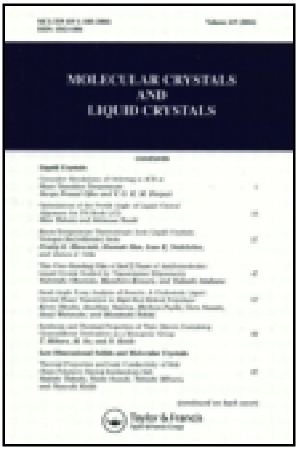

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Orientation Studies by NMR on Chlorobenzenes in Nematic Liquid Crystals

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Orientation Studies by NMR on Chlorobenzenes in Nematic Liquid Crystals

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The orientations of benzene as well as 11 different chlorine substituted benzenes have been studied in the liquid crystal solvents EBBA, ZLI 1132 and in a mixture of the two. Bond contributions to the interaction energy of the solute molecules with the solvents have been determined. They are found to be characteristic for each molecule so that a prediction of *S*-values exclusively based on the number and type of bonds as well as on bond orientation with respect to the solvent director is very imprecise. The predictions can be considerably improved if the molecular shape, i.e. location of the bonds is also considered, as suggested in an earlier approach by Van der Est *et al.*

Keywords: NMR, order of chlorobenzenes, bond contributions to orientation energy, transferability of bond contributions

1. INTRODUCTION

Very early in the development of NMR of oriented molecules Saupe[1] and later on Nehring and Saupe[2] tried to interpret degrees of order of chlorine and fluorine substituted benzenes on the basis of a simple dispersion force model in which each bond contributes additively to the interaction energy, which depends upon the bond type, the liquid crystal solvent and the angle between the bond axis and the symmetry axis of the solvent. In this model it was assumed, that bond contributions to the interaction energy are transferable i.e. within the groups of substituted benzenes they are independent of the substitution. The authors reached the conclusion that differences in orientation are mainly caused by localized contributions of bonds. Deviations from the theory were attributed to specific interactions.

Roughly twenty years later we have come back to a similar concept for interpreting degrees of order during our studies of the solvent-effect on the structure of molecules dissolved in liquid crystals.[3,4] In this theory the external orienting potential energy of a molecule is described as a sum of bond interaction tensors which are responsible for the correlated deformation of the solute as well as its orientation. The tensor is characterized by its anisotropy ΔA and its asymmetry ηA. Although for this approach it is not necessary to assume the action of dispersion forces exclusively, we arrive at a formulation of the interaction energy which is virtually identical with the approach of Saupe and Nehring, if we neglect the asymmetry of the interaction tensor ηA.

For the performance of the corrections which must be applied to the measured direct couplings in order to take into account the correlated solute deformation as well as for a prediction of order parameters it is helpful to know, whether a measured anisotropy of the bond interaction tensor is transferable i.e. whether it can be used for different molecules in the same solvent. This question can be studied particularly easily in a group of molecules which has different arrangements of a few bonds such as the various chlorobenzenes. In the present paper we have therefore analyzed the spectra of benzene as well as 11 different chlorine substituted benzenes in two different solvents which are known to display extreme behaviour in the deformation of solutes, as well as in their mixture.

2. EXPERIMENTAL

Commercially available chlorine substituted benzenes were dissolved at a concentration of 6 mole percent in the previously degassed liquid crystals ZLI 1132, EBBA and a mixture of 55% of ZLI 1132 and 45% of EBBA. The temperatures T_{NI} of the transition between the nematic and isotropic phases of each sample were determined in order to make the measurements at the same reduced temperature $T^* = T/T_{NI} = 0.88$. The spectra were recorded on a Bruker AC-250 spectrometer being locked on D_2O in the interwall space of the double wall tubes. The indirect couplings were taken from the literature or determined in the solvent perdeuterobenzene and kept fixed in the spectral analysis with the program LEQUOR[5] iterating the dipolar couplings and the chemical shift differences. As the order parameters were found to be only slightly dependent on harmonic vibration and correlated deformation as well as on small structural changes the resulting direct couplings were used without corrections in the program SHAPE,[6] and the structure was fixed [r(C-H) = 1.084 Å, r(C-C) = 1.397 Å, angles corresponding to a regular hexagon]. As far as possible only proton-proton-couplings were used, but for the tetra- and pentasubstituted benzenes information from the C-13 satellites at natural abundance had to be included in the determination of the order parameters. For C-13 enriched hexachlorobenzene only the couplings between the C-13 nuclei could be observed.

The results are summarized in Table I.

3. RESULTS AND DISCUSSION

Transferability of bond contributions

The contributions to the bond interaction tensor components Axx and Azz which determine the degrees of order of the perpendicular x- and z-axes in the benzene ring plane and Ayy perpendicular to the plane can be derived as follows:

Angle	Axx	Azz
30°,150°	$5/12\ \Delta A_n$	$-1/12\ \Delta A_n$
90°	$-4/12\ \Delta A_n$	$8/12\ \Delta A_n$

TABLE I

Experimental order and interaction tensor elements in 10**-22 J for the chlorine substituted benzenes dissolved at 6 mole % in three nematic liquid crystals. Data in brackets indicate that the solute concentration is below 6 mole %.

