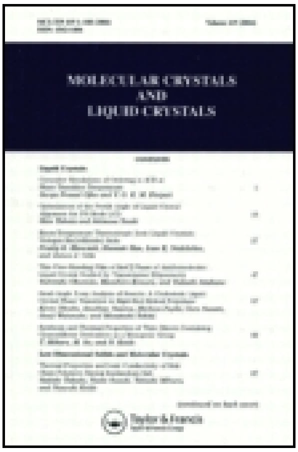

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Size and Shape Effects and the Orientation in Nematic Liquid Crystals of Solutes Having Planar Symmetry

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Size and Shape Effects and the Orientation in Nematic Liquid Crystals of Solutes Having Planar Symmetry

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Experiments performed in our laboratory have suggested that the orientational order of solutes dissolved in nematic liquid crystals results from two mechanisms: a) the interaction between the average electric field gradient experienced by the solute and its molecular quadropole moment; b) the interaction with a potential which depends on the size and shape of a molecule. We model the size and shape potential by replacing the molecule by a cavity having a simple geometrical shape and assuming that the potential experienced by each surface element of the cavity depends only on its orientation with respect to the director. We use the lengths of the projections of the solutes onto axes parallel and perpendicular to the director to approximate the dimensions of the cavity. We use two different potentials based on these assumptions and fit the parameters describing the strength of the interactions with the different surfaces using the published experimental values of the order parameters of 27 molecules having C_{2v} and higher symmetry. All solutes were dissolved in a special mixture where the electric field gradient mechanism is expected to be negligible. We measure the order parameters of 13 additional molecules with C_s symmetry, also dissolved in the same special mixture. Then, without any adjustable parameters, we use the size and shape potentials to predict the order matrices of the solutes with C_s symmetry. These order matrices contain three independent elements for each solute and thus these measurements provide a stringent test for the models. We compare both potentials and discuss the consistency of the parameters which were obtained from the different fits.

1 INTRODUCTION

Solute molecules dissolved in nematic liquid crystals are subject to anisotropic forces which cause them to orient. Usually, a rod like molecule, like allene, orders such that the long axis of the molecule is preferentially oriented parallel to the nematic director. A disc like molecule, like benzene, usually orders such that the plane of the molecule is preferentially oriented parallel to the director. The nature of the anisotropic orienting potential which the nematic environment exerts on the small solutes has been the subject of many investigations. Recently it has been suggested that this ordering results from two mechanisms: a) the electrostatic interaction between the average electric field gradient F_{ZZ} at the site of the solute and the molecular quadropolar moment of the molecule[1–4]; b) the interaction with a short range potential which depends on the size and shape of the molecule.[2,5–8]

The electric field gradient experienced by dideuterium has been measured using NMR for some pure liquid crystals and some mixtures of liquid crystals. Of particular interest are liquid crystal mixtures in which F_{ZZ}, as measured by dideuterium, is negligible. One is then tempted to assume that all molecules dissolved in these mixtures are subject to similar small electric field gradients. Therefore we shall assume that the main contribution to their orientational order results from the size and shape dependent forces, and consequently these mixtures of liquid crystal solvents can be used to investigate the size and shape anisotropic potential.

One of the liquid crystals in which dideuterium experiences a negligible electric field gradient is a mixture of 55 wt% Merck ZLI-1132 with 45 wt% EBBA-d_2. The value $F_{ZZ} \approx 0$ was measured at $T = 301.4$ K.[3] The orientational order of different molecules having different sizes and shapes dissolved in this special mixture have been obtained using proton NMR.[5,6] The first experiments involved 12 molecules having C_{3v} or higher symmetry. For this set of molecules, the order matrix $S_{\alpha\beta}$, which describes the orientational order of the molecules, contains only one independent element. In subsequent experiments the orientational order of 15 molecules having C_{2v} and D_{2h} symmetry were measured. These molecules require two independent parameters to fully characterize their orientational order.

The orientational order matrix $S_{\alpha\beta}$ of a molecule can be calculated if one assumes that the solute molecule is subject to a mean field potential $U(\Omega)$ where Ω are the angles describing the orientation of the director in a coordinate system attached to the molecule. Then $S_{\alpha\beta}$ is given by

$$S_{\alpha\beta} = \frac{\int (3 \cos \theta_\alpha \cos \theta_\beta - \delta_{\alpha\beta})\, exp\, (-U(\Omega)/k_B T) d\Omega}{2 \int exp\, (-U(\Omega)/k_B T) d\Omega} \tag{1}$$

where θ_α is the angle between the space fixed direction of the director and the α direction of a coordinate system fixed to the molecule.

A theoretical model for the short-range of $U(\Omega)$ was introduced by Van der Est et al.[2,5,8] and subsequently modified by Zimmerman and Burnell.[9] In these works, $U(\Omega)$ is assumed to depend on the size and shape of the molecule and is given by

$$U(\Omega) = 2\, k_{xy} \frac{C(\Omega)^2}{4\pi} + k_z\, C(\Omega)\, Z(\Omega) \tag{2}$$

where $C(\Omega)$ is the circumference of the projection of the molecule onto a plane (the XY plane) perpendicular to the director (the Z axis) and $Z(\Omega)$ is the length of the projection of the molecule onto the Z axis (see Figure 1). Equation 2 with $k_z = 0$ corresponds to the potential given in References 2, 5, and 8. The molecules were modeled as a collection of Van der Waals spheres centered on the sites of the nuclei.

