Multiple Quantum and High-Resolution NMR, Molecular Structure, and Order Parameters of Partially Oriented *ortho* and *meta* Dimethyl-, Dichloro-, and Chloromethylbenzenes Codissolved in Nematic Liquid Crystals

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We develop a strategy for analyzing complex nuclear magnetic resonance (NMR) spectra of several solutes codissolved in liquid-crystal phases. Spectral parameters of solutes *m*- or *o*-xylene were estimated by analyzing 2D multiple-quantum NMR spectra using a modified version of a least-squares fitting routine which adjusts chemical shifts, order parameters, structural parameters, and/or dipolar couplings independently. These estimates were used to facilitate analysis of the high-resolution spectra which contain resonances from many solutes. Calculated spectra of *m*- or *o*-xylene were subtracted from the experimental high-resolution spectra leaving resonances from the other solutes readily visible. Accurate spectral parameters of all codissolved solutes were determined from the high-resolution spectra. Order parameters and structural parameters (including vibrationally corrected parameters) of *m*- and *o*-xylene, *m*- and *o*-chlorotoluene, and *m*- and *o*-dichlorobenzene were calculated from the dipolar couplings. © 2000 Academic Press

I. INTRODUCTION

Nuclear magnetic resonance (NMR) spectroscopy of small molecules oriented in liquid-crystal solvents can yield precise information about the solute molecular geometry and second-rank orientational order parameters (*1, 2*). NMR spectroscopy is one of the few techniques available for the determination of condensed phase structures, and the method can be used to investigate possible differences between gas and condensed phase structures. In addition, rotational potential barriers in molecules such as butane (*3*) and biphenyl (*4*) can be examined.

The orientational order parameters are related to the anisotropic intermolecular forces and thus can be used to examine statistical theories of liquid crystals (*5–12*). Instead of analyzing the liquid-crystal molecules themselves, it is common to dissolve small solutes which probe these anisotropic forces. Solutes can be chosen so as to emphasize specific anisotropic

interactions (*5, 8, 9, 13*). For example, in this study the three *ortho* (and the three *meta*) solutes have similar sizes and shapes but have different multipole moments. The anisotropic short-range interactions are similar for the molecules but the long-range interactions (such as those due to the multipole moments and dispersion forces) are different; therefore, it may be possible to examine effects of long-range interactions on the anisotropic intermolecular potential. Since there is much debate as to which long-range electrostatic interactions are most significant (*5–7, 13, 14*), the order parameters determined in this study may be useful when investigating intermolecular potentials.

The differences among order parameters of solutes may be small and thus accurate measurements are required. Order parameters determined for molecules in the same liquid crystal should be measured under identical conditions. Ideally all solutes should be codissolved in the same sample tube but, due to overlap of spectral lines, extracting information from the resultant proton NMR spectrum may be impractical. It is common to dissolve solutes in different sample tubes and then to scale the results to account for variation in the solvent orientational order that results from different sample conditions (*5, 13–17*). In an effort to alleviate the problem of scaling, in this study three or four fully protonated solutes are codissolved in the same sample tube. We present some interesting NMR and spectral analysis tricks to disentangle the very complicated proton NMR spectra which result.

We develop a strategy for the analysis of high-resolution NMR spectra which contain resonances from many partially oriented solutes. In some cases 2D multiple quantum (MQ) NMR spectra are analyzed first with the aid of a spectral analysis program which adjusts resonance frequencies, order parameters, structural parameters, and/or dipolar couplings independently. Spectral parameters determined from the analysis of MQ spectra are used as initial estimates in the analysis of the complex high-resolution spectra which contain resonances

TABLE 1
Solute and Solvent Composition[a] of Samples

Sample	Solutes	Liquid-crystal solvent
1	o-Chlorotoluene/o-dichlorobenzene/TCB[b]	ZLI 1132[c]
2	o-Chlorotoluene/o-dichlorobenzene/TCB[b]	55 wt% ZLI 1132/EBBA
3	o-Chlorotoluene/o-dichlorobenzene/TCB[b]	EBBA[d]
4	o-Xylene/o-dichlorobenzene/TCB[b]	ZLI 1132[c]
5	o-Xylene/o-dichlorobenzene/TCB[b]	55 wt% ZLI 1132/EBBA
6	o-Xylene/o-dichlorobenzene/TCB[b]	EBBA[d]
7	m-Chlorotoluene/m-dichlorobenzene/TCB[b]	ZLI 1132[c]
8	m-Chlorotoluene/m-dichlorobenzene/TCB[b]	55 wt% ZLI 1132/EBBA
9	m-Chlorotoluene/m-dichlorobenzene/TCB[b]	EBBA[d]
10	m-Xylene/m-dichlorobenzene/TCB[b]	ZLI 1132[c]
11	m-Xylene/m-dichlorobenzene/TCB[b]	55 wt% ZLI 1132/EBBA
12	m-Xylene/m-dichlorobenzene/TCB[b]	EBBA[d]
13	o-Xylene/o-chlorotoluene/o-dichlorobenzene/TCB[b]	ZLI 1132[c]

[a] Total solute composition is $\approx$10 mol%.
[b] TCB refers to an internal orientational standard 1,3,5-trichlorobenzene.
[c] See Ref. (18) for chemical composition.
[d] EBBA refers to N-(p-ethoxybenzylidene)-p'-n-butylaniline.

from other solutes. The resultant analyzed spectrum is subtracted from the experimental one and resonances corresponding to the other solutes are readily visible. By analyzing proton NMR spectra and dipolar couplings of the partially oriented solutes m- and o-xylene, m- and o-chlorotoluene, and m- and o-dichlorobenzene, we determine the spectral parameters, molecular order parameters, and internuclear distances including the vibrationally corrected r_α structures.
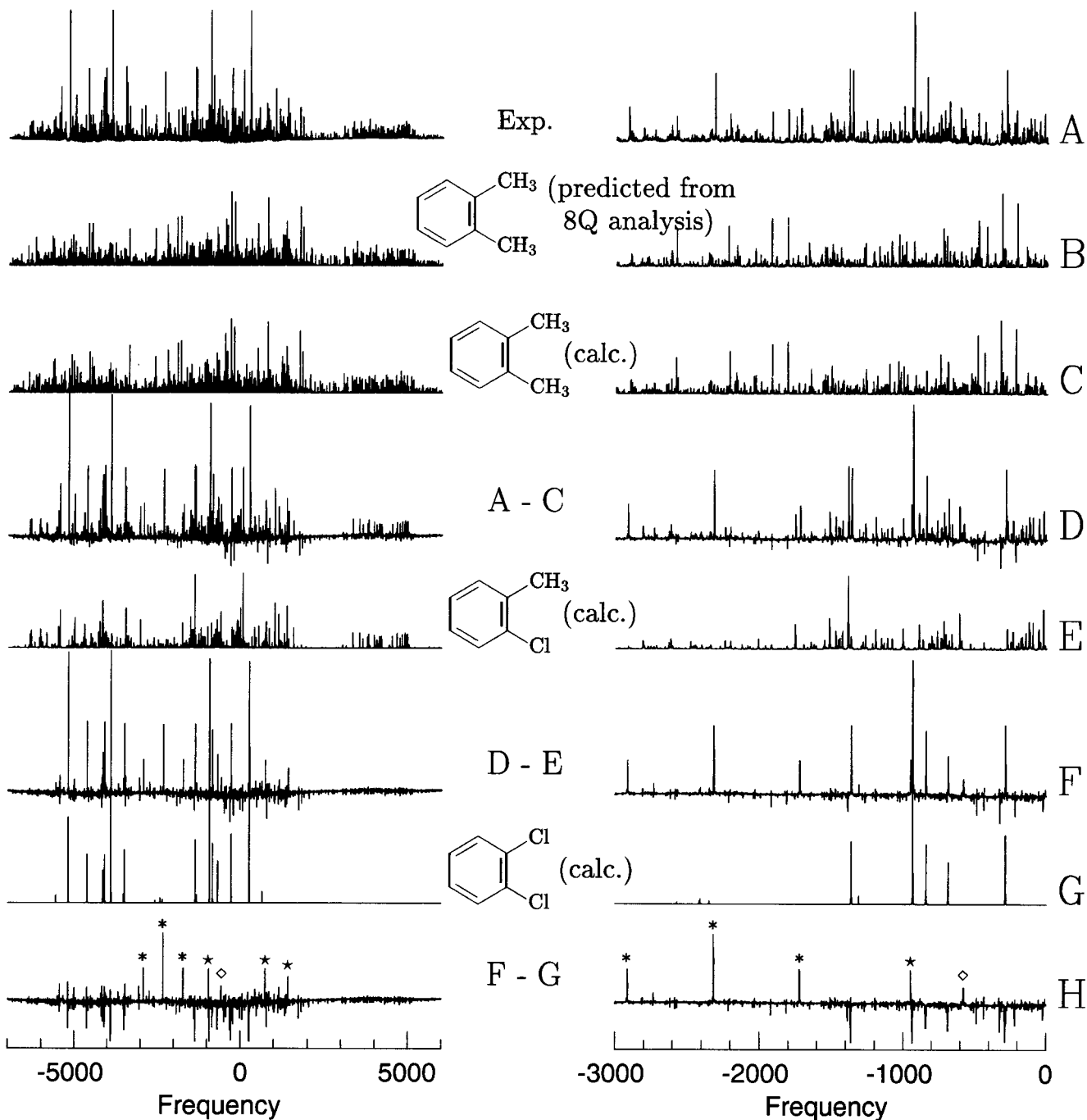
II. EXPERIMENT

The nematic liquid-crystal Merck ZLI 1132 (see Ref. (18) for chemical composition) and all solutes were used without further purification. The liquid crystal N-(p-ethoxybenzylidene)-p'-n-butylaniline (EBBA) was synthesized (19) and purified by recrystallization from cold methanol. Each of the 13 samples was prepared by dissolving three or four solutes in one of the liquid-crystal solvents: ZLI 1132; 55 wt% ZLI 1132/EBBA; or EBBA. The total solute concentration was $\approx$10 mol%. The solute 1,3,5-trichlorobenzene (TCB) which was added to each sample was used as an internal orientational standard. The composition of each sample is given in Table 1.