Solvent			**ZLI 1132**			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.1243	0.1243	-0.2485	23.6	23.6	-47.2
1-	0.0291	0.2436	-0.2727	16.2	37.5	-53.7
1,2-	0.1834	0.0886	-0.2720	31.7	22.5	-54.2
1,3-	0.2063	0.0577	-0.2640	33.0	18.3	-51.3
1,4-	-0.0453	0.3394	-0.2941	10.5	48.9	-59.4
1,2,3-	0.1898	0.0941	-0.2839	33.8	24.6	-58.4
1,3,5-	0.1416	0.1416	-0.2833	29.2	29.2	-58.4
1,2,3,4-	0.0723	0.2271	-0.2993	24.6	39.4	-64.0
1,2,3,5-	0.1123	0.1781	-0.2904	27.3	33.6	-60.9
1,2,4,5-	0.1977	0.1069	-0.3046	37.5	29.0	-66.5
1,2,3,4,5-	0.1639	0.1267	-0.2906	32.3	28.2	-60.5
(1,2,3,4,5,6-	0.1631	0.1631	-0.3262	38.3	38.3	-76.6)

Solvent			**ZLI 1132 / EBBA**			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.0898	0.0898	-0.1796	15.0	15.0	-30.0
1-	0.0057	0.2025	-0.2082	7.3	28.3	-35.6
1,2-	0.1596	0.0631	-0.2226	24.9	14.9	-39.8
1,3-	0.1941	0.0288	-0.2229	28.4	11.2	-39.6
1,4-	-0.0709	0.3101	-0.2392	0.3	41.0	-41.3
1,2,3-	0.1683	0.0676	-0.2359	26.2	15.2	-41.4
1,3,5-	0.1146	0.1146	-0.2291	20.9	20.9	-41.8
1,2,3,4-	0.0319	0.2236	-0.2555	14.5	33.9	-48.4
1,2,3,5-	0.0930	0.1526	-0.2457	20.1	26.1	-46.2
1,2,4,5-	0.1850	0.0782	-0.2632	30.9	20.4	-51.3
1,2,3,4,5-	0.1498	0.1079	-0.2577	26.9	22.8	-49.7
(1,2,3,4,5,6-	0.1421	0.1421	-0.2842	29.3	29.3	-58.6)

Solvent			**EBBA**			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.0565	0.0565	-0.1131	8.7	8.7	-17.4
1-	-0.0437	0.1835	-0.1399	-2.9	23.7	-20.8
1,2-	0.1411	0.0168	-0.1579	19.6	5.6	-25.2
1,3-	0.1953	-0.0314	-0.1638	25.6	-0.1	-25.5
1,4-	-0.1613	0.3715	-0.2102	-16.5	46.5	-30.0
1,2,3-	0.1856	0.0088	-0.1944	25.8	6.8	-32.6
1,3,5-	0.0959	0.0959	-0.1919	16.4	16.4	-32.8
(1,2,3,4-	-0.0593	0.3174	-0.2581	3.9	43.1	-47.0)
1,2,3,5-	0.0728	0.1581	-0.2309	16.6	25.4	-42.0
(1,2,4,5-	0.2220	0.0266	-0.2486	33.0	13.3	-46.3)
(1,2,3,4,5-	0.1694	0.0884	-0.2577	28.8	20.8	-49.6)

with ΔA_n = anisotropy of the interaction tensor for bond n (bond interaction parameter). For the definition of the coordinate axes see Figure 1.

With the assumption that the bond interaction parameters of similar molecules (substituted chlorobenzenes) are identical for the same liquid crystal solvent, the total interaction or order tensors for all the chlorobenzenes can be predicted from the parameters of only two different molecules determining the difference between the C—H and C—Cl bond interaction parameters. It turns out, that in a plot of