While using the potential given by Equation 2 to fit the experimental values of the order parameters, it has been implicitly assumed that the parameters k_{xy} and k_z, which characterize the strength of the potential, depend only on the liquid crystal solvent and its temperature. If this assumption is correct, one can use Equation 2 to predict, without any adjustable parameters, the order matrix of

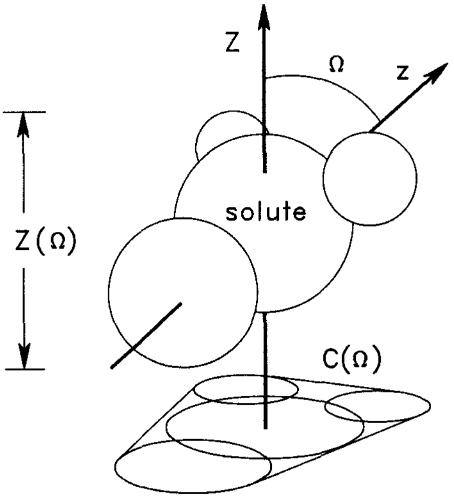

FIGURE 1 The potential given by equations 2–4 depend on the size and shape of the molecule through the projections $X(\Omega)$, $Y(\Omega)$, $Z(\Omega)$ of the molecule onto the space fixed X, Y and Z axes, and $C(\Omega)$—the circumference around the projection onto the XY plane. The Z axis corresponds to the direction of the liquid crystal director. The molecule is modelled as a collection of Van der Waals spheres.

molecules dissolved in zero electric field gradient liquid crystal solvents for which the values of k_{xy} and k_z are known.

In this paper we report the results of an investigation of the order parameter of 13 substituted benzene molecules having C_s symmetry. For these molecules $S_{\alpha\beta}$ contains three independent elements and therefore these measurements provide more stringent tests than previously available of the various assumptions and models used to describe the size and shape orientational mechanism. In this paper we also introduce another potential which depends on the size and shape of the molecules. We use both potentials to fit the published order parameters for the 27 molecules with C_{2v} and higher symmetries and the order parameters reported here for the 13 molecules having C_s symmetry.

2 SIZE AND SHAPE POTENTIALS

The anisotropic potential given by Equation 2 follows from the following considerations. First we assume that we can approximate the cavity occupied by the solute, in the liquid crystal, by a cavity having a simple geometrical shape, whose dimensions, but not its actual shape, depends on the orientation Ω of the solute. Then we assume that, due to the anisotropy of the liquid crystal solvent, the potential experienced by each surface element depends only on the angle between the normal to the surface and the director. It follows that the potential experienced by the molecule depends linearly on the surface area of the different surfaces of the cavity. Therefore we write

$$U(\Omega) = 2\, k_{xy} A_{xy}(\Omega) + k_z A_z(\Omega) \tag{3}$$

where $A_z(\Omega)$ is the total area of the surfaces of the cavity which are parallel to the director and $A_{xy}(\Omega)$ is the area of each of the two surfaces of the cavity which are perpendicular to the director. Equation 2 follows from Equation 3 if one assumes that the cavity is a cylinder whose dimensions l and r are given by $r = C(\Omega)/(2\pi)$ and $l = Z(\Omega)$.

In this paper, we test another potential also based on Equation 3. Here we assume that the cavity is a parallelepiped whose dimensions are given by $X(\Omega)$, $Y(\Omega)$, $Z(\Omega)$, where $X(\Omega)$, $Y(\Omega)$ and $Z(\Omega)$ are the projections of the molecule onto the X, Y and Z axes respectively. From Equation 3 it follows that the potential is given by

$$U(\Omega) = 2\, k_{xy} X(\Omega)\, Y(\Omega) + 2\, k_z\, (X(\Omega) + Y(\Omega))\, Z(\Omega) \tag{4}$$

In a previous paper the values of k_{xy} and k_z in Equation 2 were obtained using a least square fit of the calculated to the experimental values of the order parameters for the 12 molecules having C_{3v} and higher symmetry and the 15 molecules having C_{2v}, and D_{2h} symmetry.[9] Here we perform the same fit using Equation 4. The geometries of the molecules, the Van der Waals radii and the molecular fixed coordinate system used for each molecule are described in References 5 and 6. For molecules with C_{3v} or higher symmetry the molecular axis system was chosen such that the off-diagonal elements of the order parameter matrix $S_{\alpha\beta}$ are zero, $S_{zz} \neq 0$ and $S_{xx} = S_{yy}$. Similarly for molecules with C_{2v} and D_{2h} symmetry the molecular axes system was chosen such that $S_{\alpha\beta}$ contains no off-diagonal elements and two independent diagonal elements. The values which resulted from a least square fit using Equation 2 are $k_{xy} = 12.32$ dyn/cm and $k_z = -9.83$ dyn/cm. Using Equation 4 and the same set of 27 molecules with the same choice of molecular axes systems we obtain $k_{xy} = 10.23$ dyn/cm and $k_z = -8.87$ dyn/cm.

