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Orientational order of biaxial solutes in nematic phases Size and shape effects

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Experimental order parameters for a series of solutes with C_{2v} and D_{2h} symmetry dissolved in the nematic liquid crystal comprised of 55 wt % 1132 (Merck ZLI 1132) and 45 wt % EBBA- d_2 (N-(4-ethoxybenzylidene)-2,6-dideutero-4-n-butylaniline) are obtained from N.M.R. measurements. In this mixture the average gradient in the electric field experienced by $^2\text{H}_2$ is zero. The order parameters are calculated using a model based on short range repulsive interactions, which depend on the dimensions of the solute. The calculated values are in excellent agreement with the experimental results which suggests that these short range interactions are responsible for solute ordering in the 55 wt % 1132/EBBA- d_2 system. It is also shown that in the two component liquid crystal solvents, 1132 and EBBA- d_2 , the interaction between the molecular quadrupole moment of the solute and the mean electric field gradient due to the liquid crystal plays an important role in determining the solute ordering.

1. Introduction

Knowledge of the intermolecular forces responsible for orientational order in liquid-crystalline systems is essential for a proper understanding of these systems. Unfortunately, most of the molecules that form liquid-crystalline phases exist in many different conformations, and many parameters are necessary to describe the average molecular orientation [1]. For this reason, the study of small rigid solutes has been used to obtain information about the mechanisms which lead to orientation in partially ordered fluids. Despite the large number of solutes and liquid crystal systems which have been studied [2-5], the exact nature of the interactions involved is still not completely understood. However, recent studies on molecular hydrogen [6-9] have shown that the deuterons in D_2 and HD experience an external electric field gradient due to the liquid crystal, and that an important mechanism for the orientation of molecular hydrogen and other small solutes involves the interaction between this electric field gradient and the molecular quadrupole moment of the solute [6-8, 10].

It has also been shown [7] that in a 55 wt % 1132/EBBA mixture at 301.4 K the deuterons of D_2 experience no external electric field gradient. If it is assumed that all solutes experience this same zero electric field gradient then the interaction between the molecular quadrupole moment and the mean electric field gradient need not be considered as an orientational mechanism in this mixture. In a recent publication [10] experimental order parameters were measured for a series of small molecules with C_{3v} or higher symmetry dissolved in 55 wt % 1132/EBBA. A model was proposed for the short range repulsive interactions between the solute molecules and the liquid crystal

solvent since these interactions are expected to play a role in the ordering of the solutes. In the model the interaction potential depends on the size and shape of the solute and a force constant describing the liquid crystal environment which is assumed to be the same for all solutes. Using this model and treating the force constant as an adjustable parameter, it was shown that the experimental solute order parameters in the 55 wt % 1132/EBBA mixture could be predicted quite accurately.

The order parameters were also calculated by considering the interaction between the molecular polarizability of the solutes and the anisotropy in the mean square electric field of the liquid crystal. Good agreement between calculated and experimental values was obtained. This is not surprising because the polarizability is to a good approximation a function of molecular size and shape. In contrast the molecular quadrupole moment, which is not a bond additive property, does not correlate well with the size and shape. This suggests that if the contribution to the solute ordering from the electric field gradient–molecular quadrupole moment interaction is removed, as is the case in 55 wt % 1132/EBBA- d_2 , then any molecular property that is related to the size and shape of a solute can be used to predict its order parameters. Consequently, there is a problem distinguishing between mechanisms that depend on solute size and shape. However, for large solutes short range interactions must play an important role.

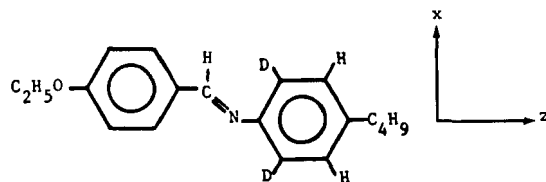


Figure 1. Structure and molecule fixed axes; EBBA- d_2 .

The main objective of the work presented here [11] is to further test the short range interaction model for the interpretation of the orientational order of solutes. For this purpose we have studied a series of molecules with C_{2v} and D_{2h} symmetry dissolved in 55 wt % 1132/EBBA- d_2 . The EBBA- d_2 (cf. figure 1) is deuterated on the aniline ring at the two positions ortho to the nitrogen and we have used the duetron spectrum to monitor the state of the liquid crystal. Experimental order parameters for the solutes of C_{3v} or higher symmetry studied in [10] have also been measured in the deuterated liquid crystal mixture. Solutes of C_{2v} and D_{2h} symmetries require two parameters to specify the average second rank tensorial orientation as opposed to solutes with C_{3v} or higher symmetry where only one parameter is necessary. Because the two independent order parameters for solutes with C_{2v} and D_{2h} symmetries must describe orientation in exactly the same environment, such solutes present a more rigorous test of the model. The two independent order parameters combined with the liquid crystal deuterium quadrupolar splittings also allow us to evaluate the validity of our assumption that all solutes experience the same average environment.

2. Experimental

The liquid crystals used were EBBA- d_2 : N-(4-ethoxybenzylidene)-2,6-dideutero-4-*n*-butylaniline; 1132: Merck ZLI 1132 (see [4] for chemical composition) and a 55 wt % 1132/EBBA- d_2 mixture. The solutes listed in table 1 were purchased from a variety of chemical suppliers. These compounds and the 1132 were used without

further purification. The EBBA- d_2 (figure 1) was synthesized by first deuterating *p-n*-butylaniline at the two positions ortho to the amine group by refluxing the hydrochloride salt in D_2O for several hours [12]. The deuterated aniline was extracted from the D_2O with ether, purified by distillation and then used to synthesize EBBA- d_2 according to the procedure in [13].

Samples for N.M.R. experiments were prepared by placing the liquid crystal into 5 mm o.d. N.M.R. tubes. The liquid crystal was then thoroughly degassed by the freeze-pump-thaw method. All samples were made by dissolving the minimum amount of solute (~ 1 mole per cent) in the liquid crystal. This concentration approximates infinite dilution where there is little disruption of the ordering of the liquid crystal molecules. The tubes were then either capped or flame sealed and thoroughly mixed in the isotropic phase using a vortex stirrer. All samples were stored in the dark to prevent degradation of the EBBA- d_2 .

Proton and deuteron N.M.R. spectra were obtained using Fourier transform techniques with a Bruker WH-400 N.M.R. spectrometer operating at 400.1 MHz for protons and 61.4 MHz for deuterons. The deuteron signal of the deuterated EBBA- d_2 was observed through the lock channel without removing the sample from the magnet, thus ensuring that both the proton and deuteron spectra were collected at exactly the same temperature. The temperature was controlled at 301.4 ± 0.3 K by means of a variable temperature gas flow unit and calibrated using the proton chemical shift differences from a sample of ethylene glycol. All samples were heated to the isotropic phase and vortexed before being placed into the probe and were usually left to equilibrate for half an hour before N.M.R. spectral acquisition.