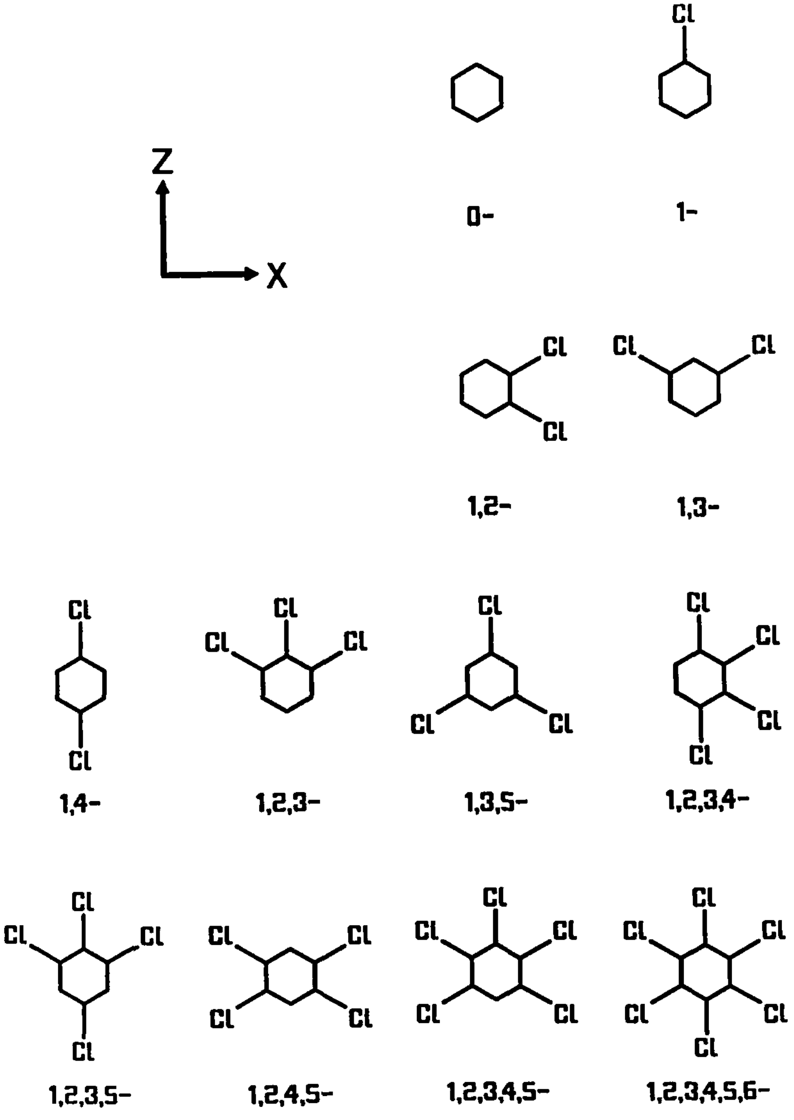

FIGURE 1 Definition of the coordinate axes of the chlorobenzene derivatives.

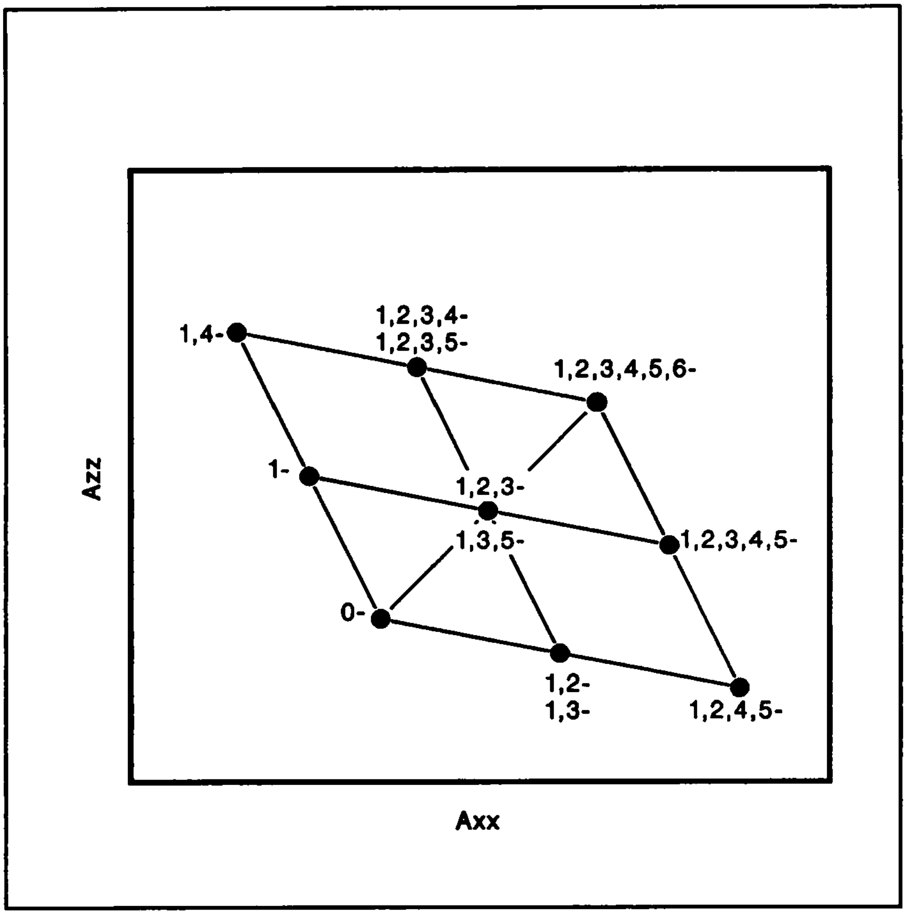

FIGURE 2 Predicted interaction tensor elements *A*zz vs *A*xx in the chlorobenzene derivatives forming a regular parallelogram pattern.

*A*zz vs *A*xx the predicted interaction parameters form a regular parallelogram pattern as shown on Figure 2 and summarized on Table II.

These predicted values as listed in Table II are compared on Figures 3, 4, 5, 6 with the experimental values of Table I. The deviations are marked by dashed lines.