Tables I and II and Figures 2 and 3 compare the experimental and calculated values for the order parameters using both Equation 2 and Equation 4. In both cases the resulting values for the order parameters are in very good agreement with the experimental results. Figure 2 shows the difference between the calculated and the experimental values of S_{zz} for the molecules with C_{3v} symmetry. By plotting these differences we emphasize the quality of the fits and the difference between the potentials. The ○ and the × correspond to fits using Equation 2 and 4 respectively. Both potentials yield comparable fits, except for hexadiyne where the fit using Equation 2 is noticeably better. The fit using Equation 2 tends to overestimate S_{zz}, while the fit using Equation 4 underestimates S_{zz}.

For the molecules with C_{2v} and D_{2h} symmetry, let S_{33}, S_{22}, S_{11} be the element of $S_{\alpha\beta}$ with the largest, intermediate and smallest absolute value respectively. Let the asymmetry parameter η be defined through $\eta = (S_{11} - S_{22})/S_{33}$. Figure 3a shows the fits for S_{33} using both models. For this case the fit using Equation 4 is better. While the fit using Equation 2 tends to overestimate S_{33}, the fit using Equation 4 does not show a trend to overestimate or underestimate the calculated values of S_{33}. Figure 3b shows a similar comparison for the asymmetry parameter η. For this case, again, the fit using Equation 4 is superior. This improvement results from the fact that, as shown in Figure 3c, Equation 4 yields a much better

TABLE I

Experimental[5] and calculated values for the other parameters of solutes with C_{3v} or higher symmetry. The molecules are ordered in increasing order of $S_{zz}(exp)$. $S_{zz}(calc)^*$ values were obtained using Equation 2 with the best fit values k_{xy} = 12.32 dyn/cm and k_z = −9.83 dyn/cm and $S_{zz}(calc)^{**}$ with Equation 4 using k_{xy} = 10.23 dyn/cm and k_z = −8.87 dyn/cm

SOLUTE	$S_{zz}(exp)$	$S_{zz}(calc)^*$	$S_{zz}(calc)^{**}$
1,3,5-TRICHLOROBENZENE	-0.2380	-0.2251	-0.2557
HEXAFLUOROBENZENE	-0.2280	-0.2154	-0.2451
1,3,5-TRIFLUOROBENZENE	-0.2014	-0.1913	-0.2192
BENZENE	-0.1756	-0.1507	-0.1735
HYDROGEN	-0.0008	0.0190	0.0187
IODOMETHANE	0.0650	0.0901	0.0872
BROMOMETHANE	0.0676	0.0775	0.0763
ACETYLENE	0.1123	0.1018	0.0998
ALLENE	0.1302	0.1317	0.1244
PROPYNE	0.1559	0.1484	0.1411
BUTYNE2	0.1943	0.2020	0.1796
2,4-HEXADIYNE	0.3664	0.3508	0.2876

fit for S_{11}—the order parameter with the smallest absolute value. Furthermore, S_{11} is underestimated using Equation 2 while such a bias does not occur for the fit using Equation 4.

3 MOLECULES WITH C_s SYMMETRY

3.1 Experimental Details

The liquid crystal solvent used was a mixture of 55 wt% Merck ZLI 1132 which is by itself a eutectic mixture of 1,4-(trans-4′-*n*-alkylcyclohexyl)-cyanobenzene (alkyl = propyl, pentyl, heptyl) and 1,4′-(trans-4′-*n*-pentylcyclohexyl)-cyanobiphenyl and 45 wt% EBBA-d_2: *N*-(4-ethoxybenzylidene)-4′-*n*-butylaniline. The solutes in Table III were purchased from various chemical suppliers and were used without further purification. The samples were prepared in 5 mm o.d. glass tubes. Each sample contained less than 5 mol % solute. The proton NMR spectra of the solutes were

TABLE II

Experimental[6] and calculated values for the order parameters of solutes with C_{2v} or D_{2h} symmetry. The molecules are ordered in increasing order of $S_{33}(exp)$, where $S_{33}(exp)$ is the element of the order tensor S_{ij} with the largest absolute value. The molecular fixed coordinate system is given in Reference 6. $S_{zz}(calc)^*$ values were obtained using Equation 2 with the best fit values k_{xy} = 12.32 dyn/cm and k_z = −9.83 dyn/cm and $S_{zz}(calc)^{**}$ with Equation 4 using k_{xy} = 10.23 dyn/cm and k_z = −8.87 dyn/cm