3. Results and discussion

The elements of the order parameter tensor are defined as

$$S_{\alpha\beta} = \langle 3 \cos \theta_\alpha \cos \theta_\beta - \delta_{\alpha\beta} \rangle / 2, \quad (1)$$

where θ_α is the angle between the α molecular fixed axis and the laboratory fixed Z axis. The order parameters of a solute may be obtained from the experimental dipolar couplings using the relation

$$D_{ab} = -(h\gamma_a\gamma_b/4\pi^2) \langle 3 \cos^2 \theta_{abZ} - 1 \rangle / r_{ab}^3, \quad (2)$$

where θ_{abZ} is the angle between the laboratory Z axis and the vector between the two nuclei a and b . We have assumed a rigid structure so that the internuclear distance r_{ab} may be factored from the average, and the remaining terms are related to the elements of the order parameter tensor. Non-trivial spectra were analysed with the computer program LEQUOR [14] to obtain the dipolar couplings and chemical shift differences. Indirect spin-spin couplings were taken from the literature. The solutes studied are listed in table 1 along with their experimental order parameters in 55 wt % 1132/EBBA- d_2 which have been calculated from the measured dipolar couplings using the computer program SHAPE [15] and a geometry from one of electron diffraction, microwave spectroscopy or N.M.R. using liquid crystal solvents (references for the J couplings and geometries are given in table 2). The definitions of the molecule fixed axes for the solutes are given in the footnotes to table 1.

The structure and the molecule fixed axis system of EBBA- d_2 are shown in figure 1. The deuteron spectrum of the EBBA- d_2 consists of four lines which arise from the quadrupolar coupling of the deuterons and the dipolar coupling between each deuteron and the adjacent ring protons [16]. The dipolar couplings between the

Table 1. Experimental and calculated order parameters (55 wt % 1132/EBBA- d_2 at 301.4 K).

Solute		$S(\text{exp})(a)$	$S(\text{calc})$			
			Fit to all results		Separate fit to each solute	
			S.R. (b)	Pol. (c)	S.R. (d)	Pol. (e)
Acetone	S_{xx}	0.0711 (2)	0.0754	0.0366	0.0729	0.0408
	S_{yy}	-0.0720 (1)	-0.0718	-0.0669	-0.0696	-0.0736
	S_{zz}	0.0009 (1)	-0.0036	0.0303	-0.0033	0.0340
Furan	S_{xx}	0.0907 (1)	0.0636	0.0469	0.0974	0.0841
	S_{yy}	-0.1365 (1)	-0.0894	-0.0770	-0.1336	-0.1383
	S_{zz}	0.0458 (2)	0.0258	0.0302	0.0362	0.0520
Thiophene	S_{xx}	0.0586 (1)	0.0547	0.0057	0.0810	0.0061
	S_{yy}	-0.1490 (4)	-0.0998	-0.0997	-0.1474	-0.1235
	S_{zz}	0.0905 (5)	0.0451	0.0940	0.0664	0.1166
Pyridine	S_{xx}	0.1093 (2)	0.0727	0.1129	0.1016	0.1067
	S_{yy}	-0.1545 (4)	-0.1138	-0.1632	-0.1566	-0.1555
	S_{zz}	0.0452 (6)	0.0412	0.0502	0.0550	0.0488
Fluorobenzene	S_{xx}	0.0507 (1)	0.0242	0.0645	0.0274	0.0760
	S_{yy}	-0.1906 (1)	-0.1384	-0.1640	-0.1804	-0.1947
	S_{zz}	0.1399 (2)	0.1142	0.0995	0.1530	0.1188
Chlorobenzene	S_{xx}	0.0070 (1)	-0.0109	0.0622	-0.0201	0.0635
	S_{yy}	-0.2037 (2)	-0.1501	-0.2196	-0.1856	-0.2229
	S_{zz}	0.1967 (3)	0.1610	0.1575	0.2057	0.1594
TTF (f)	S_{xx}	-0.081 (3)	-0.1513	-0.1299	-0.1129	-0.0499
	S_{yy}	-0.2514 (17)	-0.2570	-0.3520	-0.2189	-0.2828
	S_{zz}	0.3320 (17)	0.4083	0.4819	0.3318	0.3327
2,6-Difluoropyridine	S_{xx}	0.1529 (2)	0.1231		0.1577	
	S_{yy}	-0.1908 (2)	-0.1503		-0.1868	
	S_{zz}	0.0379 (4)	0.0272		0.0291	
Iodobenzene	S_{xx}	-0.0243 (5)	-0.0594		-0.0642	
	S_{yy}	-0.2146 (6)	-0.1735		-0.1811	
	S_{zz}	0.2389 (11)	0.2329		0.2453	
1,2-Dichlorobenzene	S_{xx}	0.0647 (1)	0.0254		0.0245	
	S_{yy}	-0.2248 (3)	-0.1754		-0.2040	
	S_{zz}	0.1601 (2)	0.1500		0.1795	
1,2-Dicyanobenzene	S_{xx}	0.063 (11)	0.0272		0.0254	
	S_{yy}	-0.247 (13)	-0.2100		-0.2255	
	S_{zz}	0.184 (24)	0.1828		0.2001	
1,3-Dichlorobenzene	S_{xx}	0.1958 (4)	0.2029		0.2092	
	S_{yy}	-0.2243 (3)	-0.1870		-0.1915	
	S_{zz}	0.0285 (7)	-0.0159		-0.0177	
1,3-Dinitrobenzene	S_{xx}	0.1961 (2)	0.2211		0.2090	
	S_{yy}	-0.2287 (2)	-0.2096		-0.1999	
	S_{zz}	0.0326 (4)	-0.0116		-0.0091	
1,4-Dichlorobenzene (g)	S_{xx}	-0.0721 (1)	-0.1046		-0.1123	
	S_{yy}	-0.2467 (4)	-0.2003		-0.2105	
	S_{zz}	0.3188 (5)	0.3049		0.3228	

Table 1 (continued).

Solute		$S(\text{exp})(a)$	$S(\text{calc})$			
			Fit to all results		Separate fit to each solute	
			S.R. (b)	Pol. (c)	S.R. (d)	Pol. (e)
1,4-Dibromobenzene (g)	S_{xx}	-0.1021 (1)	-0.1420		-0.1420	
	S_{yy}	-0.2546 (1)	-0.2173		-0.2170	
	S_{zz}	0.3567 (2)	0.3594		0.3590	
Benzene	S_{zz}	-0.1756	-0.1220	-0.1608		
1,3,5-Tri-fluorobenzene	S_{zz}	-0.2014	-0.1687	-0.1654		
1,3,5-Tri-chlorobenzene	S_{zz}	-0.2380	-0.2121	-0.2141		
1,3,5-Tri-bromobenzene	S_{zz}	-0.1886	-0.2268	-0.2434		
Hexafluorobenzene	S_{zz}	-0.2280	-0.1990	-0.1804		
2,4-Hexadiyne	S_{zz}	0.3664	0.4439	0.1846		
2-Butyne	S_{zz}	0.1943	0.2081	0.1670		
Allene	S_{zz}	0.1302	0.1197	0.1808		
Bromomethane	S_{zz}	0.0676	0.0664	0.0734		
Iodomethane	S_{zz}	0.0650	0.0786	0.0942		
Hydrogen	S_{zz}	-0.0008	0.0152	0.0109		
Acetylene	S_{zz}	0.1123	0.0825	0.0663		
Propyne	S_{zz}	0.1559	0.1314	0.1177		

(a) Order parameters obtained from the experimental dipolar coupling constants. The bracketed numbers are errors. The axis system is chosen such that z is the symmetry axis, y is perpendicular to the plane of the molecule and x is perpendicular to y and z .