In the solvent EBBA the measured values for *A*xx and *A*zz define a point which is not situated on the parallelogram side with a slope as predicted by the theory. For the construction of the parallelogram we have therefore used a set of *A*xx, *A*zz which lies on the parallelogram side with predicted slope and has minimal distance from the measured value. For the prediction of the *A*yy the measured difference between the experimental values of benzene and chlorobenzene can be used directly as a basis.

TABLE II
Predicted order and interaction tensor elements in 10**-22 J for the chlorine substituted benzenes dissolved at 6 mole % in three nematic liquid crystals.

Solvent			ZLI 1132			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.1246	0.1246	-0.2492	23.6	23.6	-47.2
1-	0.0307	0.2436	-0.2743	16.6	37.6	-54.2
1,2-	0.2557	0.0379	-0.2936	41.1	20.1	-60.7
1,3-	0.2557	0.0379	-0.2936	41.1	20.1	-60.7
1,4-	-0.0601	0.3603	-0.3002	9.6	51.6	-60.7
1,2,3-	0.1542	0.1542	-0.3084	34.1	34.1	-67.2
1,3,5-	0.1542	0.1542	-0.3084	34.1	34.1	-67.2
1,2,3,4-	0.0496	0.2757	-0.3253	27.1	48.1	-73.7
1,2,3,5-	0.0496	0.2757	-0.3253	27.1	48.1	-73.7
1,2,4,5-	0.2557	-0.0524	-0.2034	58.6	16.6	-73.7
1,2,3,4,5-	0.3829	0.0544	-0.4373	51.6	30.6	-80.2
1,2,3,4,5,6-	0.1741	0.1741	-0.3482	44.6	44.6	-86.7

Solvent			ZLI 1132 / EBBA			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.0898	0.0898	-0.1797	15.0	15.0	-30.0
1-	0.0097	0.2043	-0.2140	8.2	28.8	-35.6
1,2-	0.2204	0.0197	-0.2401	32.2	11.6	-41.2
1,3-	0.2204	0.0197	-0.2401	32.2	11.6	-41.2
1,4-	-0.0702	0.3195	-0.2493	1.4	42.6	-41.2
1,2,3-	0.1306	0.1306	-0.2611	25.4	25.4	-46.8
1,3,5-	0.1306	0.1306	-0.2611	25.4	25.4	-46.8
1,2,3,4-	0.0365	0.2480	-0.2845	18.6	39.2	-52.4
1,2,3,5-	0.0365	0.2480	-0.2845	18.6	39.2	-52.4
1,2,4,5-	0.3497	-0.0591	-0.2907	49.4	8.2	-52.4
1,2,3,4,5-	0.2590	0.0431	-0.3020	42.6	22.0	-58.0
1,2,3,4,5,6-	0.1580	0.1580	-0.3160	35.8	35.8	-63.6

Solvent			EBBA			
Solute	**Sxx**	**Szz**	**Syy**	**Axx**	**Azz**	**Ayy**
0-	0.0568	0.0568	-0.1137	8.7	8.7	-17.4
1-	-0.0267	0.1905	-0.1638	0.5	25.1	-20.8
1,2-	0.2153	-0.0125	-0.2028	29.3	4.7	-24.2
1,3-	0.2153	-0.0125	-0.2028	29.3	4.7	-24.2
1,4-	-0.1110	0.3267	-0.2157	-7.7	41.5	-24.2
1,2,3-	0.1156	0.1156	-0.2312	21.1	21.1	-27.6
1,3,5-	0.1156	0.1156	-0.2312	21.1	21.1	-27.6
1,2,3,4-	0.0093	0.2543	-0.2637	12.9	37.5	-31.0
1,2,3,5-	0.0093	0.2543	-0.2637	12.9	37.5	-31.0
1,2,4,5-	0.3718	-0.0970	-0.2748	49.9	0.7	-31.0
1,2,3,4,5-	0.2702	0.0180	-0.2882	41.7	17.1	-34.4
1,2,3,4,5,6-	0.1528	0.1528	-0.3057	33.5	33.5	-37.8

*The experimental values of benzene and monochlorobenzene were chosen as basis for the calculation of *A*yy.

**In the solvent EBBA the values for *A*xx and *A*zz of monochlorobenzene were constructed to lie on the parallelogram side with the predicted slope.