SOLUTE		$S(exp)$	$S(calc)^*$	$S(calc)^{**}$
1,2-DICYANOBENZENE	S_{yy}	-0.247	-0.228	-0.260
	S_{zz}	0.184	0.190	0.190
1,3-DINITROBENZENE	S_{xx}	0.1961	0.2477	0.2413
	S_{yy}	-0.2287	-0.2215	-0.2492
1,2-DICHLOROBENZENE	S_{yy}	-0.2248	-0.1977	-0.2262
	S_{zz}	0.1601	0.1624	0.1660
1,3-DICHLOROBENZENE	S_{xx}	0.1958	0.2173	0.2141
	S_{yy}	-0.2243	-0.2016	-0.2291
CHLOROBENZENE	S_{yy}	-0.2037	-0.1689	-0.1928
	S_{zz}	0.1967	0.1787	0.1797
2,6,-DIFLUOROPYRIDINE	S_{xx}	0.1529	0.1384	0.1443
	S_{yy}	-0.1908	-0.1740	-0.1993
FLUOROBENZENE	S_{yy}	-0.1906	-0.1646	-0.1890
	S_{zz}	0.1399	0.1361	0.144
PYRIDINE	S_{xx}	0.1093	0.0898	0.0984
	S_{yy}	-0.1545	-0.1408	-0.1619
THIOPHENE	S_{yy}	-0.1490	-0.1261	-0.1442
	S_{zz}	0.0905	0.0581	0.0683
FURAN	S_{xx}	0.0907	0.0782	0.0856
	S_{yy}	-0.1365	-0.1130	-0.1303
ACETONE	S_{xx}	0.0711	0.0925	0.0945
	S_{yy}	-0.0720	-0.0861	-0.0957
IODOBENZENE	S_{yy}	-0.2146	-0.1877	-0.2109
	S_{zz}	0.2389	0.2497	0.2464
1,4-DICHLOROBENZENE	S_{yy}	-0.2467	-0.1970	-0.2181
	S_{zz}	0.3188	0.3216	0.3077
TTF	S_{yy}	-0.2514	-0.2529	-0.2759
	S_{zz}	0.3320	0.3688	0.3369
1,4-DIBROMOBENZENE	S_{yy}	-0.2546	-0.2023	-0.2222
	S_{zz}	0.3567	0.3584	0.3429

obtained at 400 MHz using a Bruker WH400 spectrometer. The quadropolar splittings of the deuterated EBBA were measured at 61.4 MHz through the lock channel. The experiments were performed at T = 301.4 K and the temperature was controlled using a variable temperature gas flow unit.

The direct dipolar couplings between the nuclei and the chemical shifts of the nuclei were obtained from the proton spectrum using the least square program LEQUOR. Indirect spin-spin couplings were taken from the literature. Initial guesses for the dipolar coupling, which are required in order to use LEQUOR, were calculated using the potential given in Equation 2. The values of k_{xy} and k_z

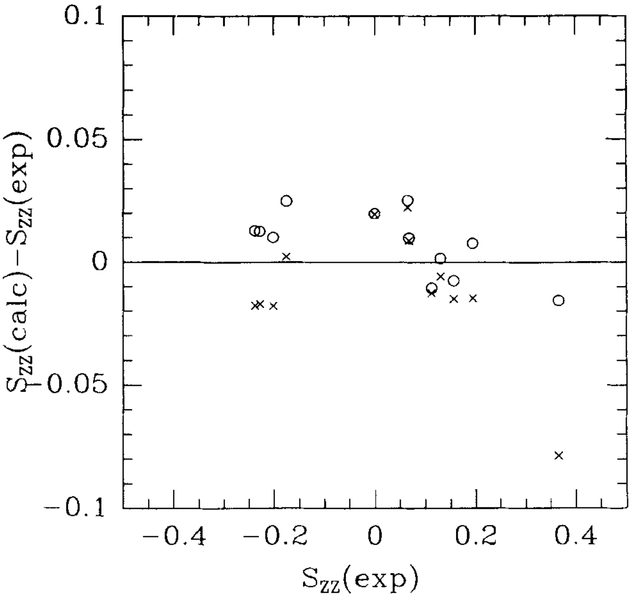

FIGURE 2 The difference between the calculated and experimental values of S_{zz} vs. the experimental values of S_{zz} for molecules with C_{3v} or higher symmetry. The ○ were calculated using Equation 2 with the best fit values $k_{xy} = 12.32$ dyn/cm and $k_z = -9.83$ dyn/cm. The × were calculated using Equation 4 with the best fit values $k_{xy} = 10.23$ dyn/cm and $k_z = -8.87$ dyn/cm.

used were the values which had been obtained from the fit to the 27 molecules, as described in the previous section. The geometrical description of the solute molecules were taken from the literature. The availability of these initial guesses for the dipolar couplings considerably simplified the analyses of the spectra. The order parameters were calculated from the dipolar couplings using the program SHAPE. The molecular fixed axes were defined such the z axis is perpendicular to the plane of the molecule and the y axis passes through the two hydrogen nuclei that are para to each other. Further details regarding the parameters used will be given elsewhere.

3.2 Results and Discussion

We have measured the values of the quadropolar splitting of the deuterated EBBA. These splittings are a measure of the degree of order in the liquid crystal solvent. The resulting values for the samples reported in this study agree to better than 5% with each other and with values previously obtained for the solutions containing the 27 solutes of higher symmetry. This agreement demonstrates that the conditions in all these experiments are similar and therefore we will use the values of k_{xy} and k_z obtained from the fits reported in the previous section in a calculation of the order parameters of the molecules with C_s symmetry. In this way we compare the experimental values of the order parameters to values which are calculated without any adjustable parameters. Table 3 and Figure 4 show a comparison between the experimental and the calculated values of the order parameters.

