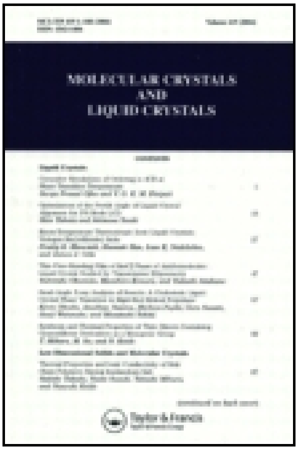

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Orientation Studies by NMR on Polycyclic Aromatic Molecules Dissolved in Nematic Liquid Crystals

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Orientation Studies by NMR on Polycyclic Aromatic Molecules Dissolved in Nematic Liquid Crystals

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The degrees of order of 7 solute polycyclic aromatic ring systems have been measured on the basis of ^{2}H-NMR spectra in the liquid crystal solvents EBBA and ZLI 1132. Bond contributions to the interaction energy of the solute molecules with the solvents have been determined. They are found to be transferable so that orientations of molecules can be predicted as long as there is no contradiction between the symmetry of a molecule based on the number and direction of bonds and the symmetry based on the position of bonds or molecular shape as e.g. in perylene.

Keywords: NMR, order of polycyclic aromatic ring systems, bond contributions to orientation energy, transferability of bond contributions

1. INTRODUCTION

In an earlier study[1] on the orientation of chlorobenzenes in nematic liquid crystals we have demonstrated that based on a description of the external orienting potential energy of the solute as a sum of bond interaction tensors,[2] the bond contributions turn out to be characteristic for each molecule and therefore are non transferable. Furthermore we have shown that for these relatively small molecules with considerable variation of molecular shape the consideration of shape allows a more precise prediction of the degrees of order.

In the present paper we are measuring the degrees of order of 7 polycyclic aromatic molecules in two different liquid crystal solvents in order to find out whether the results of the chlorobenzene study[1] are also confirmed in this group of molecules with considerably larger dimensions.

One of the studied molecules, perylene, will be of particular interest, because it has sixfold symmetry, i.e. one degree of order, if only the number and directions of bonds are considered. On the contrary, it should have two different degrees of order on the basis of the position of bonds, i.e. molecular shape. Furthermore if only the length and width but not the number of bonds are taken into account its degrees of order should be similar to the ones of the molecule pyrene which has a smaller number of bonds.

2. EXPERIMENTAL

Commercially available perdeuterated aromatic compounds benzene, triphenylene, naphthalene, anthracene, phenanthrene, perylene and pyrene were dissolved at a concentration of 2 mole percent in the previously degassed liquid crystals EBBA and ZLI 1132 in 5mm tubes. ^{2}H-spectra were recorded on a Bruker AC 250 Fourier transform NMR-spectrometer without lock. At least 3 different temperatures were measured for each sample in order to determine the signs of the splittings. For the definition of the axes of compounds, see Figure 1.

The degrees of order are obtained from the ^{2}H-spectra of the fully deuterated molecules which display doublets with splittings $\Delta\nu_i$

$$\Delta\upsilon_i = \frac{3}{2} Q_D \left[S_{xx} - \cos^2\gamma_i(S_{xx} - S_{zz}) + \frac{\eta}{3}(2S_{zz} + S_{xx} + \cos^2\gamma_i(S_{xx} - S_{zz}))\right]$$

where Q_D is the quadrupole coupling constant of the deuteron, η is the asymmetry parameter of the electric field gradient and γ_i the angle between the C—D bond and the z-axis. Additional information may be derived from splittings due to deuteron-deuteron direct couplings.

In principle, depending upon the sign of the quadrupole splitting, different sets of S-values are obtained. However, the sign of degree of order S_{zz} for the largest solute molecular axis may from experience be assumed positive. The other signs are derived from the fact that a plot of S_{zz} versus $(S_{xx} - S_{yy})$ must display a maximum.[3,4]

Since the information available in the literature on the quadrupole coupling constants Q_D and asymmetry parameters η of the studied molecules is very limited, Q_D has been assumed to be generally equal to 181kHz and η equal to 0.064 as observed in anthracene.[5]

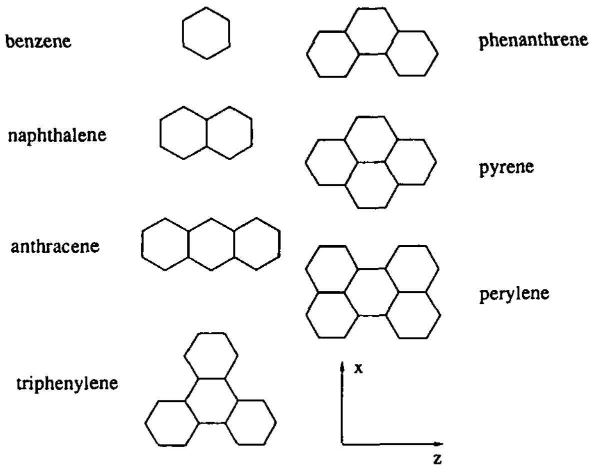

FIGURE 1 Definition of the coordinate axes of polycyclic aromatic ring systems.