(b) Order parameters calculated using a model for the short range repulsive interactions. The force constant governing the interaction has been obtained by a least squares fit of S_{xx} , S_{yy} and S_{zz} for all solutes to the experimental values.

(c) Order parameters calculated using the interaction between the molecular polarizability of the solute and the mean electric field due to the liquid crystal solvent. The anisotropy in the mean square electric field has been obtained by a least squares fit of S_{xx} , S_{yy} and S_{zz} for all solutes to the experimental values.

(d) Order parameters calculated in the same manner as (b) except that the force constant has been fitted for each solute independently.

(e) Order parameters calculated in the same manner as (c) except that the anisotropy in the mean electric field squared has been fitted independently for each solute.

(f) For TTF z is along the C-C double bond joining the two rings, x is parallel to the vector joining the sulphur atoms within one ring and y is perpendicular to x and z . TTF = tetra-thiofulvalene.

(g) For 1,4-dichlorobenzene and 1,4-dibromobenzene the z axis is chosen such that it passes through both halogen atoms. The y axis is perpendicular to the plane of the molecule and the x axis is perpendicular to y and z .

deuterons and the other spins in the molecule are not resolved and contribute to the line width. In the 55 wt % 1132/EBBA- d_2 mixture containing no solute at 301.4 K we obtain for the quadrupolar splitting $\Delta\nu_Q = 17.94$ kHz and for the dipolar coupling $D_{HD} = 774$ Hz. The contribution of J_{HD} (~ 1 Hz) to the dipolar splitting has been ignored. We define the asymmetry parameter, η_q , for the electric field gradient tensor along the CD bond as

$$\eta_q = (q_{aa} - q_{cc})/q_{bb}, \quad (3)$$

where the a axis is in the plane of the aromatic ring and perpendicular to the CD bond, b is along the CD bond and c is perpendicular to both a and b . We have assumed a value of 0.04 for η_q and 185 kHz for the quadrupolar coupling constant, e^2qQ/h . These values are consistent with those given in [3] for deuterons in similar molecules. If we also assume a value of 2.479×10^{-8} cm for the ortho HD distance [17] and 120.0° for the CCD angle the following order parameters for the aniline ring are obtained: $S_{xx} = -0.312$, $S_{yy} = -0.322$ and $S_{zz} = 0.634$. Values of S_{zz} and $S_{xx} - S_{yy}$ for the EBBA aniline ring for samples containing various solutes at a variety of temperatures are given in tables 3, 4 and 6. In all cases $S_{xx} - S_{yy}$ is approximately zero so that the rigid aniline ring has almost axially symmetric ordering. The values of $S_{xx} - S_{yy}$ shown in table 6 are in good agreement with the value of -0.013 obtained by Diehl and Tracey for the same liquid crystal [16]. It is also interesting to note that although the values of $S_{xx} - S_{yy}$ are small they are consistently negative for the pure EBBA- d_2 (cf. table 6) and consistently positive for the 55 wt % 1132/EBBA- d_2 mixture (cf. tables 3 and 4). These order parameters may be used as an internal standard in order to compare the experimental conditions between samples. However, because of the relatively large experimental errors associated with D_{HD} , we have chosen to use the quadrupolar splitting, $\Delta\nu_Q$, for such comparisons.

The order parameters of a solute in an anisotropic environment may be calculated using the following expression:

$$S_{\alpha\beta} = \frac{\int (3 \cos \theta_\alpha \cos \theta_\beta - \delta_{\alpha\beta}) \exp(-U(\Omega)/k_B T) d\Omega}{2 \int \exp(-U(\Omega)/k_B T) d\Omega}, \quad (4)$$

where $U(\Omega)$ is the mean potential describing the interaction between the solute and its environment. In the limit of low solute concentration, this potential is determined only by the solute-solvent interactions. In 55 wt % 1132/EBBA- d_2 we assume that the potential is dominated by the short range repulsive interactions and have developed a simple model for these interactions in nematic liquid crystal systems. A complete description is given in [10]. In the model the liquid crystal is treated as an elastic continuum and the solute is modelled as a collection of van der Waals spheres. The solute displaces the liquid crystal, which in turn exerts a restoring force on the solute. This is given by

$$F = -kc, \quad (5)$$

where k is the force constant and c describes the displacement of the liquid crystal. The distance c is a function of solute orientation and is calculated as the perimeter of the solute molecule projected on to a plane perpendicular to the director. The elastic energy of the continuum,

$$U_{SR} = kc^2/2, \quad (6)$$

is also a function of the orientation of the solute.

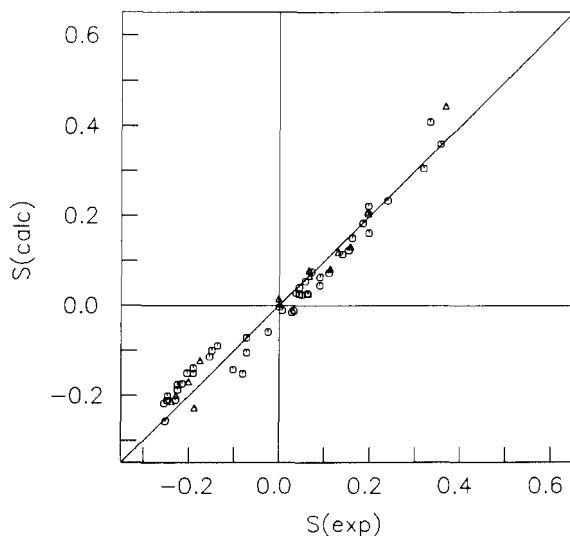


Figure 2. Short range interaction model. Experimental versus calculated order parameters for solutes in 55 wt % 1132/EBBA- d_2 . The calculated order parameters, shown in table 1, have been obtained using a model based on the short range interactions which depend on the size and shape of the solute [10]. For solutes with C_{2v} or D_{2h} symmetry the values of S_{xx} , S_{yy} and S_{zz} are plotted (circles). For solutes with C_{3v} or higher symmetry only S_{zz} is plotted (triangles). The definitions of the axes, x , y and z , are given as footnotes to table 1. The force constant describing the short range interactions has been obtained from a least squares fit to the solid line of slope 1. $T = 301.4$ K, $k = 5.55$ dyn cm $^{-1}$, $F_{zz} = 0.0$ e.s.u., correlation coefficient = 0.985.

Order parameters for the solutes given in table 1 have been calculated using expression (4) and the model for the short range interactions to obtain $U(\Omega)$. The van der Waals radii have been taken from [18]. The one adjustable parameter of the model, the force constant k , is obtained by a least squares fit of the calculated order parameters S_{xx} , S_{yy} and S_{zz} to the experimental values for all the solutes dissolved in 55 wt % 1132/EBBA- d_2 . The value of k is found to be 5.55 dyn cm $^{-1}$. The order parameters calculated from this fit are listed in table 1 and are plotted against the experimental results in figure 2. As can be seen the fit is very good, and the model is very successful in explaining the experimental results for all the solutes.