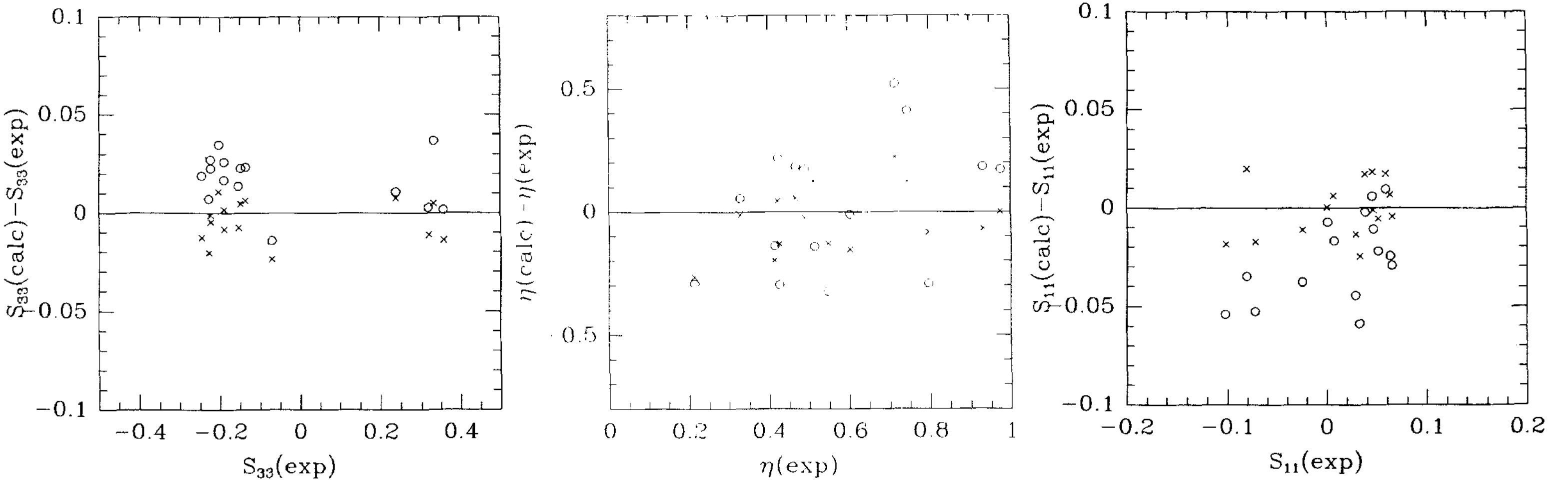

FIGURE 3 a) The difference between the calculated and experimental values of S_{33} vs. the experimental values of S_{33} for molecules with C_{2v} or D_{2h} symmetry. S_{33} is the element of the experimental order tensor S_{ij} with the largest absolute value. The ○ were calculated using Equation 2 with the best fit values k_{xy} = 12.32 dyn/cm and k_z = −9.83 dyn/cm. The × were calculated using Equation 4 with the best fit values k_{xy} = 10.23 dyn/cm and k_z = −8.87 dyn/cm. b) As in 3a for the asymmetry parameter $\eta = (S_{11} - S_{22})/S_{33}$. c) As in 3b for S_{11}—the diagonal element of S_{ij} with the smallest absolute value.

TABLE III

Experimental and calculated values for the order parameters of solutes with C_s symmetry. The molecules are ordered in increasing order of $S_{33}(exp)$, where $S_{33}(exp)$ is the element of the order tensor S_{ij} with the largest absolute value. $S(calc)^*$ values were obtained using Equation 2 with the best fit values $k_{xy} = 12.32$ dyn/cm and $k_z = -9.83$ dyn/cm and $S(calc)^{**}$ with Equation 4 using $k_{xy} = 10.23$ dyn/cm and $k_z = -8.87$ dyn/cm, obtained from the fits to the molecules with higher symmetry

SOLUTE		$S(exp)$	$S(calc)^*$	$S(calc)^{**}$
1,3-FLUOROBROMOBENZENE	S_{xx}	0.1664	0.1929	0.1934
	S_{zz}	-0.2026	-0.1946	-0.2207
	S_{xy}	0.0486	0.0684	0.0581
3-BROMOIODOBEBENZENE	S_{xx}	0.1956	0.2750	0.2661
	S_{zz}	-0.2099	-0.2152	-0.2410
	S_{xy}	0.0179	0.0207	0.0173
2-BROMOCHLOROBENZENE	S_{xx}	0.1459	0.1641	0.1686
	S_{zz}	-0.2113	-0.2003	-0.2285
	S_{xy}	0.0125	0.0298	0.0255
2-BROMOIODOBENZENE	S_{xx}	0.1362	0.1740	0.1784
	S_{zz}	-0.2119	-0.2097	-0.2381
	S_{xy}	0.0267	0.0324	0.0283
3-CHLOROIODOBENZENE	S_{xx}	0.1966	0.2527	0.2465
	S_{zz}	-0.2124	-0.2103	-0.2362
	S_{xy}	0.0289	0.0417	0.0348
2-FLUOROBENZONITRILE	S_{xx}	0.1690	0.1800	0.1818
	S_{zz}	-0.2148	-0.2041	-0.2307
	S_{xy}	0.0968	0.1176	0.0102
3-CHLOROBROMOBENZENE	S_{xx}	0.1984	0.2345	0.2293
	S_{zz}	-0.2225	-0.2052	-0.2317
	S_{xy}	0.0117	0.0210	0.01734
3-FLUOROBENZONITRILE	S_{xx}	0.1906	0.2161	0.2128
	S_{zz}	-0.2139	-0.2092	-0.2357
	S_{xy}	0.0977	0.0996	0.0839
2-CHLOROIODOBENZENE	S_{xx}	0.1532	0.1718	0.1760
	S_{zz}	-0.2234	-0.2048	-0.2325
	S_{xy}	0.0428	0.0610	0.0532
2-CHLOROBENZONITRILE	S_{xx}	0.1688	0.1830	0.1845
	S_{zz}	-0.2292	-0.2140	-0.2430
	S_{xy}	0.0693	0.0707	0.0619
3-BROMOBENZONITRILE	S_{xx}	0.2310	0.2835	0.2715
	S_{zz}	-0.2337	-0.2250	-0.2516
	S_{xy}	0.0599	0.0332	0.0287
2-BROMOBENZONITRILE	S_{xx}	0.1640	0.1845	0.1864
	S_{zz}	-0.2340	-0.2180	-0.2475
	S_{xy}	0.0595	0.0428	0.0386
3-CHLOROBENZONITRILE	S_{xx}	0.2336	0.2616	0.2515
	S_{zz}	-0.2398	-0.2203	-0.2472
	S_{xy}	0.0746	0.0536	0.0449