Proton NMR spectra of the 13 samples were acquired at 299.6 ± 0.5 K on a Bruker AMX-500 spectrometer. Acetone-d_6 in a coaxial capillary provided the deuterium lock. For high-resolution proton NMR spectra, 32K point FIDs were acquired after a single pulse, zero filled to 64K points, and processed using a Lorentzian line broadening of 1.0 Hz. Half-height linewidths were typically 2–3 Hz. For samples which contained o- or m-xylene two-dimensional selective 8Q spectra were acquired using the pulse sequence described in Refs. (20) and (21). Selective 8Q interferograms were acquired with between 1024 and 2048 increments in t_1 and for each t_1

increment 2048 points were collected in t_2; a one-dimensional 8Q spectrum was produced by zero filling to 2048 points in t_1, 2D magnitude Fourier transforming, and performing a summed projection onto the F_1 axis. Only transitions from o- or m-xylene were observed in the selective 8Q spectra because for a n-spin-$\frac{1}{2}$ system, n is the highest attainable MQ order and all other solutes have <8 spins. The intensity of MQ lines is highly dependent on the preparation time used for the 2D pulse sequence and therefore at least two 8Q spectra with preparation times between 10 and 21 ms were acquired for each sample containing o- or m-xylene in an attempt to detect all 8Q transitions. For all experiments the recycling time was 4 s.

III. SPECTRAL ANALYSIS AND STRATEGY

Unlike NMR spectra of isotropic solutions, the NMR spectra of orientationally ordered molecules contain information about nuclear dipolar couplings between pairs of spins on the same molecule; random rapid translational motion of the molecules causes intermolecular dipolar couplings to be averaged to zero. The anisotropic molecular reorientation causes the intramolecular dipolar couplings to be averaged to a nonzero value. The NMR spectrum is dependent on the flexibility and symmetry of the molecules and on the number and type of nuclear spins; in the experimental spectrum shown in Fig. 1A there are no sharp resonances observed from the liquid-crystal molecules which have more than 23 nuclear spins, no symmetry, and many conformers. Most of the resolvable lines in the spectrum are from the solute o-xylene which has only 10 spins and C_{2v} symmetry and is essentially rigid. The spectral parameters of such small solutes can be determined accurately by analyzing the experimental spectrum using the spin Hamiltonian

FIG. 1. Spectral analysis strategy: Full spectra are displayed on the left and expansions are displayed on the right. A is the experimental spectrum of Sample 13. B is the predicted *o*-xylene spectrum from the parameters determined by analysis of the 8Q spectrum (Fig. 2 and values in square brackets from Table 2). Spectrum C is calculated (using values from Table 2 and using a Lorentzian lineshape with a half-height linewidth of 2 Hz) from the fit to the high-resolution spectrum of *o*-xylene. Note that there are only minor differences between spectra B and C. Spectrum D is the difference between A and C. The negative residuals in Spectrum D are due to slight differences between the lineshapes of the calculated and experimental spectra. The calculated spectrum of *o*-chlorotoluene is E and F is the difference between D and E. Spectrum G is the calculated *o*-dichlorobenzene spectrum and H is the difference between F and G. Note that when calculated spectra are subtracted from experimental, resonances form the other molecules are readily visible. Resonances marked with an * are from TCB. Resonances indicated with a ★ are impurities and the resonance indicated with a ◇ is from the partially protonated acetone used for a field/frequency lock. The calculated spectrum of TCB is not displayed. For high-resolution spectra intensities of the calculated spectrum closely correspond with those of the experimental spectrum.

$$H = - \sum_i \nu_i I_i^Z + \sum_i \sum_{j>i} [(J_{ij} + 2D_{ij})I_i^Z I_j^Z$$

$$+ \tfrac{1}{2}(J_{ij} - D_{ij})(I_i^+ I_j^- + I_i^- I_j^+)], \qquad [1]$$

where I^Z, I^+, and I^- are the spin operators, ν_i is the resonance frequency of nucleus i, and J_{ij} and D_{ij} are the indirect and dipolar coupling constants between nuclei i and j on the same molecule.

Determining spectral parameters from a spectrum may be extremely difficult; for example, o-xylene has three resonance frequencies and 10 dipolar couplings. Without accurate estimates of such parameters, it may require months to analyze a spectrum. However, estimates of spectral parameters can be obtained from analysis of MQ NMR spectra. MQ spectra tend to be easier than high-resolution spectra to analyze since there are comparatively fewer lines (3, 4, 22–26). However, broad peaks, poor resolution, and a lack of correlation between the intensities of calculated and experimental frequencies can make analysis of the MQ spectrum somewhat difficult, but not as difficult as analysis of the high-resolution spectrum.

In a typical method of spectral analysis, the MQ spectrum is analyzed first to obtain estimates of spectral parameters and the high-resolution spectrum is then analyzed to obtain the more accurate spectral parameters. The spectral parameters are adjusted in a least-squares routine by minimizing the square of the difference between calculated and experimental frequencies; within the least-squares routine, the nonequivalent D_{ij} are adjusted independently. However, because of the sparsity of lines, fitting D_{ij} independently may be problematic when analyzing MQ and some simple high-resolution spectra; spectral parameters may be meaningless even though the spectrum appears to be "fit." The problem can be overcome by realizing that D_{ij} can be related to molecular orientational order parameters $S_{\beta\xi}$ and structural parameters.

For the essentially inflexible molecules in this study the D_{ij} can be calculated from

$$D_{ij} = -\frac{\mu_0 \hbar \gamma_i \gamma_j}{8\pi^2} \sum_{\beta\xi} S_{\beta\xi} \left\langle \frac{\cos\theta_\beta \cos\theta_\xi}{r_{ij}^3} \right\rangle, \qquad [2]$$

where the angle brackets indicate a statistical average over all intramolecular motions, β and ξ are the molecular fixed x, y, and z axes, r_{ij} is the internuclear distance between nuclei i and j, and θ_β and θ_ξ are the angles between the internuclear vector and the molecular β and ξ axes. $S_{\beta\xi}$ is equal to $\tfrac{1}{2}\langle 3\cos\theta_{\beta Z}\cos\theta_{\xi Z} - \delta_{\beta\xi}\rangle$ where the angle brackets indicate a statistical average over all orientations of the molecule and $\theta_{\beta Z}$ and $\theta_{\xi Z}$ are the angles between the magnetic field direction Z and molecular β and ξ axes.

The least-squares routine has been modified so that $S_{\beta\xi}$, structural parameters, and/or D_{ij} for an arbitrary molecule can be adjusted independently; within the fitting routine D_{ij} are

calculated from $S_{\beta\xi}$ and structural parameters. If a D_{ij} is to be adjusted independently, it is not calculated but allowed to freely vary. Thus the dependence of the D_{ij} on $S_{\beta\xi}$ is removed. Derivatives of the line positions with respect to D_{ij} are calculated analytically. The derivatives of the line positions with respect to $S_{\beta\xi}$ and structural parameters are calculated using finite difference and structural data obtained from other studies. This is similar to a fitting method presented in Refs. (4) and (24); however, the fitting routine described in Refs. (4) and (24) was designed for a specific molecule and only allowed for adjustment of S_{zz} and $S_{xx} - S_{yy}$. It should be noted that line positions are very sensitive to minor changes in structural parameters and thus reasonably good estimates of proton positions are required for this method to succeed. With this new version of the least-squares program it is possible to adjust D_{ij} independently from $S_{\beta\xi}$ and structural parameters; this is useful, for example, if the molecule has internal rotations where the potential barrier is uncertain or if specific structural parameters are not well known. By using the new least-squares program the number of adjustable parameters required to analyze the spectrum is significantly reduced which greatly simplifies the analysis; o-xylene has 10 independent D_{ij} which require adjustment but only 2 independent $S_{\beta\xi}$ and a few structural parameters which require adjustment. The analysis of the very complex o-xylene 8Q spectra required less than a week. In contrast, the analysis of the complex 8Q spectra of p-xylene (reported in a previous paper (27)) which was analyzed without the aid of the new version of the least-squares program required a month.