The low symmetry of the solutes studied here may also help to distinguish between various mechanisms which correlate roughly with the size and shape of the solute. With this in mind we have calculated order parameters using as the orienting mechanism the interaction between the polarizability of the solute and the mean electric field due to the liquid crystal. Unfortunately the low symmetry of the solutes also makes determination of their polarizability tensors more difficult because one needs to measure three properties of the solute which depend on the three independent elements of the polarizability tensor, α_0 , α_{zz} and $\alpha_{xx} - \alpha_{yy}$ [19]. In some recent publications [19–21] the authors have combined measurements of the Kerr and Cotton–Mouton effects with light scattering measurements to obtain the elements of the polarizability tensors of six of the solutes used here. In table 2 we present polarizabilities for these solutes extrapolated to zero frequency along with calculated values for TTF and static polarizabilities from the literature for the solutes of C_{3v} symmetry. The interaction between the polarizability of the solute and an electric field

Table 2. Solute polarizabilities and references.

Solute	Polarizability $\times 10^{24}/\text{cm}^3$			Reference	<i>J</i> coupling reference (a)	Structure reference (a)
	α_{xx}	α_{yy}	α_{zz}			
Acetone	7.15	5.16	7.05	[20]	[27]	[28]
Furan	7.75	5.36	7.48	[21] (b)	[29]	[30]
Thiophene	9.51	7.27	10.93	[21] (b)	[29]	[31]
Pyridine	11.94	6.21	11.02	[20]	[32]	[33]
Fluorobenzene	11.88	6.32	11.37	[19] (c)	[34]	[35]
Chlorobenzene	14.52	7.42	15.84	[20]	[36]	[37] (d)
TTF	17.62	4.96	25.74	[38]	[39]	[39]
Benzene	11.73	11.73	6.54	[40]		
1,3,5-Trifluorobenzene	11.56	11.56	6.19	[41] (c)		
1,3,5-Trichlorobenzene	18.88	18.88	11.36	[42] (b)		
1,3,5-Tribromobenzene	22.39	22.39	13.34	[42] (b)		
Hexafluorobenzene	12.18	12.18	6.19	[41, 43] (c)		
Hydrogen	0.71	0.71	1.01	[44, 45]		
Iodomethane	6.47	6.47	8.92	[41] (c)		
Bromomethane	4.81	4.81	6.74	[41] (c)		
Propyne	4.54	4.54	7.57	[40]		
Acetylene	2.78	2.78	4.53	[40]		
2-Butyne	5.29	5.29	9.51	[40]		
2,4-Hexadiyne	7.78	7.78	12.42	[46, 40] (e)		
Allene	4.47	4.47	9.02	[41] (c)		
2,6-Difluoropyridine					[47]	[48] (d)
Iodobenzene					[36]	[17] (f)
1,2-Dichlorobenzene					[49]	[50] (d)
1,2-Dicyanobenzene					[51]	[51] (d)
1,3-Dichlorobenzene					[52]	[50] (d)
1,3-Dinitrobenzene					[53]	[54, 55] (d)
1,4-Dichlorobenzene					[56]	[56]
1,4-Dibromobenzene					[57]	[57]

(a) *J* coupling and structure references for solutes with C_{3v} or higher symmetry are given in [10].

(b) Extrapolated to zero frequency using frequency dependence of benzene given in [40].

(c) Extrapolated to zero frequency.

(d) The structure has been calculated from data in the given reference(s).

(e) The polarizability has been estimated using data from the given references.

(f) Regular hexagon assumed.

due to the liquid crystal is given by

$$U(\Omega) = -(1/3)(\langle E_{\parallel}^2 \rangle - \langle E_{\perp}^2 \rangle) \sum_{\beta, \gamma=x, y, z} \alpha_{\beta\gamma} (3 \cos \theta_{\beta Z} \cos \theta_{\gamma Z} - \delta_{\beta\gamma}) / 2, \quad (7)$$

where β, γ are molecule fixed axes and $\Omega = \Omega(\theta_{\beta Z}, \theta_{\gamma Z})$. We have used expressions (4) and (7) and the polarizabilities in table 2 to calculate order parameters for the solutes. The value of the anisotropy in the mean electric field squared has been adjusted in a least squares fit of S_{xx} , S_{yy} and S_{zz} to the experimental values. The results of this calculation are listed in table 1 and plotted in figure 3. The value of the square root of the anisotropy in the mean square electric field, $(\langle E_{\parallel}^2 \rangle - \langle E_{\perp}^2 \rangle)^{1/2}$, obtained from the fit is $4.52 \times 10^7 \text{ V cm}^{-1}$. As can be seen, the agreement between the experimental and calculated values is quite good, although a somewhat better fit is obtained with the short range interaction model (cf. figure 2). As with the solutes of C_{3v} or higher symmetry [10] we are unable to distinguish clearly between the polarizability

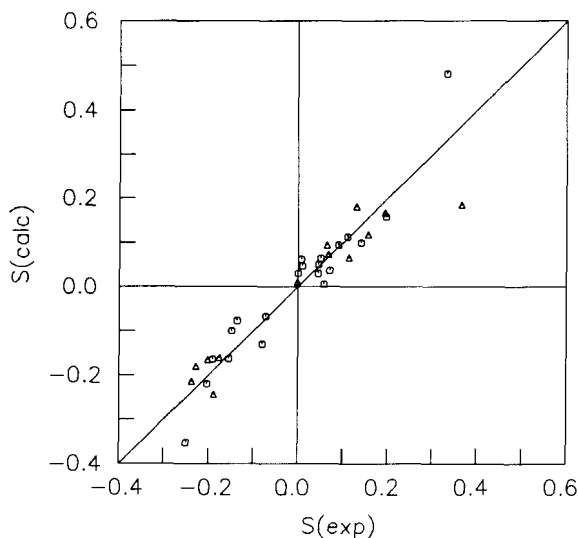


Figure 3. Polarizability–electric field interaction. Experimental versus calculated order parameters for solutes in 55 wt % 1132/EBBA- d_2 . The calculated order parameters, shown in table 1, have been obtained using the interaction between the polarizability tensor of the solute (given in table 2) and the mean electric field squared due to the liquid crystal. For solutes with C_{2v} or D_{2h} symmetry the values of S_{xx} , S_{yy} and S_{zz} are plotted (circles). For solutes with C_{3v} or higher symmetry only S_{zz} is plotted (triangles). The anisotropy in the mean electric field squared has been obtained from a least squares fit to the line of slope 1. $T = 301.4$ K, $(\langle E_{\parallel}^2 \rangle - \langle E_{\perp}^2 \rangle)^{1/2} = 4.52 \times 10^7$ V cm $^{-1}$, $F_{zz} = 0.0$ e.s.u., correlation coefficient = 0.941.

mechanism and the short range interaction mechanism because both are functions of the size and shape of the solutes.

In the above comparisons between experiment and theory we have assumed that all solutes experience the same mean field. There is no reason to expect that all solutes will be governed by exactly the same mean field, as each may sample a slightly different distribution of local environments. For example, it is well known that various tetrahedral solutes experience different local magnetic susceptibility anisotropies and therefore must lie in different average environments [22]. However, for the solutes with C_{2v} or D_{2h} symmetry any two of the three non-zero order parameters are independent of each other. Since all three order parameters must depend on the environment in the same way, they should be predicted exactly by the model if the form of the potential is correct. Thus we have calculated order parameters for the solute with C_{2v} and D_{2h} symmetry by fitting the force constant for each solute separately. The order parameters obtained from this calculation are presented in table 1 and the force constants are shown in table 3. As can be seen, the agreement between the experimental and calculated order parameters is excellent. This demonstrates very clearly that the scatter in figure 1 is primarily due to our assumption that each solute experiences exactly the same mean field and that the form of our potential is correct.