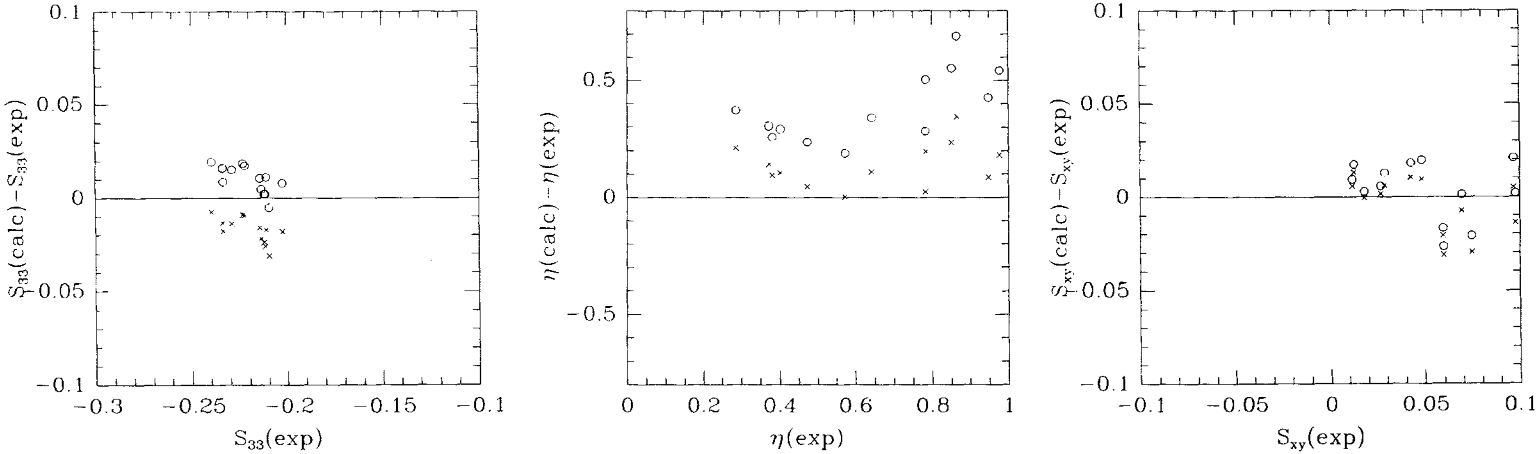

FIGURE 4 a) The difference between the calculated and experimental values of S_{33} vs. the experimental values of S_{33} for molecules with C_s symmetry. The ○ were calculated using Equation 2 with the values $k_{xy} = 12.32$ dyn/cm and $k_z = -9.83$ dyn/cm which were obtained from the fit for the molecules with C_{2v} and higher symmetry. The × were calculated using Equation 4 with the values $k_{xy} = 10.23$ dyn/cm and $k_z = -8.87$ dyn/cm which were also obtained from the fits to the molecules with higher symmetry. b) As in 4a for the asymmetry parameter $\eta = (S_{11} - S_{22})/S_{33}$. c) As in 4a for S_{xy}.

Both models, as Figure 4a demonstrates, yield values for S_{33} which are in very good agreement with the experimental results. As in the case for the 27 molecules of higher symmetry Equation 2 overestimates S_{33} and Equation 4 underestimates S_{33}. Figure 4b shows the results for the asymmetry parameter η. In both cases the calculated value of η is slightly overestimated. However, Equation 4 yields much better values for η. Finally, Figure 4c shows that both Equation 2 and Equation 4 yield comparable values for the off diagonal element S_{xy}. Although the values of S_{xy} are small, and consequently some of the fractional errors are large, both models calculate these values with the correct sign and with reasonable accuracy.

Figures 5 show the comparison for the same set of 13 molecules for a calculation in which the parameters k_{xy} and k_z are obtained from a least square fit of the calculated values of the order parameters of these C_s molecules to the experimental values. Using Equation 2 the resulting values are $k_{xy} = 8.45$ dyn/cm and $k_z = -12.27$ dyn/cm. Using Equation 4 the values are $k_{xy} = 9.40$ dyn/cm and $k_z = -6.67$ dyn/cm. In this case Equation 4 yields better fits than does Equation 2. The fits for S_{33} using Equation 4 are excellent and do not show any systematic deviations. Also the fit for η is much superior when Equation 4 is used. Both equations yield comparable fits for S_{xy}.