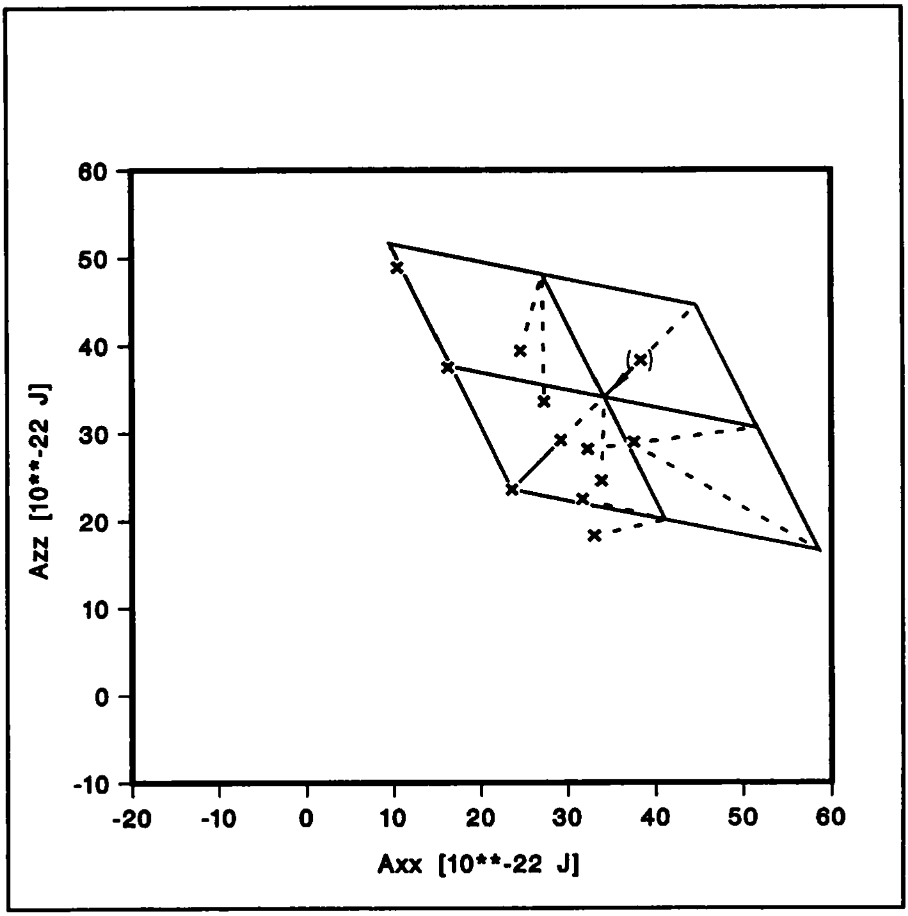

FIGURE 3 Interaction tensor elements Azz vs Axx in 10^{-22} J of the chlorobenzene derivatives dissolved in ZLI 1132 (see Table II). The deviations between predicted and experimental values (X) are marked by the broken lines. Data in brackets indicate that the solute concentration is below 6 mole %. Arrows indicate the expected change with increasing concentration.

In general, we observe considerable deviations between the predicted and the measured Axx and Azz values. The following trends can be seen in all solvents:

—In 22 out of 28 cases the measured Axx and Azz are smaller than the ones predicted by the theory, indicating a kind of saturation i.e. a decrease of bond interaction parameters with increasing number of substituents.

—For each of the molecular pairs (1,2- and 1,3-dichlorobenzene), (1,2,3,- and 1,3,5-trichlorobenzene) and (1,2,3,4,- and 1,2,3,5-tetrachlorobenzene) the theory predicts one unique set of Axx, Ayy and Azz for one particular solvent. The experiment shows, that this rule is far from being fulfilled for Axx and Azz. On the other hand for Ayy the deviations are considerably smaller.