We have also calculated order parameters using the polarizability–electric field mechanism and fitted the anisotropy in the mean electric field squared for each solute. The order parameters obtained from this calculation are shown in table 1 and the anisotropies in the mean square electric field are shown in table 3. Although the

Table 3. Force constants, electric fields and liquid crystal deuteron splittings (55 wt % 1132/EBBA- d_2 at 301.4 K).

Solute	$k/(\text{dyn cm}^{-1})(a)$	$\langle E_{\parallel}^2 - E_{\perp}^2 \rangle \times 10^{-15}$ ($\text{V}^2 \text{cm}^{-2})(b)$	$\Delta\nu_Q/\text{kHz}(c)$	$D_{\text{HD}}/\text{Hz}(d)$	$S(\text{l.c.})(e)$	
					S_{zz}	$S_{xy} - S_{yz}$
(1) Acetone	5.37	2.26	16.91	738	0.610	0.016
(2) Furan	8.54	3.74	17.93	778	0.643	0.016
(3) Thiophene	8.47	2.54	17.46	750	0.620	0.014
(4) Pyridine	7.90	1.92	17.18	755	0.624	0.018
(5) Fluorobenzene	7.48	2.46	17.65	765	0.633	0.016
(6) Chlorobenzene	7.03	2.05	17.81	733	0.606	0.006
(7) TTF	4.50	1.29	17.82	750	0.620	0.010
(8) 2,6-Difluoropyridine	7.12		16.89	743	0.614	0.017
(9) Iodobenzene	5.83		17.58	733	0.606	0.009
(10) 1,2-Dichlorobenzene	6.64		17.68	750	0.620	0.010
(11) 1,2-Dicyanobenzene	6.09		17.77	765	0.633	0.014
(12) 1,3-Dichlorobenzene	5.72		17.75	750	0.620	0.011
(13) 1,3-Dinitrobenzene	5.24		17.64	773	0.639	0.018
(14) 1,4-Dichlorobenzene	5.87		17.60	753	0.623	0.013

(15)		5.55					
	1,4-Dibromobenzene		17.84	765	0.633	0.014	
	Benzene		17.51	715	0.591	0.005	
	1,3,5-Trifluorobenzene		17.81	743	0.614	0.009	
	1,3,5-Trichlorobenzene		17.76	693	0.573	-0.003	
	1,3,5-Tribromobenzene		17.59	753	0.623	0.013	
	Hexafluorobenzene		16.95	733	0.606	0.015	
	2,4-Hexadiyne		17.76	693	0.573	-0.003	
	2-Butyne		17.59	753	0.622	0.013	
	Allene		17.69	735	0.608	0.008	
	Bromomethane		17.47	730	0.604	0.009	
	Iodomethane		17.70	780	0.645	0.019	
	Acetylene		17.54	752	0.622	0.014	
	Propyne		17.65	705	0.583	0.001	

(a) k is the force constant which governs the short range interactions (see text). The values of k presented have been obtained by a least squares fit of the calculated values of S_{xx} , S_{yy} and S_{zz} for the given solute to the experimental values.

(b) $\langle E_{ij}^2 - E_i^2 \rangle$ is the anisotropy in the mean electric field squared due to the liquid crystal (see text). The values presented have been obtained by a least squares fit of the calculated values of S_{xx} , S_{yy} and S_{zz} of the given solute to the experimental values.

(c) ΔV_Q is the quadrupolar splitting of the deuterons ortho to the nitrogen in the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 mixture (see figure 1). (d) D_{HFD} is the dipolar coupling between the deuterons and the adjacent protons of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 mixture (see figure 1).

(e) $S(\text{l.c.})$ refers to the order parameters of the aniline ring of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 (see figure 1).

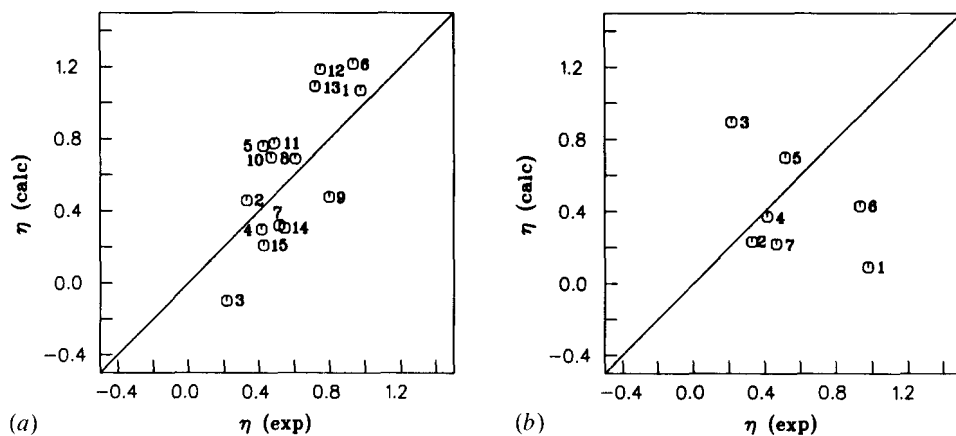


Figure 4. Asymmetry parameters for C_{2v} and D_{2h} solutes. Experimental versus calculated values of the asymmetry parameter: $\eta = (S_{11} - S_{22})/S_{33}$ (see text) for solutes with C_{2v} or D_{2h} symmetry in 55 wt% 1132/EBBA- d_2 . (a) Short range interaction model: The asymmetry parameters have been calculated using a model for the short range interactions. The force constant describing the interaction has been adjusted separately for each solute (see tables 1 and 3). $T = 301.4$ K, $F_{zz} = 0.0$ e.s.u., correlation coefficient = 0.7620. The solid line of slope 1 has been drawn to aid the eye. The labelling of the points refers to table 3. (b) Polarizability model: The asymmetry parameters have been calculated using the interaction between the polarizability tensor of the solute and the mean electric field squared due to the liquid crystal. The mean electric field has been adjusted separately for each solute (see tables 1 and 3). $T = 301.4$ K, $F_{zz} = 0.0$ e.s.u., correlation coefficient = -0.4795. The solid line of slope 1 has been drawn to aid the eye. The labelling of the points refers to table 3.

agreement with the experimental values is good, in most cases it is not as good as that obtained using the short range interaction model.

In order to see more clearly how well the relationships between the order parameters for each solute are predicted we define an asymmetry parameter

$$\eta = (S_{11} - S_{22})/S_{33} \quad (8)$$

such that for the experimental order parameters $|S_{33}| > |S_{22}| > |S_{11}|$. This definition ensures that η calculated from the experimental order parameters lies between zero and one. Figure 4 shows the comparison between the experimental values of η and those calculated from the separate fits to each solute in table 1 for both the short range and polarizability interaction models. As can be seen from figure 4(a), although there are some deviations, the correlation is reasonably good for the short range interaction model. By comparison the asymmetry parameters calculated using the polarizability-electric field mechanism (cf. figure 4(b)) do not agree as well with experiment. While this may be a result of inaccuracies in the polarizabilities we have used, it is unlikely that this could account for all of the discrepancy. Because the values of k and $(\langle E_{\parallel}^2 \rangle - \langle E_{\perp}^2 \rangle)$ have been adjusted separately for each solute, the scatter in figures 4(a) and (b) arises entirely because of inaccuracies in the form of the potential. These results suggest that the polarizability-electric field mechanism cannot account for all of the orientation of the solutes, although it cannot be ruled out entirely. This is also consistent with the results of a recent study by Emsley *et al.* [23] on anthracene dissolved in several liquid crystals. They found that dispersion forces, which depend

on the solute polarizability, could not account for the solute order parameters. However, it should be pointed out that they did not take the molecular quadrupole moment–electric field gradient mechanism into account.