These comparisons demonstrate that the two models, both based on the size and shape of the solute molecules, are capable of producing excellent agreement between experimental and calculated values for the order parameters of molecules having C_s symmetry. The model based on Equation 4 yields better values for the smaller order parameters than does the model based on Equation 2.

4 DISCUSSION

We have used two different potentials which depend on the size and shape of the solute molecules to calculate the order parameter matrix $S_{\alpha\beta}$ for molecules dissolved in a liquid crystal mixture in which the orientation of the solutes is expected to correlate with their size and shape. Both potentials are based on the assumption that the potential depends linearly on the areas of the different surfaces of a cavity containing the solute molecules. The difference between the potentials is related to the way one estimates this surface area. In one case we assumed that the cavity has a cylindrical shape and in the other case we model it as a parallelepiped. Both potentials yield very good fits to the experimentally determined values of the order parameters for molecules with C_{2v} and higher symmetry. The potential based on the $X(\Omega)$, $Y(\Omega)$ and $Z(\Omega)$ projections yielded better fits for the asymmetry parameter than the potential based on the projection $Z(\Omega)$ and the circumference $C(\Omega)$.

In order to apply a stringent test to both potentials we measured the orientational order of 13 molecules having C_s symmetry. For these solutes the potential is required to yield good values for the three independent parameters which describe the orientational order of the molecule. The order parameters were calculated using the values of k_{xy} and k_z which were previously determined from the solutes with higher symmetries. The agreement between experimental and calculated values is very good. As expected, even better fits were obtained when the parameters

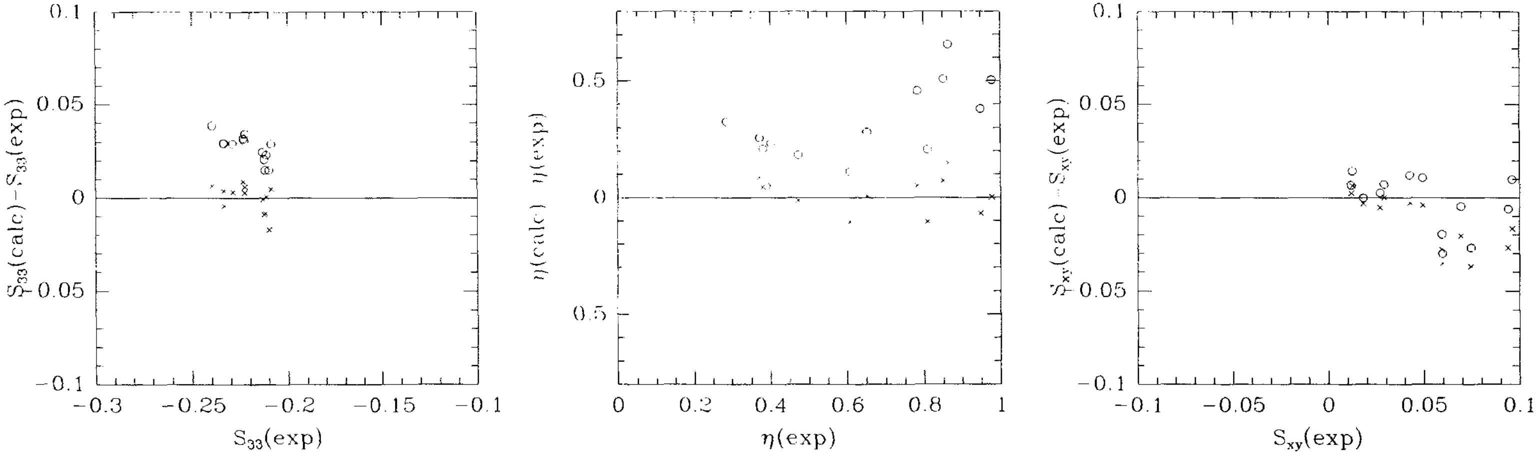

FIGURE 5 a) The difference between the calculated and experimental values of S_{33} vs. the experimental values of S_{33} for molecules with C_s symmetry. The parameters were obtained from a least square fit using only the molecules having C_s symmetry. The ○ were calculated using Equation 2 with the best fit values $k_{xy} = 8.45$ dyn/cm and $k_z = -12.27$ dyn/cm. The × were calculated using Equation 4 with the best fit values $k_{xy} = 9.40$ dyn/cm and $k_z = -6.67$ dyn/cm. b) As in 5a for the asymmetry parameter $\eta = (S_{11} - S_{22})/S_{33}$. c) As in 5a for S_{xy}.

were adjusted in a separate least squares fit to $S_{\alpha\beta}$ for these C_s molecules. In both cases the potential based on the $X(\Omega)$, $Y(\Omega)$ and $Z(\Omega)$ yielded better fits for the values of the asymmetry parameter.

While performing these analyses we have implicitly assumed that the parameters k_{xy} and k_z should be the same for the different molecules. The ability to use these potentials to predict the order parameter of other molecules dissolved in zero electric field gradient mixtures hinges on the question of whether the parameters k_{xy} and k_z depend on the type or size or symmetry of the molecules. The success of the calculations for the C_s molecules using the parameters obtained from the molecules with higher symmetry suggests that such a transfer of parameters is justified. To further explore this transferability we have also performed a fit to k_{xy} and k_z separately for the three groups of molecules, where the groups are characterized by the number of independent components in the order matrix. The resulting values, summarized in Table 4, show that the potential based on $C(\Omega)$ and $Z(\Omega)$ yields more consistent values for k_z while the other potential yields more consistent values for k_{xy}. Table 4 also shows the values of k_{xy} and k_z obtained from the fits to the 27 molecules having C_{2v} and higher symmetry.