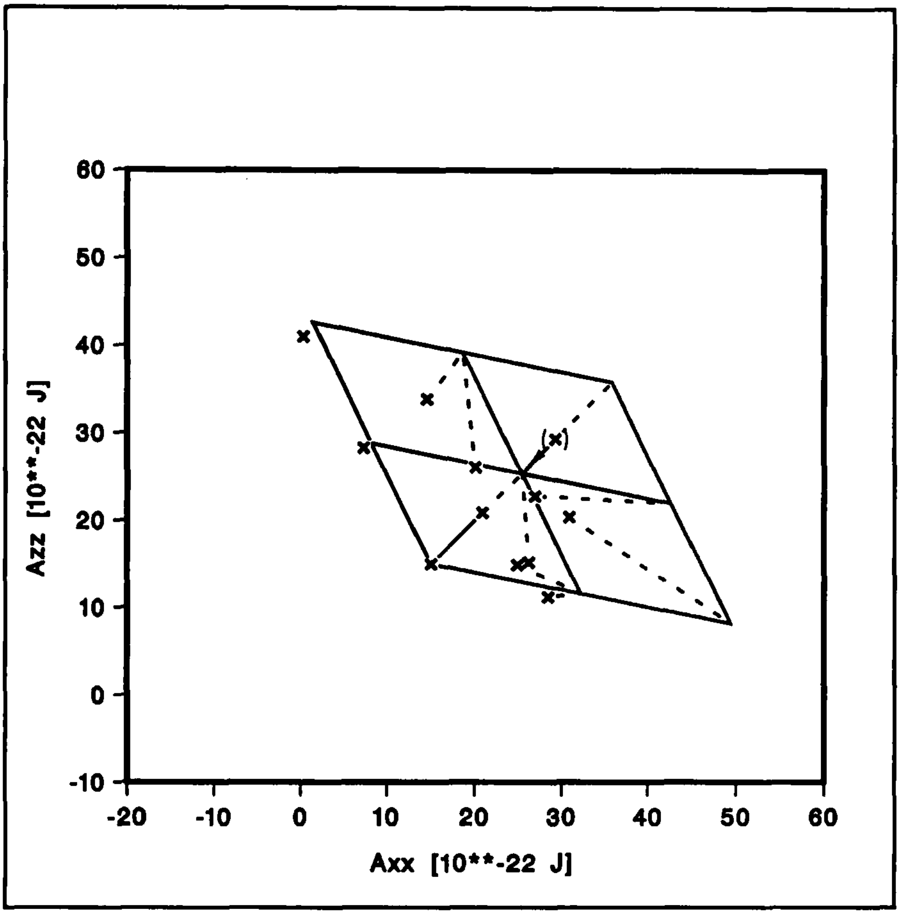

FIGURE 4 Interaction tensor elements Azz vs Axx in 10^{-22} J of the chlorobenzene derivatives dissolved in ZLI 1132 (55%)/EBBA (45% (see Table II). The deviations between predicted and experimental values (X) are marked by the broken lines. Data in brackets indicate that the solute concentration is below 6 mole %. Arrows indicate the expected change with increasing concentration.

—In the solvent ZLI 1132 the value of $|Ayy|$ is generally smaller than predicted. The deviation increases with the number of Cl-substituents. In the solvent EBBA there is an opposite trend, so that in the mixture of the two solvents the deviations are minimized.

All our results show, that the bond contributions to the interaction energy i.e. to the degree of order are non-transferable. This means, that not only the number, type and orientation of bonds but also their positions within the molecule or the molecular shape must be considered. We have therefore reanalyzed our data on the basis of an approach formulated originally by Van der Est *et al.*[7]

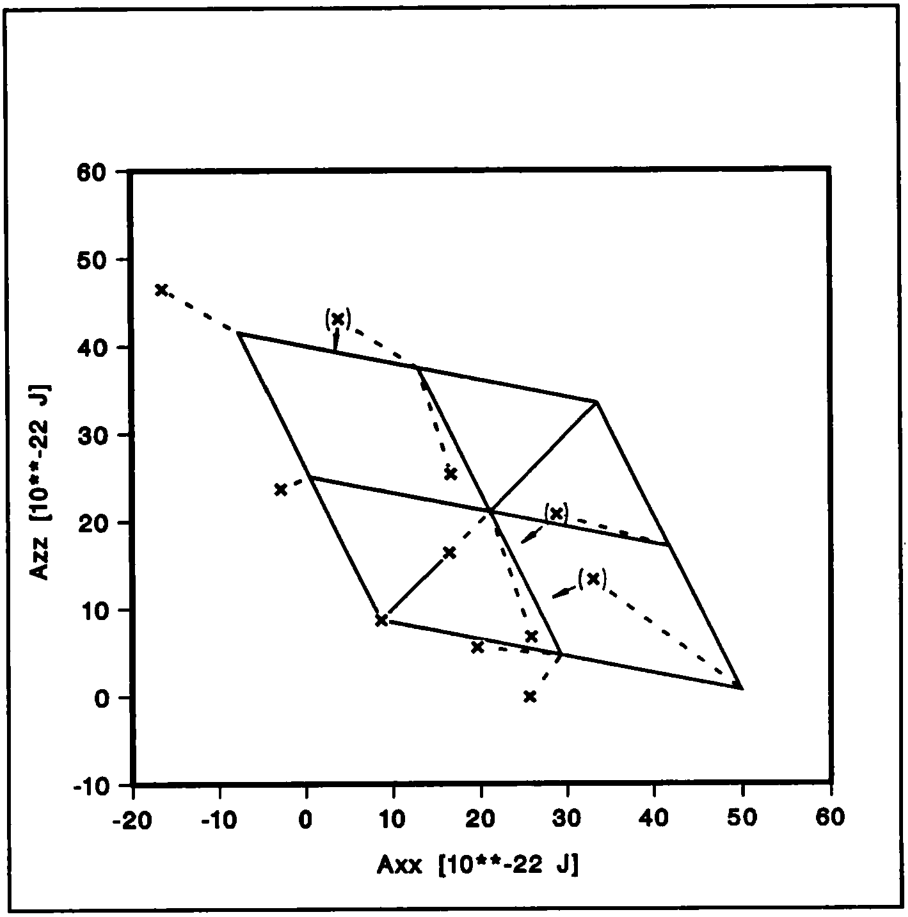

FIGURE 5 Interaction tensor elements Azz vs Axx in 10^{-22} J of the chlorobenzene derivatives dissolved in EBBA (see Table II). The deviations between predicted and experimental values (X) are marked by the broken lines. Data in brackets indicate that the solute concentration is below 6 mole %. Arrows indicate the expected change with increasing concentration.

Consideration of molecular shape

In the approach of Van der Est *et al.*[7] one part of the potential responsible for the solute orientation is assumed to have a long range which is due to the interaction between the solute quadrupole moment and the solvent mean electric field gradient. This part can be minimized by choosing a liquid crystal solvent mixture (55% ZLI 1132 and 45% EBBA) in which measurements on molecular hydrogen have proved the near absence of the field gradient.

