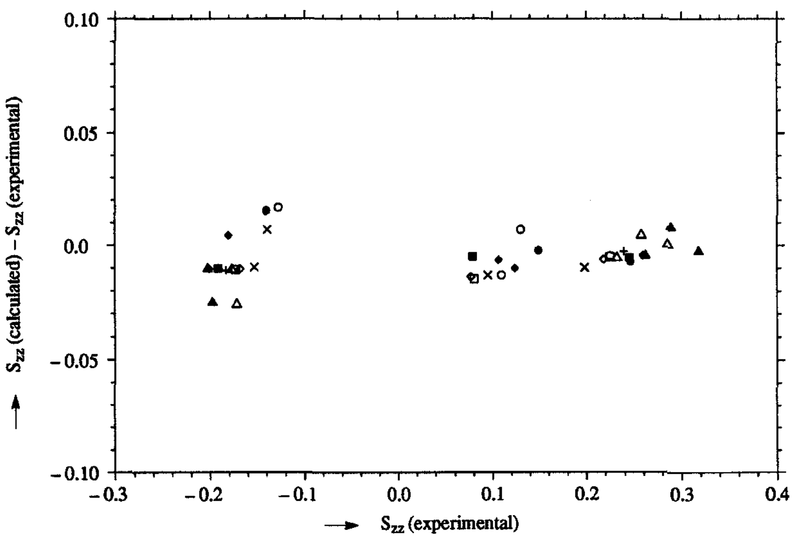
The differences between calculated and experimental values for S_{zz} are presented in figure 3 (*a*). The agreement is remarkably good, all absolute differences being less than 0·05. For all molecules, except hydrogen, benzene, and acetylene, the relative error in the values of the order parameter S_{zz} is less than 15 per cent. From table 4 and figures 3 (*b*) and (*c*) it can be seen that the values for the order parameters S_{xx} and S_{yy} of 1,4-dichlorobenzene and 1,4-dibromobenzene, calculated from the force constant obtained from the fit for a particular sample, are consistently too small and too large, respectively. The minimum circumference model of van der Est *et al.* yields equally good values for the order parameters of the solutes in our present zero-efg mixtures as for the same solutes dissolved in 55 wt% 1132/EBBA-d_2 at 301·4 K [20]. This strongly supports the notion that the short range interactions described by the van der Est *et al.* model can indeed be taken to be responsible for the solute ordering in mixtures in which the average efg as experienced by molecular deuterium is zero.

The extension of the single parameter van der Est *et al.* model which adds an anisotropic surface interaction to the potential gives a much better fit to a collection of 46 solutes in the 55 wt% 1132/EBBA-d_2 mixture [24]. Thus, it is interesting to apply this newer model to our results. The new potential has the form

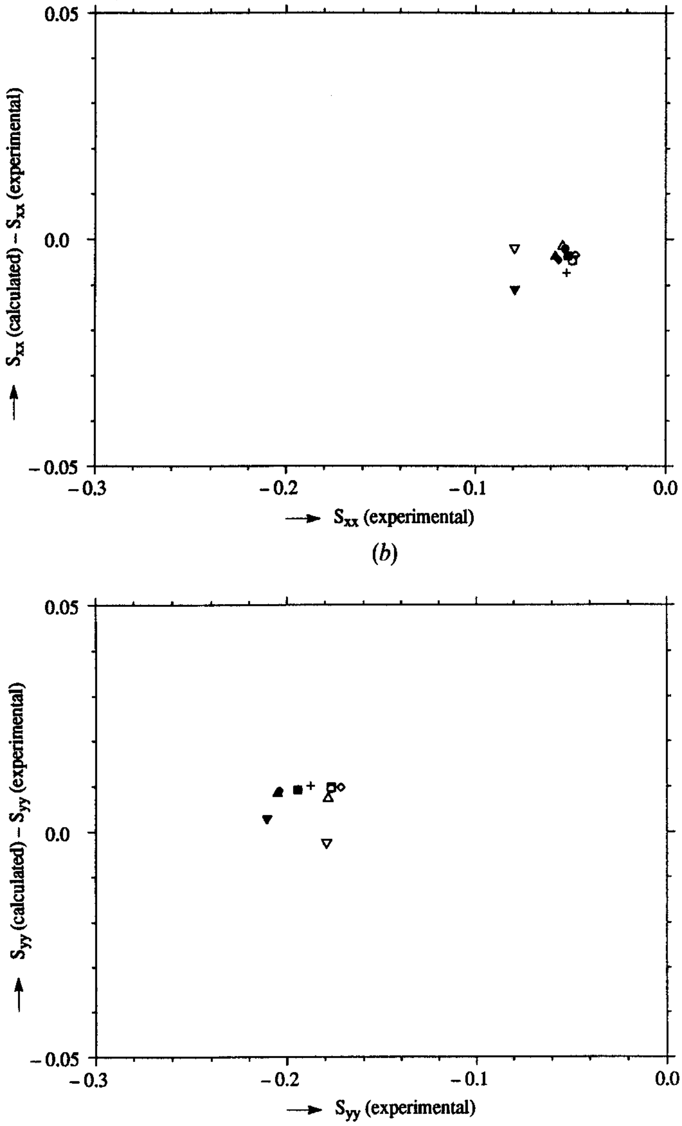
$$U=\tfrac{1}{2}k_1C^2-\tfrac{1}{2}k_2\int C(Z)\,dZ, \qquad (2)$$