In the above discussion we have shown that the small scatter in the points in figure 1 arises primarily because our assumption that each solute experiences exactly the same average environment is not strictly true. In a recent publication [24] on solutes with C_{3v} or higher symmetry dissolved in 5CB- $\alpha, \beta d_4$ it was shown that the effects of fairly large variations in temperature and solute concentration could be accounted for by scaling F_{zz} and k from their dependences on the quadrupolar splittings of the liquid crystal deuterons. Thus, if the small variation in k between samples arises because of variations in the experimental conditions we can use the quadrupolar splittings of the deuterons in the liquid crystal to correct k . In table 4 we present liquid crystal splittings and experimental order parameters for furan and thiophene as a function of temperature in the 55 wt % 1132/EBBA- d_2 mixture. We have obtained the value of k for each solute at each temperature by fitting the calculated order parameters to the experimental values and in figure 5 we have plotted k versus $\Delta\nu_Q$ for the two solutes. It is clear from the plot that the dependence of k on $\Delta\nu_Q$ is roughly linear over the range that we have measured, and the slope is to a good approximation the same for both solutes. It is also apparent that the small variation in the liquid crystal splittings shown in table 3 cannot account for the variation in k from one sample to another. These results suggest that the solutes are governed by slightly different force constants because they sample different distributions of local environments and not because of variations in the experimental conditions.

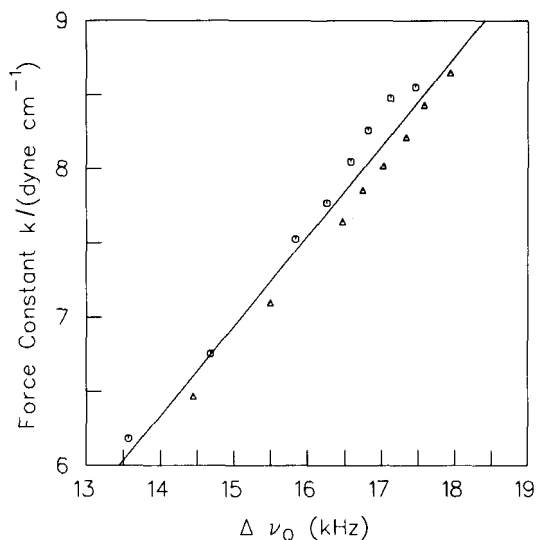


Figure 5. Force constant in 55 wt % 1132/EBBA- d_2 . The force constant describing the short range interactions between solvent and solute versus the quadrupolar splitting of the deuterons of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 . The variation in both quantities is obtained by varying the temperature. The value of the force constant is that obtained from a least squares fit of the calculated order parameters to the experimental values for furan (circles) and thiophene (triangles). The slope and the intercept of the best straight line through the points are: $0.6049 \text{ dyn cm}^{-1} \text{ kHz}^{-1}$; $-2.13 \text{ dyn cm}^{-1}$. $F_{zz} = 0.0 \text{ e.s.u.}$; $T = 301.4 \text{ K}$; correlation coefficient = 0.9817.

Table 4. Furan and thiophene in 55 wt % 1132/EBBA- d_2 : experimental solute and liquid crystal order parameters, liquid crystal deuteron quadrupolar splittings and dipolar coupling constants.

Solute	Temperature (K)	S(solute)			$\Delta\nu_Q/\text{kHz}(b)$	$D_{HD}/\text{Hz}(c)$	S(l.c.)(d)	
		S_{xx}	S_{yy}	S_{zz}			$S_{xx} - S_{yy}$	S_{zz}
Furan	304	0.0907 (1)	-0.1365 (1)	0.0457 (2)	17.93	778	0.643	0.016
	306	0.0884 (1)	-0.1335 (2)	0.0452 (3)	17.58	732	0.605	0.008
	308	0.0863 (1)	-0.1311 (4)	0.0448 (5)	17.33	715	0.591	0.007
	310	0.0841 (1)	-0.1285 (2)	0.0443 (3)	17.02	698	0.577	0.006
	312	0.0820 (1)	-0.1258 (1)	0.0437 (2)	16.74	722	0.597	0.014
	314	0.0798 (1)	-0.1227 (1)	0.0430 (2)	16.46	698	0.577	0.011
	320	0.0735 (1)	-0.1152 (4)	0.0418 (5)	15.49	663	0.548	0.012
325	0.0669 (1)	-0.1055 (6)	0.0389 (7)	14.44	628	0.519	0.013	
Thiophene	304	0.0586 (1)	-0.1490 (4)	0.0905 (5)	17.46	750	0.620	0.014
	306	0.0572 (1)	-0.1459 (2)	0.0887 (3)	17.12	715	0.591	0.009
	308	0.0559 (1)	-0.1427 (2)	0.0868 (3)	16.81	732	0.605	0.016
	310	0.0545 (1)	-0.1395 (2)	0.0850 (3)	16.57	715	0.591	0.014
	312	0.0531 (1)	-0.1363 (2)	0.0832 (3)	16.25	698	0.577	0.013
	314	0.0517 (1)	-0.1326 (2)	0.0809 (3)	15.83	663	0.548	0.008
	320	0.0469 (1)	-0.1206 (4)	0.0737 (5)	14.68	610	0.504	0.007
325	0.0423 (4)	-0.1113 (17)	0.0690 (21)	13.57	575	0.475	0.009	

(a) The temperature reported is the dial setting of the temperature control unit. A dial setting of 304 K corresponds to an actual probe temperature of $301.4 \text{ K} \pm 0.3 \text{ K}$.

(b) $\Delta\nu_Q$ is the quadrupolar splitting of the deuterons ortho to the nitrogen in the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 mixtures (see figure 1).

(c) D_{HD} is the dipolar coupling between the deuterons and the adjacent protons of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 mixture (see figure 1).

(d) $S(\text{l.c.})$ is the order parameter tensor of the aniline ring of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 .