The second hard core short range repulsive contribution is described by a Hooke's law force constant for the restoring force $F(\Omega)$ of the liquid crystal solvent which is deformed by the solute. Deformation parallel to the liquid crystal director does

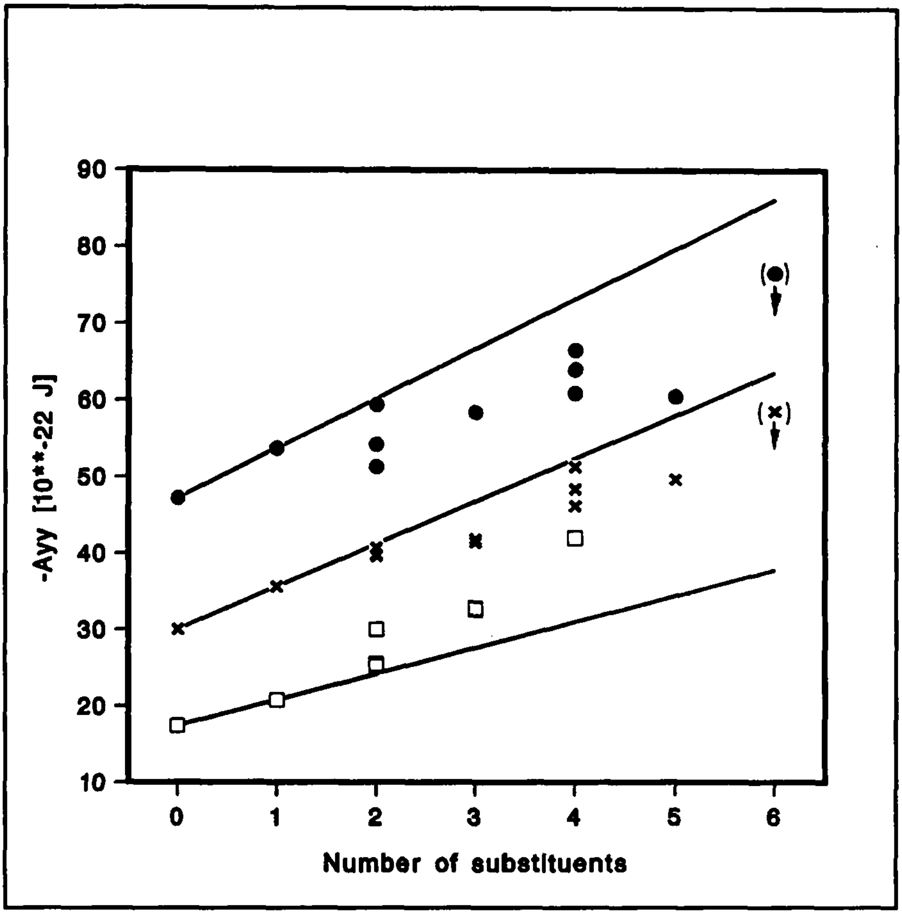

FIGURE 6 Interaction tensor elements perpendicular to the ring plane of the chlorobenzene derivatives dissolved in ZLI 1132 (●), ZLI 1132/EBBA (X) and EBBA (☐) as a function of the number of substituents. The straight lines are calculated according to the transferability assumption using benzene and monochlorobenzene as basis. Data in brackets indicate that the solute concentration is below 6 mole %. Arrows indicate the expected change with increasing concentration.

not require energy. Consequently the important parameters determining the restoring force

$$F(\Omega) = -k\int_0^{2\pi} r(\alpha,\Omega)\, d\alpha = -k\, c(\Omega)$$

are the circumference $c(\Omega)$ of the deformed tube and the Hooke's constant k.

Using the maximum circumference procedure for all the chlorobenzenes in the mixture ZLI 1132/EBBA we have performed least squares iterative determinations of the force constants. For the exactly determined problems with C_3-symmetry the order parameters are reproduced precisely by one free parameter as expected. For

TABLE III
Iterated order parameters for the chlorobenzenes dissolved in ZLI 1132 (55%)/ EBBA (45%) according to the maximum circumference procedure of V.d.Est et al.[7] and resulting force constants in mdyn/Å.

Solute	Sxx	Szz	Syy	k
0-	0.0898	0.0898	-0.1796	4.452
1-	0.0243	0.1938	-0.2181	4.467
1,2-	0.1575	0.0668	-0.2244	4.199
1,3-	0.1931	0.0308	-0.2240	3.778
1,4-	-0.0506	0.3021	-0.2515	4.296
1,2,3-	0.1645	0.0746	-0.2390	4.088
1,3,5-	0.1144	0.1144	-0.2289	3.238
1,2,3,4-	0.0301	0.2245	-0.2545	4.003
1,2,3,5-	0.0776	0.1612	-0.2388	3.386
1,2,4,5-	0.2070	0.0303	-0.2373	3.331
1,2,3,4,5-	0.1675	0.0754	-0.2428	3.419
1,2,3,4,5,6-	0.1421	0.1421	-0.2841	4.428

molecules with two independent *S*-values, the agreement between calculated and experimental data is not as good. The largest deviations are found for 1,2,4,5-tetra- and pentachlorobenzene. Still, the agreement is considerably better than in the first approach which does not consider molecular shape. The results are summarized in Table III and Figure 7. A second fit with an average force constant for all molecules (Table IV) increases the average deviations of *S*-values by a factor of approximately 1.5.