In previous experiments the deuteron spectra of perdeuterated 4-*n*-pentyl-4′-cyanobiphenyl (5CB), itself a nematic liquid crystal, were obtained in the same zero electric field gradient mixture used in the studies reported here.[7] It is of interest to examine the question whether this long molecule, which also exists in many conformations, can be described by the above potentials and whether the resulting parameters are consistent with the values obtained from the fits to the small solutes. The method used to calculate the quadropolar splitting of 5CB has been previously

TABLE IV

The values of the parameters k_{xy} and k_z (in dyn/cm) obtained from fits in which the molecules were grouped according to the symmetry of the molecules. The values on the left were obtained using Equation 2 and those on the right using Equation 4. Also shown are the values obtained for 2 fits for 5CB performed with 2 different fixed values of E_{tg} (in kJ/mol)

	Equation 2			Equation 4	
SYMMETRY	k_{xy}	k_z		k_{xy}	k_z
C_{2v} and higher	12.32	-9.83		10.23	-8.87
C_{3v} and higher	12.87	-10.00		9.00	-11.7
C_{2v} & D_{2h}	11.67	-10.42		10.50	-8.15
C_s	8.45	-12.27		9.40	-6.67
5CB (E_{tg}=2.09)	15.20	-12.92		14.36	-8.38
5CB (E_{tg}=2.91)	12.51	-9.04		12.05	-4.84

described in detail.[7,12-14] One of the difficulties associated with these calculations results from the fact that the value of E_{tg}, the energy difference between the gauche and trans states, is not well known. One can fix E_{tg} to different values and obtain fits of comparable quality but with different values of k_{xy} and k_z.

As shown in Reference 9, it is possible to obtain a very good fit to the spectra of 5CB (RMS = 1003 Hz) by varying E_{tg} and using Equation 2 with the values $k_{xy} = 12.32$ dyn/cm and $k_z = -9.83$ dyn/cm obtained from the fit of the molecules with C_{2v} and higher symmetry. The resulting value of $E_{tg} = 2.91$ kJ/mol is in acceptable agreement with the commonly used gas phase value $E_{tg} = 2.09$ kJ/mol.[10,11] However, a fit using Equation 4 and the parameters obtained from the small solutes yields unsatisfactory results for the spectrum of 5CB (RMS = 3214 Hz). Therefore, in this case, in order to obtain a good fit one must adjust the values of k_{xy} and k_z. Figure 6 shows such fits, obtained using Equation 4, varying k_{xy} and k_z and fixing E_{tg} to $E_{tg} = 2.09$ kJ/mol and $E_{tg} = 2.91$ kJ/mol. The resulting fits are better than the corresponding fits using Equation 2 shown in Reference 9. The fitted values for the parameters k_{xy} and k_z are also shown in Table 4. For the fits with the gas phase value $E_{tg} = 2.09$ kJ/mol both Equation 2 and Equation 4 yield values for k_{xy} and k_z which equally deviate from the values obtained for the small solutes. For $E_{tg} = 2.91$ kJ/mol the deviation of the fitted values of k_{xy} and k_z from the corresponding values obtained from the fits for the small solutes is smaller when Equation 2 is used compared to the case where Equation 4 is used.

These results demonstrate that size and shape potentials are capable of yielding excellent fits for both small solutes as well as a long flexible molecule like 5CB. In all cases the fits using Equation 4 are superior.

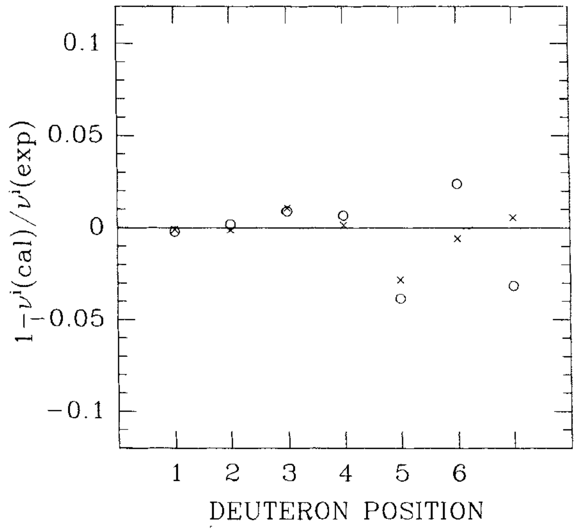

FIGURE 6 The fractional difference between the experimental and calculated quadropolar couplings for 5CB. Positions 1–5 are along the alkyl chain. Positions 6 and 7 are in the rings. The calculated values were obtained using Equation 4. The ○ were calculated using $k_{xy} = 14.36$ dyn/cm (fitted), $k_z = -8.38$ dyn/cm (fitted) and $E_{tg} = 2.09$ kJ/mol (fixed). The × were calculated using $k_{xy} = 12.05$ dyn/cm (fitted), $k_z = -4.84$ dyn/cm (fitted) and $E_{tg} = 2.91$ kJ/mol (fixed).

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