where the potential of equation (1) is modified by adding the second term in which the integral goes from the minimum to the maximum value of Z. Z is the projected length of the solute along the director, and $C(Z)$ is the circumference of the solute at position Z.

As discussed above, a reasonable way of comparing results in different sample tubes is to multiply the k parameters by the scaling factor needed to give an exact fit to 1,3,5-trichlorobenzene in that tube using a $P_2(\cos\vartheta)$ potential. The results of using such a procedure in simultaneous fits of equation (2) to all samples of a given zero-efg mixture are reported in figure 4. The newer model fits smaller order parameters such as S_{xx} and S_{yy} better than does the single parameter one. For both liquid crystal mixtures the fit is excellent for all order parameters, including S_{xx} and S_{yy}. The values obtained for the 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture at 316 K (using sample 2 as a reference) are $k_1=2\cdot75\pm0\cdot13\times10^{-3}\,\mathrm{N\,m^{-1}}$ and $k_2=20\cdot8\pm1\cdot7\times10^{-3}\,\mathrm{N\,m^{-1}}$; for the 56·6 wt% 1132/43·5 wt% EBBA-d_2 mixture at 322 K (using sample 1 as a reference) they are $k_1=2\cdot54\pm0\cdot14\times10^{-3}\,\mathrm{N\,m^{-1}}$ and $k_2=30\cdot4\pm2\cdot0\times10^{-3}\,\mathrm{N\,m^{-1}}$. These numbers are in fair agreement with the previous results obtained for a fit to 46 solutes dissolved in



(*a*)



(*b*)

(*c*)

Figure 4. The difference between the calculated and experimental values versus the experimental values of order parameters. The calculated results have been obtained using equation (2) and the best fit numbers $k_1 = 2{\cdot}75 \times 10^{-3}\,\mathrm{Nm}^{-1}$ and $k_2 = 20{\cdot}8 \times 10^{-3}\,\mathrm{Nm}^{-1}$ (sample 2) for the 30·0 wt% EBBA-d_2/70·0 wt% 5CB-α,β-d_4 mixture at 316 K and $k_1 = 2{\cdot}54 \times 10^{-3}\,\mathrm{Nm}^{-1}$ and $k_2 = 30{\cdot}4 \times 10^{-3}\,\mathrm{Nm}^{-1}$ (sample 1) for the 56·5 wt% 1132/EBBA-d_2 mixture at 322 K. Molecular deuterium has not been included in the fits. The symbols have the same meaning as in figure 3. (*a*) Fits to S_{zz}. (*b*) Fits to S_{xx}. (*c*) Fits to S_{yy}.

the 55 wt% 1132/45 wt% EBBA-d_2 mixture at 301·4 K ($k_1 = 2{\cdot}04 \pm 0{\cdot}16 \times 10^{-3}\,\mathrm{Nm}^{-1}$, $k_2 = 48 \pm 2 \times 10^{-3}\,\mathrm{Nm}^{-1}$) [24]. The difference in the ratio k_1/k_2 for the three different zero-efg solvents seems to be significant. A study of the temperature dependence of the orientation potential in these zero-efg mixtures is currently under way [28].

4. Conclusion

In summary, the mean field approximation provides a proper framework for the description of the orientation of a variety of molecules greatly differing in size and flexibility, dissolved in a nematic environment. When studied in zero-efg mixtures, these solutes, as well as the solvent molecules themselves, appear to experience the same single orienting mechanism in different mixtures. In a zero-efg solvent, the order parameters S_{zz} of solutes, or the quadrupolar line splittings associated with solvent deuteron sites can be predicted with about 10 per cent accuracy by a simple scaling procedure. All that is required is the measurement in one zero-efg solvent of a reference compound, together with the compound under investigation, and in the second zero-efg solvent the measurement of the reference compound alone. In addition, the order parameters can be predicted with a mean field model based on short range repulsive interactions, which depend on the size and shape anisotropy of the solute. The calculated values agree well with the experimental results, which strongly indicates that precisely these short range interactions are responsible for solute ordering in zero-efg nematic solvents.

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