For each sample there were at least three solutes which contributed to the high-resolution spectrum. Resonances from any one particular solute could not be easily identified (e.g., Fig. 1A). We present below a strategy for dealing with such complicated situations and the analysis of these complex spectra is exemplified for Sample 13 (o-xylene/o-chlorotoluene/o-dichlorobenzene/TCB in ZLI 1132) in Figs. 1 and 2. For samples which contained o- or m-xylene the 8Q spectrum was analyzed first using the modified version of the fitting program. $S_{\beta\xi}$ and resonance frequencies were adjusted until a reasonable fit to the 8Q spectrum was obtained. Then using the original version of the MQ analysis program D_{ij} and resonance frequencies were determined. The values obtained are presented in Table 2 (in square brackets) for Sample 13 and in Table 3 for the other samples. The calculated 8Q spectrum is compared with the experimental in Fig. 2. The high-resolution spectrum predicted from the analysis of the 8Q spectrum of o-xylene is displayed in Fig. 1B. By comparing the experimental Fig. 1A with the predicted one there are many resonances which can be immediately assigned. In most cases only minor adjustments to the spectral parameters determined from the 8Q analysis were required to fit the high-resolution spectrum, even with the presence of resonances from the other molecules. The spectral parameters obtained from the fit to the high-resolution spectra are presented in Table 2 for Sample 13 and in the Table 3 for
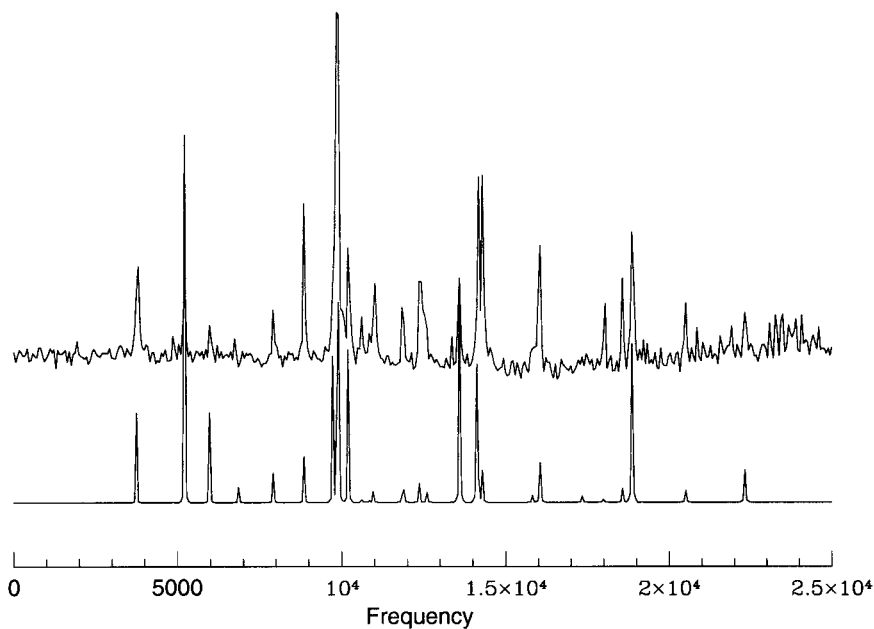
FIG. 2. The experimental +8-quantum spectrum (top) is of Sample 13. Only resonances from o-xylene are observed; for an n-spin-$\frac{1}{2}$ system, n is the highest attainable MQ order. The calculated +8-quantum spectrum of o-xylene (from values in square brackets from Table 2) is on the bottom. Note that the linewidth in the experimental spectrum is approximately 50 Hz and the intensities of the calculated spectrum do not correspond with those of the experimental.

the other samples. Figures 1B and 1C compare the calculated high-resolution spectra of the prediction from the fit to the 8Q and the fit to the experimental high-resolution spectrum.

After analysis of the high-resolution spectrum the resultant fitted spectrum of either o- or m-xylene was subtracted from the experimental one and resonances from the other solutes could be identified (see Fig. 1D). For samples which did not contain o- or m-xylene analysis of the high-resolution spectrum begins with this step in the strategy. The initial dipolar couplings for the o- or m-chlorotoluenes were calculated from the order parameters of o- or m-xylene. The off-diagonal order parameter was set to zero. In the spectra of the o- and m-chlorotoluene, there is a group of resonances up frequency from the main portion of the spectrum (for o-chlorotoluene see Figs. 1D and 1E). The fine structure is due to the D_{ij} between methyl and ring protons and by assigning some of these resonances certain D_{ij} could be roughly determined which aided in the identification of resonances in the main portion of the spectrum. Once a few resonances within the main portion of the spectrum were correctly assigned the spectrum was analyzed quickly.

Again after the high-resolution spectrum of chlorotoluene was fit and subtracted from the experimental spectrum, resonances from dichlorobenzene were easily identified (e.g., Figs. 1F and 1G). In Fig. 1H only a few resonances remain after the fitted o-xylene, o-chlorotoluene, and o-dichlorobenzene spectra are subtracted from the experimental one. The remaining

resonances correspond to TCB, acetone-d_5 (from lock), and an unknown impurity.

We employed a unique strategy whereby we analyzed the most complex spectrum first by roughly determining molecular parameters and eventually spectral parameters from a fit to the 8Q spectrum; spectral parameters from this fit were used as initial estimates for the analysis of the high-resolution spectrum. The estimates were accurate enough to readily assign lines and easily solve the complex spectrum. The calculated spectrum was subtracted from the experimental one and resonances corresponding to the other solutes were easily identified and the spectral parameters determined. This very successful strategy was employed for analysis of high-resolution spectra and spectral parameters are presented in Tables 2 and 3.

We wish to emphasize that one of the objectives of this study is to determine accurate $S_{\beta\xi}$ and structural parameters and thus precise D_{ij} are required. Because of the relatively poor resolution (linewidth $\approx$ 50 Hz), possible correlations between some D_{ij}, and sparsity of lines in the MQ spectra, the D_{ij} from analysis of the MQ spectra are rather imprecise. Thus it is prudent to analyze the complex high-resolution spectra. Some of the D_{ij} from the MQ analysis differ significantly (e.g., from the data presented in Table 3, for Sample 4 o-xylene in ZLI 1132 the D_{12} and D_{56} differ by about 80 Hz and for Sample 5 o-xylene in 55 wt% 1132/EBBA the D_{13}, D_{23}, and D_{25} differ by up to 100 Hz) from those determined from the high-

TABLE 2
Fitting Parameters and RMS Errors from Analysis of High-Resolution and MQ NMR Spectra of Sample 13[a]

Parameter[b]	o-Dichlorobenzene[c]	o-Chlorotoluene[d]	o-Xylene[e]	TCB
$D_{1,2}$	−1200.30(09)	−1145.14(06)	−1147.51(03) [−1157.53]	198.59(01)
$D_{1,3}$	−163.97(11)	−169.31(10)	−175.93(04) [−169.98]	—
$D_{1,4}$	−84.76(21)	−94.01(07)	−101.17(06) [−101.20]	—
$D_{1,5}$	—	−102.17(04)	−103.08(02) [−108.11]	—
$D_{1,8}$	—	—	−710.74(02) [−711.40]	—
$D_{2,3}$	−649.78(21)	−720.68(06)	−774.72(05) [−789.86]	—
$D_{2,4}$	—	−170.79(11)	—	—
$D_{2,5}$	—	−83.95(04)	−82.10(03) [−80.59]	—
$D_{2,8}$	—	—	−139.95(03) [−144.10]	—
$D_{3,4}$	—	−1177.36(06)	—	—
$D_{3,5}$	—	−144.66(03)	—	—
$D_{4,5}$	—	−718.62(03)	—	—
$D_{5,6}$	—	1533.32(01)	1495.65(01) [1507.09]	—
$J_{1,2}$	8.06	7.93(09)	7.52(07) [—]	—
$J_{1,3}$	1.52	1.64	1.29(08) [—]	—
$J_{1,4}$	0.35	0.29	0.55(10) [—]	—
$J_{1,5}$	—	0.40	0.47(05) [—]	—
$J_{1,8}$	—	—	−0.66(04) [—]	—
$J_{2,3}$	7.45	7.54	7.20(10) [—]	—
$J_{2,4}$	—	1.47(11)	—	—
$J_{2,5}$	—	−0.60	−0.57(06) [—]	—
$J_{2,8}$	—	—	0.27(06) [—]	—
$J_{3,4}$	—	7.57(09)	—	—
$J_{3,5}$	—	0.40	—	—
$J_{4,5}$	—	−0.82(05)	—	—
$J_{5,8}$	—	—	0.48(02) [—]	—
$(\nu_1)^f$	−2392.96(27)	−2371.91(09)	−2363.55(05) [−2363.6]	−2317.02(02)
$(\nu_2)^f$	−2480.69(29)	−2441.83(09)	−2432.16(06) [−2432.2]	—
$(\nu_3)^f$	—	−2470.72(06)	—	—
$(\nu_4)^f$	—	−2391.22(06)	—	—
$(\nu_5)^f$	—	258.00(03)	−204.36(02) [−207.5]	—
RMS error	0.421	0.301	0.419 [7.79]	0.028
Number of lines assigned	18	188	437 [23]	3

[a] For atom numbering refer to Fig. 3. Numbers in round brackets are standard deviations in the last two reported digits of varied parameters. Equivalent D_{ij} are not reported.

[b] Dipolar couplings, J couplings, resonance frequencies, and RMS errors are in hertz.

[c] J couplings are not varied during analysis of spectrum. Values taken from Ref. (53).

[d] Some J couplings are not varied during analysis of spectrum. Values taken from Ref. (54).

[e] Values in square brackets are from the analysis of the 8-quantum spectrum. J couplings were set to zero for the MQ analysis.

[f] Frequency is referenced to an arbitrary zero and is increasing to high field.

resolution spectra. These discrepancies would have a significant effect on the calculated $S_{\beta\xi}$ and structural parameters.