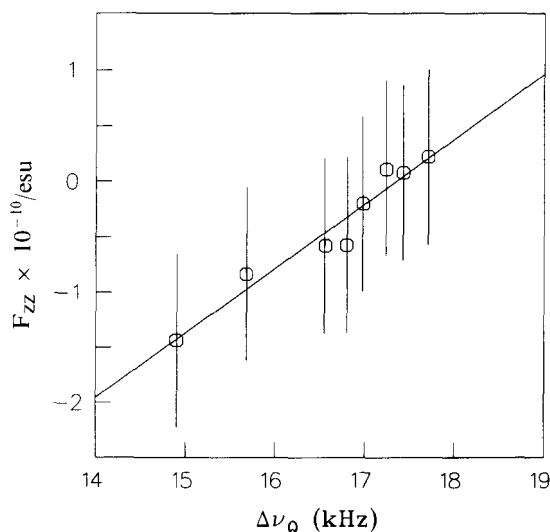


Figure 6. Electric field gradients in 55 wt % 1132/EBBA- d_2 . The measured electric field gradient versus the quadrupolar splitting of the deuterons of the EBBA- d_2 contained in the 55 wt % 1132/EBBA- d_2 . The electric field gradient is calculated [6–8] from the spectrum of D_2 dissolved in 55 wt % 1132/EBBA- d_2 . The variation in both quantities is obtained by varying the temperature. The slope and intercept of the best straight line through the points are 5.84×10^9 e.s.u. kHz $^{-1}$ and -1.01×10^{11} e.s.u.; correlation coefficient = 0.970.

We have also measured the spectrum of D_2 as a function of temperature in the 55 wt % 1132/EBBA- d_2 mixture. From these results we have calculated [6–8] the electric field gradient as a function of the liquid crystal splittings. The results of this calculation are shown in figure 6. It is clear that to a good approximation the electric field gradient also varies linearly with the liquid crystal splitting. It is also interesting to note that the best line through the points does not pass through the origin. Since both the electric field gradient and the liquid crystal splitting must go to zero at the nematic to isotropic phase transition temperature, the plot we have shown cannot be linear over the entire nematic range of the liquid crystal. It is also clear from the figure that over the range of liquid crystal splittings measured for the other samples at 301.4 K (cf. table 3) the electric field gradient experienced by D_2 is very small. Thus, if all solutes experience the same field gradient as D_2 , mechanisms involving this field gradient may be safely ignored for our samples. However, the possibility remains that each solute experiences a somewhat different distribution of local fields and hence a different mean electric field gradient.

The low symmetry of the solutes studied here also allows a more critical investigation of the contribution to the orientational order of the molecular quadrupole moment–electric field gradient mechanism. However, such an investigation is difficult because of the small number of molecular quadrupole moments which have been measured or calculated for molecules with C_{2v} and D_{2h} symmetry. We have chosen to study two of the solutes, furan and thiophene, for which measured values of the molecular quadrupole moments have been published [25] and are shown in table 5. The order parameters of the two solutes have been measured in 1132 and EBBA- d_2 where the electric field gradients are known to be large [6, 7, 10]. We have also measured order parameters in EBBA- d_2 for the solutes of C_{3v} or higher symmetry which were

Table 5. Molecular quadrupole moments.

Solute	Molecular quadrupole moment/ (10^{-26} e.s.u. cm ²) (a)	Reference
(1) Benzene	-7.80 ± 2.2	Average of values from [58] and [59]
(2) 1,3,5-Trifluorobenzene	0.94	[58]
(3) 1,3,5-Trichlorobenzene	-3.24	[60]
(4) 1,3,5-Tribromobenzene	-4.80	[60]
(5) Hexafluorobenzene	9.50	[43]
(6) 2,4-Hexadiyne	2.59 (b) 2.15 (c)	Estimate (this work)
(7) 2-Butyne	2.38 (b) 1.62 (c)	Estimate (this work)
(8) Allene	2.60 (b) 1.56 (c)	Estimate (this work)
	7.35	Upper limit [26]
(9) Bromomethane	4.64 ± 1.1	Average of values from [61, 62]
(10) Iodomethane	5.35	[62]
(11) Hydrogen	0.66	[63]
(12) Acetylene	5.5 ± 2.5	Average of values from [63, 64]
(13) Propyne	4.82	[65]
(14) Furan	Q_{xx} 5.9 Q_{yy} -6.1 Q_{zz} 0.2	[25]
(15) Thiophene	Q_{xx} 6.6 Q_{yy} -8.3 Q_{zz} 1.7	[25]

(a) For benzene, bromomethane and acetylene the value presented is an average of the largest and smallest values reported in the literature.

(b) Estimated from solute order parameter in 1132.

(c) Estimated from solute order parameter in EBBA- d_2 .

studied in [10]. These results are shown in table 6 along with the experimental order parameters from [10] for the solutes with C_{3v} or higher symmetry dissolved in 1132. In order to calculate order parameters for these solutes in 1132 and EBBA- d_2 we require both the force constant, k , and the electric field gradient, F_{zz} , for the two solvents. We have assumed as previously [10] that all solutes experience the same electric field gradient as D₂ and that the value of k is the same as that found for the 55 wt % 1132/EBBA- d_2 mixture. If these assumptions are correct and if the exponential in expression (4) can be expanded as a Taylor series and truncated after the linear term then the difference between the order parameters in either 1132 or EBBA- d_2 and the 55 wt % 1132/EBBA- d_2 mixture represents the contribution to the orientation from the molecular quadrupole moment–electric field gradient mechanism. In figures 7 and 8 we have plotted calculated versus experimental values for $S(\text{EBBA-}d_2) - S(55 \text{ wt } \% 1132)$ and $S(1132) - S(55 \text{ wt } \% 1132)$. Considering that there are no adjustable parameters and that differences in order parameters are being plotted, the agreement between the experimental and calculated values is really quite good. As can be seen, all three components of the order parameter tensor are predicted well for furan (labelled with circles) and thiophene (labelled with triangles) in both liquid crystals and all of the points (with the exception of the ones corresponding to 1,3,5-trifluorobenzene where Q_{mol} is reported to be small and positive (cf. table 5)) lie in the correct quadrant. The considerable scatter in the points is

Table 6. Solutes in 1132 and EBBA-d₂ at 301.4 K: solute and liquid crystal order parameters, liquid crystal deuteron quadrupolar splittings and dipolar couplings.

Solute	S(solute)(a)			$\Delta\nu_{\rho}/\text{kHz}(b)$	$D_{HD}/\text{Hz}(c)$	S(l.c.)(d)	
	S(1132)	S(EBBA-d ₂)	S_{zz}			$S_{xx} - S_{yy}$	
(1) Benzene	-0.2519	-0.1157	0.680	21.29	823	0.680	-0.005
(2) 1,3,5-Trifluorobenzene	-0.2590	-0.1744	0.680	21.22	823	0.680	-0.004
(3) 1,3,5-Trichlorobenzene	-0.2878	-0.2038	0.686	20.92	830	0.686	0.000
(4) 1,3,5-Tribromobenzene	-0.2883	-0.1848	0.666	21.30	805	0.666	-0.009
(5) Hexafluorobenzene	-0.2144	-0.3144	0.641	20.58	775	0.641	-0.010
(6) 2,4-Hexadiyne	0.4270	0.3144	0.690	21.46	835	0.690	-0.004
(7) 2-Butyne	0.2592	0.1524	0.678	21.32	820	0.678	-0.006
(8) Allene	0.1979	0.0925	0.672	21.33	813	0.672	-0.008
(9) Bromomethane	0.0947	0.0368	0.689	21.24	833	0.689	-0.002
(10) Iodomethane	0.0915	0.0280	0.678	21.22	820	0.678	-0.005
(11) Hydrogen	0.0082	-0.0111	0.623	21.18	753	0.623	-0.020
(12) Acetylene	0.1912	-0.0585	0.670	21.25	810	0.670	-0.008
(13) Propyne	0.2763	0.0553	0.649	21.28	785	0.649	-0.014
(14) Furan	0.1727	0.0017	0.673	21.48	814	0.673	-0.009
	-0.2063	-0.0565					
	0.0336	0.0548					
(15) Thiophene	0.1118	-0.0082	0.690	21.04	834	0.690	0.000
	-0.1990	-0.0737					
	0.0871	0.0819					

(a) For the solutes with C_{3v} or higher symmetry S_{zz} is given. The order parameters for these solutes in 1132 are taken from [10].