It is particularly interesting to note, that the approach which takes into account molecular shape is able to predict at least qualitatively the differences between the pairs (1,2- and 1,3-dichlorobenzene) as well as (1,2,3,4- and 1,2,3,5-tetrachlorobenzene).

CONCLUSIONS

Our measurements on substituted chlorobenzenes demonstrate very clearly, that anisotropies of bond interaction tensors are characteristic for each molecule, and therefore non-transferable. Although the degree of order of a molecule may still be attributed additively to the contributions of its individual bonds, these contributions must be determined separately for each solute in every solvent. The fact that an approach in which not only the number and type of bonds as well as their orientation, but also their location within the molecule, i.e. the molecular shape is considered, gives a much better prediction of all the S-values indicates why the simple transferability model fails.

For the correction of the solvent effects on the structure of oriented molecules the failure of the transferability of interaction parameters has limited adverse consequences, because these parameters are determined separately in each structural analysis by the program MASTER[8] from the direct coupling constants.

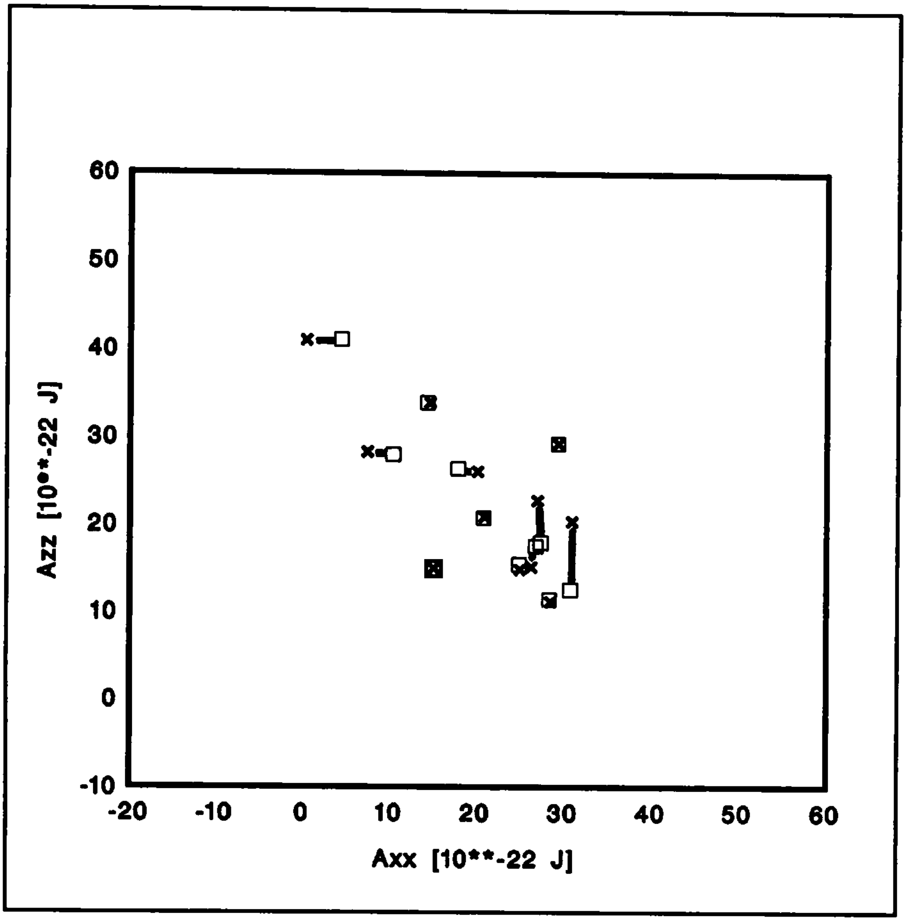

FIGURE 7 Interaction tensor elements *A*zz vs *A*xx in 10^{-22} J of the chlorobenzene derivatives dissolved in ZLI 1132 (55%)/EBBA (45%) calculated according to the maximum circumference procedure of V.d.Est *et al.*[7] The deviations between calculated (□) and experimental (X) values are marked by the solid lines. (Table III)

TABLE IV

Calculation of order parameters with fixed force constant k = 3.9 mdyn/Å according to the maximum circumference procedure of V.d.Est et al.[7] in ZLI 1132 (55%)/EBBA (45%).

Solute	Sxx	Szz	Syy
0-	0.0809	0.0809	-0.1617
1-	0.0265	0.1708	-0.1974
1,2-	0.1479	0.0650	-0.2128
1,3-	0.1988	0.0301	-0.2290
1,4-	-0.0408	0.2758	-0.2350
1,2,3-	0.1581	0.0733	-0.2314
1,3,5-	0.1290	0.1290	-0.2580
1,2,3,4-	0.0309	0.2192	-0.2501
1,2,3,5-	0.0818	0.1802	-0.2620
1,2,4,5-	0.2400	0.0238	-0.2638
1,2,3,4,5-	0.1868	0.0784	-0.2652
1,2,3,4,5,6-	0.1308	0.1308	-0.2616

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