IV. MOLECULAR STRUCTURE AND ORDER PARAMETERS

A. Calculations

Except for o-chlorotoluene, relative positions of the nuclei (Table 4) and $S_{\beta\xi}$ (Tables 5 and 6) were calculated from a simultaneous fit to the D_{ij} determined for the solute in all three liquid crystals. Since the spectrum of o-chlorotoluene in EBBA (Sample 3) was of poor quality, molecular parameters for o-chlorotoluene were calculated using D_{ij} from o-chlorotolu-

ene dissolved in ZLI 1132 and 55 wt% ZLI 1132/EBBA. The $S_{\beta\xi}$ of o-chlorotoluene in EBBA were calculated using the structure determined from the other liquid crystals. Calculations were performed using Eq. [2], a priori estimates (28), and a least-squares minimization routine NL2SNO (29), which minimizes the square of the difference between experimental and calculated D_{ij}. The a priori estimates are values of structural parameters (taken from other studies) that have an associated error and are adjusted in the least-squares routine; large deviations from the a priori estimates are discouraged by the least-squares criteria.

Dipolar couplings within the methyl group and between methyl and ring protons are an average over the methyl rota-

TABLE 3
Fitting Parameters and RMS Errors from Analysis of High-Resolution and MQ NMR Spectra[a]

Solute	Parameter[b]	Liquid crystal		
		Merck ZLI 1132	55 wt% ZLI 1132/EBBA	EBBA
		Sample 1	Sample 2	Sample 3
o-Dichlorobenzene	$D_{1,2}$	−1182.09(05)	−887.83(02)	−791.22(03)
	$D_{1,3}$	−161.98(06)	−113.68(03)	−68.16(03)
	$D_{1,4}$	−84.41(11)	−55.62(06)	−16.93(18)
	$D_{2,3}$	−643.54(12)	−427.11(06)	−135.99(18)
	$(J_{1,2})^c$	8.06	8.06	8.06
	$(J_{1,3})^c$	1.52	1.52	1.52
	$(J_{1,4})^c$	0.35	0.35	0.35
	$(J_{2,3})^c$	7.45	7.45	7.45
	$(\nu_1)^d$	−2160.66(15)	−2334.90(08)	−2436.27(23)
	$(\nu_2)^d$	−2245.63(14)	−2373.25(08)	−2476.69(23)
	RMS error	0.230	0.125	0.103
	Number of lines assigned	19	20	14
o-Chlorotoluene	$D_{1,2}$	−1124.97(05)	−910.64(05)	−950.84(05)
	$D_{1,3}$	−166.82(09)	−122.84(10)	−91.58(28)
	$D_{1,4}$	−92.91(07)	−59.00(09)	−20.37(28)
	$D_{1,5}$	−100.78(04)	−68.02(05)	−44.95(27)
	$D_{2,3}$	−712.98(06)	−452.76(07)	−153.44(27)
	$D_{2,4}$	−168.91(10)	−110.81(10)	−60.99(29)
	$D_{2,5}$	−82.72(04)	−61.45(05)	−56.53(27)
	$D_{3,4}$	−1159.40(06)	−866.88(06)	−810.02(06)
	$D_{3,5}$	−142.29(03)	−113.15(03)	−120.61(28)
	$D_{4,5}$	−705.83(03)	−573.11(03)	−628.72(04)
	$D_{5,6}$	1510.26(02)	1121.67(02)	1031.86(02)
	$J_{1,2}$	8.24(08)	7.86(10)	8.15(31)
	$(J_{1,3})^e$	1.64	1.64	1.64
	$(J_{1,4})^e$	0.29	0.29	0.29
	$(J_{1,5})^e$	0.40	0.40	0.40
	$(J_{2,3})^e$	7.54	7.54	7.54
	$J_{2,4}$	1.62(11)	1.32(12)	2.04(20)
	$(J_{2,5})^e$	−0.60	−0.60	−0.60
	$J_{3,4}$	7.58(07)	7.55(09)	7.54(11)
	$(J_{3,5})^e$	0.40	0.40	0.40
	$J_{4,5}$	−0.83(05)	−0.97(06)	−0.77(07)
	$(\nu_1)^d$	−2139.28(09)	−2301.41(12)	−2371.73(70)
	$(\nu_2)^d$	−2206.71(09)	−2333.93(12)	−2420.63(69)
	$(\nu_3)^d$	−2234.88(06)	−2365.16(06)	−2457.61(08)
	$(\nu_4)^d$	−2157.64(06)	−2289.40(07)	−2339.36(08)
	$(\nu_5)^d$	−19.02(03)	−106.06(04)	−193.17(04)
	RMS error	0.309	0.337	0.379
	Number of lines assigned	220	200	156
TCB	$D_{1,3}$	195.81(04)	148.90(05)	131.33(01)
	$(\nu_1)^d$	−2084.23(09)	−2232.41(13)	−2317.31(01)
	RMS error	0.091	0.131	0.002
	Number of lines assigned	3	3	3
		Sample 4	Sample 5	Sample 6
o-Dichlorobenzene	$D_{1,2}$	−1208.43(03)	−987.27(06)	−877.21(08)
	$D_{1,3}$	−165.02(04)	−124.94(07)	−74.47(09)
	$D_{1,4}$	−85.64(07)	−60.29(15)	−18.97(55)
	$D_{2,3}$	−655.06(07)	−464.04(16)	−143.58(54)
	$(J_{1,2})^c$	8.06	8.06	8.06
	$(J_{1,3})^c$	1.52	1.52	1.52
	$(J_{1,4})^c$	0.35	0.35	0.35

TABLE 3—*Continued*

		Liquid crystal		
Solute	Parameter[b]	Merck ZLI 1132	55 wt% ZLI 1132/EBBA	EBBA
	$(J_{2,3})^c$	7.45	7.45	7.45
	$(\nu_1)^d$	−2562.42(09)	−3495.31(19)	−3682.95(68)
	$(\nu_2)^d$	−2651.38(09)	−3552.21(19)	−3744.86(68)
	RMS error	0.154	0.246	0.248
	Number of lines assigned	20	17	12
o-Xylene[f]	$D_{1,2}$	−1157.11(03) [−1083.9]	−979.16(03) [−987.9]	−968.23(03) [−967.2]
	$D_{1,3}$	−177.32(04) [−177.0]	−140.23(04) [−240.7]	−116.66(04) [−115.2]
	$D_{1,4}$	−102.07(05) [−90.8]	−76.60(06) [−53.0]	−54.33(07) [−62.2]
	$D_{1,5}$	−103.89(03) [−79.6]	−83.42(04) [−90.5]	−72.64(04) [−69.8]
	$D_{1,8}$	−716.87(02) [−696.6]	−619.37(03) [−616.0]	−641.37(03) [−638.2]
	$D_{2,3}$	−780.36(05) [−705.7]	−588.10(06) [−505.4]	−419.47(05) [−419.8]
	$D_{2,5}$	−82.70(03) [−58.6]	−69.81(04) [13.4]	−68.71(04) [−76.4]
	$D_{2,8}$	−141.16(03) [−156.3]	−121.96(04) [−189.6]	−125.94(04) [−118.4]
	$D_{5,6}$	1508.17(01) [1425.5]	1271.18(01) [1284.2]	1247.47(01) [1245.3]
	$D_{5,8}$	−252.05(01) [−237.4]	−184.40(01) [−183.0]	−117.93(01) [−119.5]
	$J_{1,2}$	7.50(06) [—]	7.77(07) [—]	7.44(08) [—]
	$J_{1,3}$	1.50(06) [—]	1.41(07) [—]	1.37(07) [—]
	$J_{1,4}$	0.54(09) [—]	0.57(11) [—]	0.27(11) [—]
	$J_{1,5}$	0.44(05) [—]	0.43(06) [—]	0.61(08) [—]
	$J_{1,8}$	−0.69(04) [—]	−0.73(05) [—]	−0.74(05) [—]
	$J_{2,3}$	7.39(09) [—]	7.50(10) [—]	7.46(10) [—]
	$J_{2,5}$	−0.86(06) [—]	−0.69(07) [—]	−0.56(09) [—]
	$J_{2,8}$	0.37(06) [—]	0.37(07) [—]	0.26(08) [—]
	$J_{5,8}$	0.42(02) [—]	0.40(03) [—]	0.44(03) [—]
	$(\nu_1)^d$	−2534.15(05) [−2533.7]	−3429.84(05) [−3429.7]	−3557.98(06) [−3556.7]
	$(\nu_2)^d$	−2603.67(05) [−2592.6]	−3500.48(05) [−3507.6]	−3649.12(05) [−3641.0]
	$(\nu_5)^d$	−377.71(02) [−369.7]	−1236.73(03) [−1232.8]	−1376.92(03) [−1373.6]
	RMS error	0.377 [9.18]	0.413 [14.88]	0.403 [3.02]
	Number of lines assigned	501 [22]	427 [22]	374 [24]
TCB	$D_{1,3}$	200.07(07)	164.55(01)	145.88(02)
	$(\nu_1)^d$	−2486.79(17)	−3396.67(01)	−3566.11(04)
	RMS error	0.174	0.011	0.038
	Number of lines assigned	3	3	3
		Sample 7	Sample 8	Sample 9
m-Dichlorobenzene	$D_{1,2}$	−1342.52(05)	−1122.42(05)	−1095.21(05)
	$D_{1,3}$	−318.61(11)	−275.32(11)	−296.05(12)
	$D_{1,4}$	−144.36(07)	−99.39(07)	−37.55(07)
	$D_{2,4}$	−56.33(09)	−26.31(10)	32.63(10)
	$(J_{1,2})^g$	8.10	8.10	8.10
	$(J_{1,3})^g$	2.00	2.00	2.00
	$(J_{1,4})^g$	1.80	1.80	1.80
	$(J_{2,4})^g$	0.40	0.40	0.40
	$(\nu_1)^d$	−2339.57(08)	−2435.74(08)	−3850.49(09)
	$(\nu_2)^d$	−2240.18(14)	−2328.10(14)	−3677.43(14)
	$(\nu_4)^d$	−2022.96(10)	−2137.61(11)	−3453.63(11)
	RMS error	0.265	0.262	0.270
	Number of lines assigned	28	26	26
m-Chlorotoluene	$D_{1,2}$	−1559.06(23)	−1247.31(56)	−1144.35(36)
	$D_{1,3}$	−339.72(10)	−287.14(14)	−303.61(12)
	$D_{1,4}$	−103.68(10)	−80.27(18)	−54.05(11)
	$D_{1,5}$	−90.38(06)	−77.53(10)	−83.24(07)
	$D_{2,3}$	−1249.99(30)	−1079.54(68)	−1157.04(35)
	$D_{2,4}$	−44.05(07)	−22.98(09)	19.81(08)
	$D_{2,5}$	−72.88(07)	−59.46(10)	−50.72(14)
	$D_{3,4}$	−168.14(09)	−116.83(18)	−54.63(12)
	$D_{3,5}$	−177.47(10)	−118.44(12)	−12.42(12)
	$D_{4,5}$	−919.22(03)	−770.59(18)	−798.88(04)
	$D_{5,6}$	1655.06(02)	1426.57(10)	1531.65(03)