(b) $\Delta\nu_{\rho}$ is the quadrupolar splitting of the deuterons in EBBA-d₂.

(c) D_{HD} is the dipolar coupling between the deuterons and adjacent protons in EBBA-d₂.

(d) S(l.c.) is the order parameter tensor of the aniline ring of EBBA-d₂.

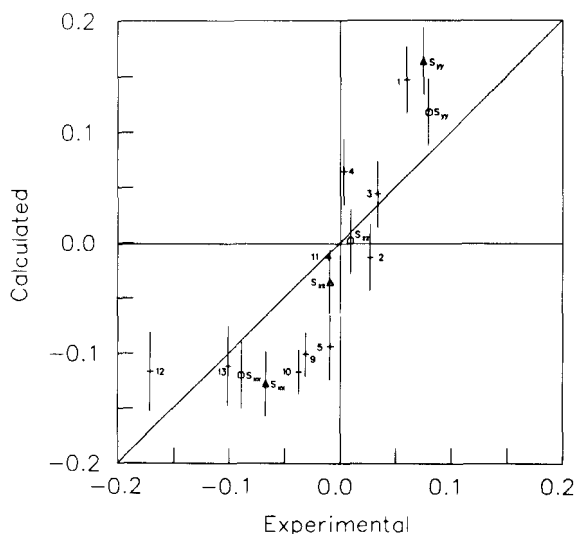


Figure 7. Electric field gradient–molecular quadrupole moment mechanism EBBA- d_2 . Experimental versus calculated values of $S(\text{EBBA-}d_2)\text{-}S(55 \text{ wt } \% \text{ 1132/EBBA-}d_2)$ for furan (circles), thiophene (triangles) and solutes with C_{3v} or higher symmetry. $S(\text{EBBA-}d_2)$ is the order parameter of the solute in EBBA- d_2 and $S(55 \text{ wt } \% \text{ 1132/EBBA-}d_2)$ is the order parameter of the solute in 55 wt % 1132/EBBA- d_2 . For the solutes with C_{3v} or higher symmetry only S_{zz} is plotted. The calculated order parameters have been obtained using a model for the short range interactions [10] and the interaction between the molecular quadrupole moment of the solute and the mean electric field gradient of the solvent. The labelling of the points refers to table 5. The error bars are meant to represent the maximum possible error from Q_{mol} in the calculated values, and have been calculated as follows. Where more than one literature value for Q_{mol} is available, the error bar represents the order parameters calculated using the limits of the literature values. Where only one literature value is available, the accuracy of Q_{mol} is taken to be equal to that of a similar molecule. For example the benzene value has been used for all benzene derivatives. 55 wt % 1132/EBBA- d_2 : $T = 301.4 \text{ K}$, $k = 5.55 \text{ dyn cm}^{-1}$, $F_{zz} = 0.0 \text{ e.s.u.}$ EBBA- d_2 : $T = 301.4 \text{ K}$, $k = 5.55 \text{ dyn cm}^{-1}$, $F_{zz} = -5.75 \times 10^{11} \text{ e.s.u.}$, correlation coefficient = 0.858.

most likely a result of our assumption of the transferability of the force constant and electric field gradient and the errors associated with the molecular quadrupole moments which are reflected in the error bars on the points. For three of the solutes, 2,4-hexadiyne, 2-butyne and allene, no values for the molecular quadrupole moments have been reported in the literature. For these solutes we have calculated molecular quadrupole moments from the experimental values of $S(1132)\text{-}S(55 \text{ wt } \% \text{ 1132})$ and $S(\text{EBBA-}d_2)\text{-}S(55 \text{ wt } \% \text{ 1132})$. The results of these calculations are shown in table 5. There is little variation between the two values obtained for each solute and the signs of the molecular quadrupole moments are consistent with the molecular structure. The value obtained for allene is also consistent with the upper limit reported in [26]. These results demonstrate very clearly the importance of the electric field gradient–molecular quadrupole moment mechanism for the ordering of solutes in these two liquid crystals.

4. Conclusion

We have shown that the ordering of solutes with C_{2v} and D_{2h} symmetry dissolved in 55 wt % 1132/EBBA- d_2 depends on the size and shape of the solute. The elements

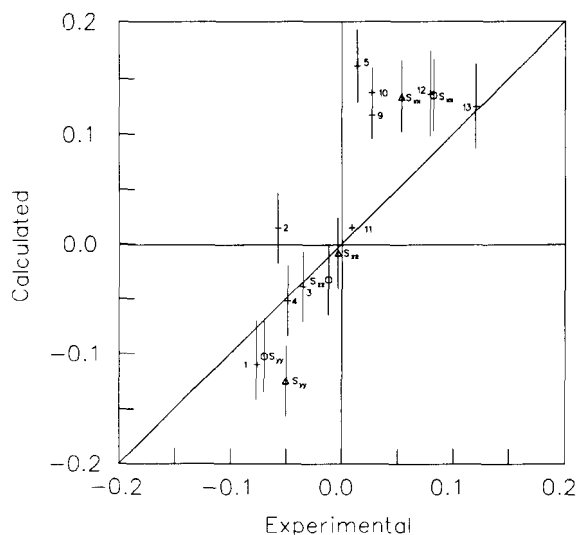


Figure 8. Electric field gradient-molecular quadrupole moment mechanism 1132. Experimental versus calculated values of $S(1132)-S(55 \text{ wt } \% 1132/\text{EBBA}-d_2)$ for furan (circles), thiophene (triangles) and solutes with C_{3v} or higher symmetry. $S(1132)$ is the order parameter of a given solute in 1132 and $S(55 \text{ wt } \% 1132/\text{EBBA}-d_2)$ is the order parameter of a given solute in 55 wt % 1132/EBBA- d_2 . The values of $S(1132)$ for the solutes with C_{3v} or higher symmetry have been taken from [10]. The calculated and experimental values have been obtained and are labelled in the same manner as for figure 7. 55 wt % 1132/EBBA- d_2 : $T = 301.4 \text{ K}$, $k = 5.55 \text{ dyn cm}^{-1}$, $F_{zz} = 0.0 \text{ e.s.u.}$. 1132: $T = 301.4 \text{ K}$, $k = 5.55 \text{ dyn cm}^{-1}$, $F_{zz} = 6.07 \times 10^{11} \text{ e.s.u.}$, correlation coefficient = 0.833.

of the order parameter tensor of the solute can be predicted quite accurately using a model for the short range repulsive interactions which is based on the dimensions of the solute. The order parameters are predicted less well using the interaction between the mean electric field due to the liquid crystal and the polarizability of the solute, which is approximately proportional to the size and shape. In the component liquid crystals 1132 and EBBA- d_2 we have shown that the interaction between the molecular quadrupole moment of the solute and the mean electric field gradient due to the liquid crystal plays an important role. These results support the conclusion that orientation of solutes in 55 wt % 1132 is dominated by short range repulsive interactions.

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