TABLE 3—*Continued*

Solute	Parameter[b]	Liquid crystal		
		Merck ZLI 1132	55 wt% ZLI 1132/EBBA	EBBA
	$(J_{1,2})^h$	8.09	8.09	8.09
	$(J_{1,3})^h$	1.10	1.10	1.10
	$(J_{1,4})^h$	2.71	2.71	2.71
	$(J_{1,5})^h$	0.00	0.00	0.00
	$(J_{2,3})^h$	7.53	7.53	7.53
	$(J_{2,4})^h$	0.39	0.39	0.39
	$J_{2,5}$	−0.05(14)	−0.02(20)	0.57(27)
	$(J_{3,4})^h$	1.65	1.65	1.65
	$J_{3,5}$	−1.10(20)	−0.75(27)	−0.50(27)
	$J_{4,5}$	−0.84(06)	−0.42(09)	−0.47(08)
	$(\nu_1)^d$	−2277.75(13)	−2375.82(22)	−3775.89(19)
	$(\nu_2)^d$	−2198.39(10)	−2290.13(14)	−3620.80(12)
	$(\nu_3)^d$	−2322.36(12)	−2377.84(23)	−3715.48(20)
	$(\nu_4)^d$	−2005.36(07)	−2106.64(09)	−3397.48(08)
	$(\nu_5)^d$	−54.42(04)	−91.77(06)	−1401.47(06)
	RMS error	0.350	0.426	0.409
	Number of lines assigned	159	134	146
TCB	$D_{1,3}$	205.51(02)	165.28(06)	142.13(06)
	$(\nu_1)^d$	−2137.15(05)	−2234.33(14)	−3586.12(15)
	RMS error	0.046	0.148	0.158
	Number of lines assigned	3	3	3
		Sample 10	Sample 11	Sample 12
m-Dichlorobenzene	$D_{1,2}$	−1288.85(03)	−1029.43(02)	−1151.31(05)
	$D_{1,3}$	−305.41(07)	−252.94(05)	−311.24(11)
	$D_{1,4}$	−139.17(04)	−90.88(03)	−39.17(06)
	$D_{2,4}$	−54.49(07)	−23.63(04)	34.71(09)
	$(J_{1,2})^g$	8.10	8.10	8.10
	$(J_{1,3})^g$	2.00	2.00	2.00
	$(J_{1,4})^g$	1.80	1.80	1.80
	$(J_{2,4})^g$	0.40	0.40	0.40
	$(\nu_1)^d$	−3057.83(06)	−3684.85(04)	−3842.65(08)
	$(\nu_2)^d$	−2962.75(09)	−3583.56(06)	−3661.69(13)
	$(\nu_4)^d$	−2757.10(07)	−3417.19(04)	−3419.55(10)
	RMS error	0.198	0.127	0.240
	Number of lines assigned	31	28	26
m-Xylene[f]	$D_{1,2}$	−1382.31(04) [−1372.0]	−1080.34(03) [−1139.49]	−1211.96(07) [−1204.28]
	$D_{1,3}$	−334.82(27) [−323.3]	−263.28(21) [−284.55]	−308.63(53) [−313.64]
	$D_{1,4}$	−128.69(04) [−120.4]	−95.53(03) [−96.28]	−77.29(06) [−76.55]
	$D_{1,5}$	−99.84(04) [−118.4]	−78.03(03) [−82.87]	−87.66(11) [−87.67]
	$D_{1,8}$	−225.32(03) [−198.9]	−159.57(04) [−155.71]	−80.20(10) [−79.16]
	$D_{2,4}$	−38.93(07) [−44.4]	−25.50(06) [−21.86]	0.45(09) [1.31]
	$D_{2,5}$	−89.22(04) [−97.9]	−67.51(03) [−68.98]	−62.34(04) [−61.60]
	$D_{4,5}$	−884.83(01) [−885.2]	−697.73(01) [−744.20]	−821.09(01) [−820.94]
	$D_{5,6}$	1827.38(01) [1825.2]	1426.23(01) [1510.85]	1596.53(01) [1597.69]
	$D_{5,8}$	−127.65(01) [−126.7]	−100.66(01) [−107.32]	−118.42(01) [−118.43]
	$J_{1,2}$	7.69(20) [—]	7.24(17) [—]	7.06(40) [—]
	$J_{1,3}$	1.03(12) [—]	0.87(08) [—]	0.72(99) [—]
	$J_{1,4}$	1.70(08) [—]	1.87(07) [—]	1.76(11) [—]
	$J_{1,5}$	−0.55(08) [—]	−0.48(07) [—]	−0.20(22) [—]
	$J_{1,8}$	−0.70(06) [—]	−0.70(08) [—]	−0.97(24) [—]
	$J_{2,4}$	0.53(13) [—]	0.46(11) [—]	0.63(17) [—]
	$J_{2,5}$	0.30(06) [—]	0.32(05) [—]	0.31(08) [—]
	$J_{4,5}$	−0.77(02) [—]	−0.71(02) [—]	−0.73(02) [—]
	$J_{5,8}$	−0.22(02) [—]	−0.22(01) [—]	−0.30(02) [—]

TABLE 3—*Continued*

		Liquid crystal		
Solute	Parameter[b]	Merck ZLI 1132	55 wt% ZLI 1132/EBBA	EBBA
	$(\nu_1)^d$	−2975.53(03) [−2975.4]	−3571.06(03) [−3571.1]	−3647.19(06) [−3647.2]
	$(\nu_2)^d$	−2907.24(07) [−2917.5]	−3536.71(05) [−3561.6]	−3571.89(07) [−3579.3]
	$(\nu_4)^d$	−2711.86(04) [−2708.1]	−3353.38(04) [−3352.1]	−3352.63(05) [−3361.7]
	$(\nu_5)^d$	−767.40(02) [−770.8]	−1336.21(02) [−1358.2]	−1395.72(02) [−1400.0]
	RMS error	0.304 [5.85]	0.305 [10.01]	0.384 [11.48]
	Number of lines assigned	402 [24]	501 [25]	440 [22]
TCB	$D_{1,3}$	197.80(04)	151.74(05)	149.66(07)
	$(\nu_1)^d$	−2860.41(11)	−3497.34(13)	−3565.45(18)
	RMS error	0.119	0.132	0.186
	Number of lines assigned	3	3	3

[a] For atom numbering refer to Fig. 3. Numbers in round brackets are standard deviations in the last two reported digits of varied parameters.

[b] Dipolar couplings, *J* couplings, resonance frequencies, and RMS errors are in hertz.

[c] Parameters not varied during analysis of spectrum. Values taken from Ref. (*53*).

[d] Frequency is referenced to an arbitrary zero and is increasing to high field.

[e] Parameters not varied during analysis of spectrum. Values taken from Ref. (*54*).

[f] Values in square brackets are from the analysis of the 8-quantum spectrum. *J* couplings were set to zero for the MQ analysis.

[g] Parameters not varied during analysis of spectrum. Values taken from Ref. (*60*).

[h] Parameters not varied during analysis of spectrum. Values taken from Ref. (*61*).

tion; D_{ij} were calculated for each 15° rotation of the methyl group. For *o*-xylene we used the Case II rotational potential and potential parameters reported by Burnell and Diehl (*30*); the potential was expanded as a Fourier series about the rotation angles α_1 and α_2 of the two methyl groups

$$V = V_3(1 - \cos 3\alpha_+ \cos 3\alpha_-) + V_a \cos 6\alpha_+$$
$$+ V_g \cos 6\alpha_- + V_6(1 - \cos 6\alpha_+ \cos 6\alpha_-) + \cdots,$$

[3]

where $\alpha_+ = \frac{1}{2}(\alpha_1 + \alpha_2)$, $\alpha_- = \frac{1}{2}(\alpha_1 - \alpha_2)$, and $V_3 = 8.4$, $V_a = 1.21$, $V_g = 1.55$, and $V_6 = 0.0$ kJ/mol. The potential minimum $\alpha_1 = 0$ (and $\alpha_2 = 0$) is where proton 5 (and 10) of the methyl group is in the plane of the benzene ring and adjacent to proton 4 (and 1) (see Fig. 3 for atom numbering). For *o*-chlorotoluene only the threefold potential is used; α_2, V_a, V_g, and V_6 are fixed at zero; V_3 is fixed at 6 kJ/mol (*31, 32*). For *m*-chlorotoluene the methyl group was modeled with a sixfold potential $V = V_6(1 - \cos 6\alpha)/2$ where V_6 is fixed at 60 J/mol (*31*) and the minimum in the potential is where one proton is perpendicular to the benzene ring. For *m*-xylene each methyl group was independently modeled with this same sixfold potential.

Since the D_{ij} are related to $\langle r^{-3} \rangle$, molecular vibrations will affect the experimental observations. The effect of vibrations on the experimental data will be different for different experimental techniques. Therefore to compare data determined from various experimental methods results

should be "vibrationally corrected."[1] The effect on the dipolar couplings from normal mode vibrations is calculated using a Taylor expansion of D_{ij} about the equilibrium position

$$D_{ij} = D_{ij}^e + \sum_\delta \left(\frac{\partial D_{ij}}{\partial \delta} \right)_e \langle \Delta\delta \rangle$$
$$+ \frac{1}{2} \sum_\delta \left(\frac{\partial^2 D_{ij}}{\partial \delta^2} \right)_e \langle \Delta\delta^2 \rangle + \cdots,$$

[4]

where D_{ij}^e is the dipolar coupling at equilibrium, δ is the x', y', and z' internuclear axes, $\langle \Delta\delta \rangle$ is the average vibrational amplitude (anharmonic) in the δ direction, and $\langle \Delta\delta^2 \rangle$ is the corresponding mean-square amplitude (harmonic). The average structure determined by subtracting the contributions from harmonic vibrations, the r_α structure, has been established as a suitable physical basis for comparing results (*38–41*). The average r_α structures determined from different techniques are usually in good agreement with each other. A calculation of $S_{\beta\xi}$ and the r_α structural parameters (Tables 4, 5, and 6) was performed using

[1] In this study molecules are in an anisotropic condensed phase; the anisotropy of the phase affects vibrational motions (orientational–vibrational correlations). Corrections have been calculated for simple molecules such as CH_4 (*33*), acetylene (*34*), benzene (*35*), chlorobenzene (*35*), and CH_3F (*36*). For molecules with a large $S_{\beta\xi}$, the orientational–vibrational correlations will have a very small effect ($\approx 0.2\%$) on the observed D_{ij} (*35, 37*). Normal mode bond vibrations have a larger effect ($\approx 2.0\%$) on the observed D_{ij} (*37*) and thus we have attempted to correct for these effects only.

TABLE 4
Structural Parameters from Fits to Dipolar Couplings[a]

Parameter[b]		o-Dichlorobenzene	o-Chlorotoluene	o-Xylene	m-Dichlorobenzene	m-Chlorotoluene	m-Xylene	TCB[c]
r(C1-C2)	n	1.3799(15)	1.3849(30)	1.3751(59)	1.4039(05)	1.3846(12)	1.3991(42)	1.3908
	v	1.3793(13)	1.3839(34)	1.3764(62)	1.4041(06)	1.3857(14)	1.4013(34)	—
r(C2-C3)	n	1.4025(15)	1.3982(23)	1.3820[e]	1.4039(05)	1.3818(12)	1.3991(42)	1.3908
	v	1.4001(13)	1.3938(26)	1.3820[e]	1.4041(06)	1.3830(14)	1.4013(34)	—
r(C3-C4)	n	1.3799(15)	1.3890(30)	1.3751(59)	1.3921(06)	1.3880(12)	1.3884(23)	1.3908
	v	1.3793(13)	1.3909(33)	1.3764(62)	1.3920(06)	1.3889(15)	1.3896(22)	—
r(C4-C5)	n	1.3822(16)	1.3840(30)	1.3771(58)	(1.3872)[d]	1.3901(12)	(1.3941)[d]	1.3908
	v	1.3826(14)	1.3836(34)	1.3764(62)	(1.3872)[d]	1.3904(15)	(1.3930)[d]	—
r(C5-C6)	n	(1.4050)[d]	(1.3850)[d]	(1.3880)[d]	(1.3872)[d]	(1.3860)[d]	(1.3941)[d]	1.3908
	v	(1.4054)[d]	(1.3839)[d]	(1.3924)[d]	(1.3872)[d]	(1.3870)[d]	(1.3930)[d]	—
r(C6-C1)	n	1.3822(16)	1.385[e]	1.3771(58)	1.3921(06)	1.382[e]	1.3884(23)	1.3908
	v	1.3826(14)	1.385[e]	1.3764(62)	1.3920(06)	1.382[e]	1.3896(22)	—
r(C1-H1)	n	1.0819(15)	1.0754(30)	1.0732(18)	1.0846(05)	1.0860(12)	1.0793(41)	1.0940
	v	1.0826(13)	1.0753(33)	1.0726(19)	1.0847(06)	1.0886(14)	1.0776(33)	—
r(C2-X)	n	1.0890(15)	1.0830(36)	1.0912(59)	1.0913(06)	1.0898(12)	1.0898(44)	1.7326
	v	1.0883(13)	1.0842(39)	1.0944(60)	1.0912(06)	1.0899(14)	1.0916(36)	—
r(C3-H3)	n	1.0890(15)	1.0909(35)	1.0912(59)	1.0846(05)	1.0838(12)	1.0793(41)	1.0940
	v	1.0883(13)	1.0909(39)	1.0944(60)	1.0847(06)	1.0845(14)	1.0776(33)	—
r(C4-X)	n	1.0819(15)	1.0733(19)	1.0732(18)	1.7355[e]	1.5096(22)	1.5139(20)	1.7326
	v	1.0826(13)	1.0726(21)	1.0726(19)	1.7355[e]	1.5140(26)	1.5193(20)	—
r(C5-X)	n	1.733[e]	1.5202(48)	1.5288(20)	1.0911(06)	1.0860(12)	1.0913(22)	1.0940
	v	1.733[e]	1.5250(53)	1.5294(21)	1.0910(06)	1.0915(15)	1.0883(21)	—
r(C6-X)	n	1.733[e]	1.751[e]	1.5288(20)	1.7355[e]	1.746[e]	1.5139(20)	1.7326
	v	1.733[e]	1.751[e]	1.5294(21)	1.7355[e]	1.746[e]	1.5193(20)	—
r(C7-H5)	n	—	1.1051(18)	1.1054(20)	—	1.1014(07)	1.1083(09)	—
	v	—	1.1037(20)	1.1045(18)	—	1.0942(09)	1.1006(09)	—
∢(C1C2C3)	n	119.54(07)	119.10(26)	118.97(13)	(120.59)[d]	120.77(10)	(121.02)[d]	122.00
	v	119.65(06)	118.69(34)	118.97(14)	(120.65)[d]	120.85(12)	(120.84)[d]	—
∢(C2C3C4)	n	119.54(07)	118.94(19)	118.97(13)	118.40(06)	119.63(13)	118.75(28)	118.00
	v	119.65(06)	119.57(30)	118.97(14)	118.37(06)	119.84(15)	119.17(23)	—
∢(C3C4C5)	n	121.01(12)	122.00[e]	122.24(15)	122.40(11)	119.67(19)	121.34(26)	122.00
	v	120.86(10)	122.00[e]	122.35(16)	122.34(11)	119.55(22)	120.19(22)	—
∢(C4C5C6)	n	(119.43)[d]	117.50[e]	(118.78)[d]	(117.80)[d]	(118.72)[d]	(118.78)[d]	118.00
	v	(119.48)[d]	117.50[e]	(118.67)[d]	(117.89)[d]	(119.06)[d]	(120.42)[d]	—
∢(C5C6C1)	n	(119.43)[d]	121.40[e]	(118.78)[d]	122.40(11)	121.50[e]	121.34(26)	122.00
	v	(119.48)[d]	121.40[e]	(118.67)[d]	122.34(11)	121.50[e]	120.19(22)	—
∢(C6C1C2)	n	121.01(12)	(121.04)[d]	122.24(15)	118.40(06)	119.69(16)	118.75(28)	118.00
	v	120.86(10)	(120.83)[d]	122.35(16)	118.37(06)	119.16(19)	119.17(23)	—
∢(C2C1H1)	n	121.10(14)	121.86(48)	120.00(48)	120.67(06)	120.33(17)	120.43(80)	121.00
	v	120.99(12)	121.50(54)	120.36(50)	120.83(07)	120.61(22)	120.32(62)	—
∢(C3C2X)	n	120.46(12)	119.96(33)	118.82(19)	119.70(03)	118.78(11)	119.48(45)	119.00
	v	120.33(10)	119.72(43)	118.85(20)	119.67(03)	118.61(12)	119.57(35)	—
∢(C2C3H3)	n	120.46(12)	119.65(24)	118.82(19)	120.67(06)	121.30(11)	120.43(80)	121.00
	v	120.33(10)	118.71(36)	118.85(20)	120.83(07)	121.29(13)	120.32(62)	—
∢(C3C4X)	n	121.10(14)	119.64(12)	120.00(48)	118.75[e]	120.34(13)	119.50(27)	119.00
	v	120.99(12)	119.69(13)	120.36(50)	118.75[e]	120.55(15)	119.96(21)	—
∢(C4C5X)	n	118.99[e]	118.88(14)	119.94(24)	(121.09)[d]	120.43(19)	(120.60)[d]	121.00
	v	118.99[e]	118.65(16)	119.03(25)	(121.05)[d]	120.09(22)	(119.78)[d]	—
∢(C1C6X)	n	118.99[e]	116.90[e]	119.94(24)	118.75[e]	119.30[e]	119.50(27)	119.00
	v	118.99[e]	116.90[e]	119.03(25)	118.75[e]	119.30[e]	119.96(21)	—
∢(CXC7H5)	n	—	110.48(23)	110.21(23)	—	110.67(09)	110.98(12)	—
	v	—	111.73(26)	111.53(24)	—	111.78(11)	111.73(15)	—
RMS error[f]		0.5630	0.5148	0.7022	0.2372	0.2989	0.2204	—
RMS error[g]		0.4914	0.5667	0.7337	0.2385	0.3466	0.2281	—
A priori estimates[h]		i	j	k	l	m	n	c
r(C1-C2)		1.3760(02)	1.38200(025)	1.38700(015)	1.4040(02)	1.38500(025)	1.40400(015)	1.3908
r(C2-C3)		1.3960(02)	1.38500(025)	1.3820[e]	1.4040(02)	1.38300(025)	1.40400(015)	1.3908
r(C3-C4)		1.3760(02)	1.38300(025)	1.38700(015)	1.3920(02)	1.39000(025)	1.39200(015)	1.3908

TABLE 4—*Continued*

Parameter[b]	o-Dichlorobenzene	o-Chlorotoluene	o-Xylene	m-Dichlorobenzene	m-Chlorotoluene	m-Xylene	TCB[c]
r(C4-C5)	1.3850(02)	1.39300(025)	1.38800(015)	1.3873(02)[d]	1.39000(025)	1.3873(02)[d]	1.3908
r(C5-C6)	1.4078(02)[d]	1.38990(025)[d]	1.3978(03)[d]	1.3873(02)[d]	1.38510(025)[d]	1.3873(02)[d]	1.3908
r(C6-C1)	1.3850(02)	1.385[e]	1.38800(015)	1.3920(02)	1.3820[e]	1.39200(015)	1.3908
r(C1-H1)	1.0870(02)	1.08000(025)	1.0820(01)	1.0850(02)	1.08500(025)	1.08500(015)	1.0940
r(C2-X)	1.0840(02)	1.0800(03)	1.0820(01)	1.0910(02)	1.0910(02)	1.0910(01)	1.7326
r(C3-H3)	1.0840(02)	1.0800(03)	1.0820(01)	1.0850(02)	1.08500(025)	1.08500(015)	1.0940
r(C4-X)	1.0870(02)	1.08000(016)	1.0820(02)	1.7355	1.51200(045)	1.51200(025)	1.7326
r(C5-X)	1.7330[e]	1.5100(04)	1.5260(015)	1.0910(02)	1.09100(025)	1.0910(01)	1.0940
r(C6-X)	1.7330[e]	1.751[e]	1.5260(015)	1.7355[e]	1.7460[e]	1.51200(025)	1.7326
r(C7-H5)	—	1.09600(025)	1.0960(01)	—	1.09880(025)	1.09880(015)	—
∢(C1C2C3)	120.30(05)	119.65(05)	119.60(05)	121.10(05)[d]	121.100(055)	121.100(025)[d]	122.00
∢(C2C3C4)	120.30(05)	119.75(05)	119.60(05)	118.10(05)	119.000(055)	118.100(025)	118.00
∢(C3C4C5)	119.90(02)	122.0[e]	121.20(01)	122.30(05)	119.000(055)	122.300(025)	122.00
∢(C4C5C6)	119.80(05)[d]	117.50[e]	120.00(05)[d]	118.10(05)[d]	118.570(055)[d]	118.100(025)[d]	118.00
∢(C5C6C1)	119.80(05)[d]	121.40[e]	120.00(05)[d]	122.30(05)	121.50[e]	122.300(025)	122.00
∢(C6C1C2)	119.90(02)	119.70(05)[d]	121.20(01)	118.10(05)	120.23(04)	118.100(025)	118.00
∢(C2C1H1)	120.28(02)	120.15(05)	119.50(03)	120.70(05)	120.700(055)	120.700(025)	121.00
∢(C3C2X)	120.10(05)	120.18(05)	120.40(05)	119.45(05)	119.450(055)	119.450(025)	119.00
∢(C2C3H3)	120.10(05)	120.13(05)	120.40(05)	120.70(05)	120.700(055)	120.700(025)	121.00
∢(C3C4X)	120.28(02)	119.40(01)	119.50(03)	118.75[e]	121.100(055)	121.100(025)	119.00
∢(C4C5X)	118.99[e]	119.90(05)	120.00(05)	120.95(05)[d]	120.950(055)	120.950(025)[d]	121.00
∢(C1C6X)	118.99[e]	116.90[e]	120.00(05)	118.75[e]	119.30[e]	121.100(025)	119.00
∢(CXC7H5)	—	111.00(04)	110.90(02)	—	111.120(025)	111.12(01)	—

[a] Refer to Fig. 3 for structure and atom numbering of molecules. Bond distances (r) in Å and bond angles (∢) in degrees. In the least squares fit to experimental dipolar couplings the weight given to each dipolar coupling is $(1/\text{error})^2$ where the errors are reported in Table 3.

[b] Parameters which are indicated with "n" are calculated with no vibrational corrections to dipolar couplings and parameters indicated with "v" are calculated with vibrational corrections.

[c] Structural parameter not adjusted. From Ref. (55).

[d] Dependent parameter is calculated from the bond angles and lengths of the carbon skeleton.

[e] Parameter not adjusted during fit.

[f] RMS error in hertz between calculated and experimental dipolar couplings.

[g] RMS error in hertz between vibrationally corrected and experimental dipolar couplings.

[h] For the least squares fitting routine the weight associated with the *a priori* estimates is $(1/\text{error})^2$ where the errors are reported in brackets.

[i] r_α structure from Ref. (53).

[j] Structure from Refs. (54) and (56).

[k] Structure from Refs. (30) and (57).

[l] r_α structure from Ref. (58).

[m] Structure taken from Ref. (59) and *m*-dichlorobenzene (58).

[n] Structure taken from *m*-dichlorobenzene (58).

a version of the least-squares routine modified to include the subroutine VICO (42, 43), which corrects for the nonnegligible effects of normal mode molecular vibrations on D_{ij} using Eq. [4]. Mean square amplitudes $\langle \Delta\delta^2 \rangle$ were calculated using the program MSAV (44) from normal mode vibrational analysis using force constants from Refs. (45) and (46).

B. Molecular Structure

One of the goals of this study is to report accurate $S_{\beta\xi}$ which in turn could be utilized when examining statistical theories. Since D_{ij} are products of order and geometric parameters, it is essential when determining accurate $S_{\beta\xi}$ to carefully consider the molecular structure. Thus we have determined geometric parameters using *a priori* estimates and vibrationally and nonvibrationally corrected D_{ij}. The relative values of the proton coordinates reported in Table 4 are from simultaneous fits to the D_{ij} obtained in three different liquid crystals for each molecule except for *o*-chlorotoluene. The use of more than one liquid crystal provides extra independent equations to the fitting procedure.

Unfortunately r_α structural data for only *o*- and *m*-dichlorobenzene could be found in the literature. Even though the *a priori* estimates for the other molecules were obtained from a combination of data from various other studies, it is noteworthy that most of the calculated structural values (vibrationally and nonvibrationally corrected) do not differ greatly from these *a priori* estimates. However, there are

TABLE 5
Order Parameters from Fits to Dipolar Couplings[a]

Solute	Order parameter[b]		Mercek ZLI1132	55 wt% ZLI 1132/EBBA	EBBA
			Sample 1	Sample 2	Sample 3
o-Dichlorobenzene	S_{zz}	n	0.17132(67)	0.13099(50)	0.12676(45)
		v	0.17232(59)	0.13180(44)	0.12773(39)
	$S_{xx} - S_{yy}$	n	0.34056(38)	0.24319(25)	0.16231(12)
		v	0.34343(33)	0.24525(22)	0.16369(11)
o-Chlorotoluene	S_{zz}	n	0.16600(56)	0.13327(45)	0.14387(50)
		v	0.16984(64)	0.13654(51)	0.14767(56)
	$S_{xx} - S_{yy}$	n	0.34678(39)	0.24827(27)	0.18577(39)
		v	0.35486(64)	0.25419(31)	0.19101(44)
	S_{xz}	n	−0.00037(16)	0.00468(15)	0.01128(25)
		v	−0.00125(67)	0.00363(59)	0.00949(78)
TCB	S_{zz}	n	−0.26436	−0.20103	−0.17730
			Sample 4	Sample 5	Sample 6
o-Dichlorobenzene	S_{zz}	n	0.17527(69)	0.14611(56)	0.14081(50)
		v	0.17630(60)	0.14702(49)	0.14189(44)
	$S_{xx} - S_{yy}$	n	0.34743(38)	0.26802(30)	0.17843(14)
		v	0.35038(33)	0.27028(26)	0.17995(12)
o-Xylene	S_{zz}	n	0.16646(71)	0.14369(61)	0.14859(61)
		v	0.16956(76)	0.14637(65)	0.15138(66)
	$S_{xx} - S_{yy}$	n	0.35394(46)	0.28468(34)	0.24869(22)
		v	0.35912(49)	0.28877(36)	0.25212(24)
TCB	S_{zz}	n	−0.27012	−0.22217	−0.19696
			Sample 7	Sample 8	Sample 9
m-Dichlorobenzene	S_{zz}	n	0.05755(18)	0.02678(16)	−0.03363(16)
		v	0.05809(18)	0.02702(17)	−0.03399(16)
	$S_{xx} - S_{yy}$	n	0.48431(25)	0.39784(22)	0.36841(22)
		v	0.48777(25)	0.40067(22)	0.37099(23)
m-Chlorotoluene	S_{zz}	n	0.04365(20)	0.02255(17)	−0.01916(17)
		v	0.04561(25)	0.02374(21)	−0.01930(20)
	$S_{xx} - S_{yy}$	n	0.48878(33)	0.40026(28)	0.38199(29)
		v	0.49674(40)	0.40663(33)	0.38766(34)
	S_{xz}	n	0.02617(30)	0.01539(28)	0.00259(35)
		v	0.02632(35)	0.01583(32)	0.00369(41)
TCB	S_{zz}	n	−0.27747	−0.22314	−0.19190
			Sample 10	Sample 11	Sample 12
m-Dichlorobenzene	S_{zz}	n	0.05581(14)	0.02422(10)	−0.03567(15)
		v	0.05633(15)	0.02444(10)	−0.03605(15)
	$S_{xx} - S_{yy}$	n	0.46513(24)	0.36476(19)	0.38717(23)
		v	0.46846(24)	0.36740(20)	0.38989(24)
m-Xylene	S_{zz}	n	0.03912(46)	0.02550(35)	−0.00036(34)
		v	0.03921(37)	0.02557(28)	−0.00047(28)
	$S_{xx} - S_{yy}$	n	0.48225(64)	0.37482(51)	0.41029(61)
		v	0.49831(55)	0.38034(44)	0.41663(52)
TCB	S_{zz}	n	−0.26706	−0.20488	−0.20207

[a] For axis definitions see Fig. 3. For corresponding structural parameters refer to Table 4. Numbers in round brackets are standard deviations in the last two reported digits of varied parameters.

[b] Order parameters which are indicated with "n" are calculated with no vibrational corrections to dipolar couplings and parameters indicated with "v" are calculated with vibrational corrections.

some exceptions; it is difficult to ascertain the nature of the discrepancies but it is most likely due to the inaccuracies with the *a priori* estimates.

Since we used *a priori* estimates from the structures of other molecules and since D_{ij} are products of order and geometric parameters, the error associated with the resulting structure is difficult to determine. Bond angles are probably not accurate to better than 0.2° and CH bond distances to 0.01 Å. Thus the statistical uncertainties (68% confidence level) reported in Table 4 are optimistic.

TABLE 6
Order Parameters for Solutes in Sample 13 from Fits to Dipolar Couplings[a]

Order parameter[b]		o-Dichlorobenzene	o-Chlorotoluene	o-Xylene	TCB
S_{zz}	n	0.17412(69)	0.16894(57)	0.16503(71)	−0.26812
	v	0.17514(60)	0.17286(65)	0.16811(76)	—
$S_{xx} - S_{yy}$	n	0.34494(42)	0.35172(40)	0.35116(46)	—
	v	0.34785(37)	0.35990(65)	0.35628(49)	—
S_{xz}	n	—	−0.00017(16)	—	—
	v	—	−0.00108(69)	—	—

[a] For axis definitions see Fig. 3. For corresponding structural parameters refer to Table 4. Numbers in round brackets are standard deviations in the last two reported digits of varied parameters.

[b] Order parameters which are indicated with "n" are calculated with no vibrational corrections to dipolar couplings and parameters indicated with "v" are calculated with vibrational corrections.

C. Order Parameters

It is generally accepted that anisotropic short-range repulsive forces are primarily responsible for the orientational ordering of liquid crystals, i.e., forces which can be related to size, shape, and conformation of the molecules (12, 47–52). Controversy has arisen over the importance of anisotropic longer range interactions (5–8). The spectra in this paper have been recorded in such a manner that the $S_{\beta\xi}$ obtained can be used to explore various models for the anisotropic potential. In many previous studies solutes dissolved in the same liquid crystal were in different sample tubes; thus to examine the $S_{\beta\xi}$ of the molecules an orientational scaling parameter was required for each solute to account for different sample conditions (5, 13–17). In this study several solutes are codissolved in the same sample (similar to the sample preparation described in Ref. (17)); $S_{\beta\xi}$ among these solutes can be directly compared without scaling. The $S_{\beta\xi}$ calculated both with and without vibrational corrections are reported in Tables 5 and 6.

If it is assumed that the two groups of disubstituted benzenes have similar sizes and shapes and that the short-range interactions are the same for the group of m-disubstituted and the same for the group of o-disubstituted benzenes, then any differences among the $S_{\beta\xi}$ within the groups are a result of the long-range interactions. As an example, we examine the S_{zz} values determined in the three liquid-crystal samples employed in this study. In the 55 wt% mixture, the S_{zz} within the group of m-disubstituted molecules and within the group of o-disubstituted molecules are all approximately equal (Fig. 4). This has also been observed in previous studies with the p-disubstituted and monosubstituted benzenes (8) and is taken as evidence that all long-range interactions are negligible in this particular liquid-crystal mixture (12).

In the component liquid crystals the S_{zz} are dispersed. This is most likely due to the influence of long-range electrostatic interactions, especially those arising from the solute molecular quadrupoles interacting with the charge distribution on other molecules (8, 12). A detailed quantitative analysis of the aniso-
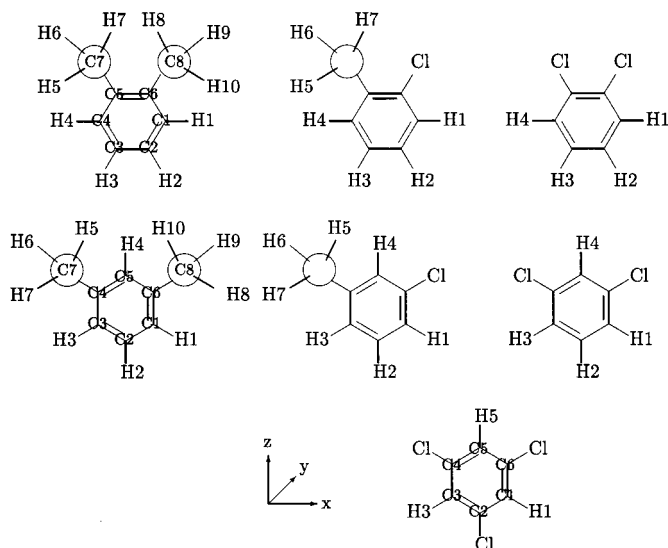
FIG. 3. Coordinate system and atom numbering of solute molecules.
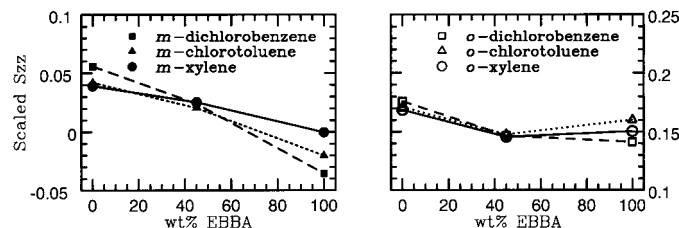
FIG. 4. Scaled nonvibrationally corrected S_{zz} of o- and m-disubstituted benzenes. The scaled S_{zz} for o-dichlorobenzene in samples 1, 4, and 13, in samples 2 and 5, and in samples 3 and 6 coincide. The scaled S_{zz} for m-dichlorobenzene in samples 7 and 10, in samples 8 and 11, and in samples 9 and 12 coincide. Note that the S_{zz} of m-disubstituted benzenes are all approximately equal in the 55 wt% ZLI1132/EBBA mixture. This is also apparent for the o-disubstituted benzenes. Note that, due to overlap of spectral lines, all solutes could not be dissolved in the same sample tube. Thus for solutes in different sample tubes, the S_{zz} values were scaled using the ratio of TCB dipolar couplings from samples 4, 5, or 6 to TCB dipolar couplings in the sample of interest.

tropic intermolecular potential using the vibrationally corrected $S_{\beta\xi}$ will be presented in a subsequent publication.

V. SUMMARY

In this paper we have determined spectral, orientational order, and structural parameters (including vibrationally corrected $S_{\beta\xi}$) for *o*- and *m*-disubstituted benzenes codissolved in various liquid crystals. Resonance frequencies and $S_{\beta\xi}$ for *o*- and *m*-xylene were estimated by analyzing the 8Q spectra using a modified version of the least-squares fitting routine which could adjust $S_{\beta\xi}$, structural parameters, and/or D_{ij} independently. With this modified version of the program the time required for analysis was greatly reduced. More accurate resonance frequencies and D_{ij} were then determined with the original MQ program and used as initial estimates when accurately determining spectral parameters from the high-resolution spectra. After the high-resolution spectra were fit, the calculated spectrum was subtracted from the experimental one and resonances from the other molecules were identifiable. The spectra of the other molecules were then analyzed one by one and subtracted from the experimental spectrum. This is one of the very few studies where many solutes were codissolved in a liquid-crystal mixture and where MQ spectroscopy and analysis of the MQ spectra by adjusting $S_{\beta\xi}$ were utilized in a successful attempt to simplify the analysis of high-resolution spectra.

ACKNOWLEDGMENTS

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