TABLE I

Experimental order and interaction tensor elements in 10^{-22}J for polycyclic aromatic ring systems dissolved at 2 mole % in nematic liquid crystals at 305K ($T^* = T/T_{NI} = 0.88$).

solute in ZLI 1132	S_{XX}	S_{ZZ}	A_{XX}	A_{ZZ}
benzene	0.133(1)	0.133(1)	26.2(2)	26.2(2)
naphthalene	0.0052(4)	0.325(1)	23.4(3)	53.4(3)
anthracene	−0.1314(4)	0.504(2)	18.6(9)	80.9(9)
triphenylene	0.197(3)	0.197(1)	65.1(27)	65.1(27)
phenanthrene	−0.034(4)	0.398(1)	28.8(19)	68.6(13)
pyrene	0.025(3)	0.344(1)	37.2(15)	65.8(12)
perylene	0.055(3)	0.321(1)	43.2(17)	66.6(13)

solute in EBBA	S_{XX}	S_{ZZ}	A_{XX}	A_{ZZ}
benzene	0.0622(4)	0.0622(4)	9.6(1)	9.6(1)
naphthalene	−0.0689(2)	0.304(0)	0.2(0)	40.1(0)
anthracene	−0.2461(6)	0.596(2)	−12.4(7)	85.4(7)
triphenylene	0.162(2)	0.162(2)	37.8(7)	37.8(7)
phenanthrene	−0.124(5)	0.436(1)	2.7(14)	60.6(6)
pyrene	−0.037(3)	0.354(0)	15.7(1)	53.5(0)
perylene	−0.072(4)	0.414(1)	17.0(6)	63.9(4)

Hexagonal symmetry was assumed for all the aromatic rings. For the errors of order parameters only experimental uncertainties are taken into account.

The resulting experimental S-values in two different liquid crystal solvents are presented in Table I.

3. RESULTS AND DISCUSSION

TRANSFERABILITY OF BOND CONTRIBUTIONS

For planar molecules each bond n contributes additively to the molecular interaction tensor with components $A_{\mu\mu}$:

$$A_{xx} = \Sigma_n \, \Delta A_n (2/3 - \cos^2\Theta_n)$$

$$A_{yy} = \Sigma_n \, \Delta A_n/3$$

$$A_{zz} = \Sigma_n \, \Delta A_n (2/3 - \sin^2\Theta_n)$$

where ΔA_n is the anisotropy of the interaction tensor of bond n and Θ_n is the angle between the direction of bond n and the molecular z-axis.[2] In agreement with earlier results[6] the asymmetries of bond interaction tensors are neglected.

All the molecules considered consist of C—D and C—C bonds exclusively. If we assume that in all the molecules these bonds are similar, there are only two different parameters ΔA_{CD} and ΔA_{CC} determining the degrees of order of all the solutes in one particular solvent according to the relations[2]

$$U^{ext} = -\frac{3}{2}\sum_{\alpha,\beta} A_{\alpha\beta}\,(\cos\Theta_\alpha\,\cos\Theta_\beta)$$

and

$$S_{\alpha\beta} = \frac{1}{Z_c}\int\frac{1}{2}(3\cos\Theta_\alpha\,\cos\Theta_\beta - \delta_{\alpha\beta})\exp(-U^{ext}/k_BT)\,d\Omega$$

$$Z_c = \int\exp(-U^{ext}/k_BT)\,d\Omega$$

where Θ_α is the angle between the molecular axis α and the liquid crystal director.

The resulting ΔA values are summarized in Table II.

A comparison of the molecular interaction tensor components A_{xx} and A_{zz} for the two liquid crystals in Figure 2 shows a general trend of reduction from the solvent ZLI 1132 to EBBA.

For the molecules benzene, triphenylene and also perylene the two parameters ΔA_{CD} and ΔA_{CC} cannot be derived separately because the equations for the molecular order tensor are linearly dependent. We have therefore based our test of transferability on the values obtained from anthracene.

In Table III respectively, Figure 3 and 4, we present the results of the analysis. With the exception of perylene the deviations from transferability are moderate leading to average errors of predicted S-values of the order of 0.02 in the solvent ZLI 1132 (Figure 5) and 0.04 in EBBA (Figure 6).

As pointed out in the introduction the case of perylene is particularly interesting. It displays two quite different S-values which are close to the ones of pyrene which has equal "length" and "width" but larger number of bonds.

TABLE II

Bond interaction tensor elements in 10^{-22}J for polycyclic aromatic ring systems dissolved at 2 mole percent in nematic liquid crystals at 305K ($T^* = T/T_{NI} = 0.88$).

	ZLI 1132		EBBA	
solute	ΔA_{CD}	ΔA_{CC}	ΔA_{CD}	ΔA_{CC}
naphthalene	−3.3	23.4	−10.6	18.7
anthracene	−4.8	21.6	−13.4	22.1
phenanthrene	−8.2	23.4	−17.5	22.8
pyrene	−4.9	18.8	−10.6	16.5

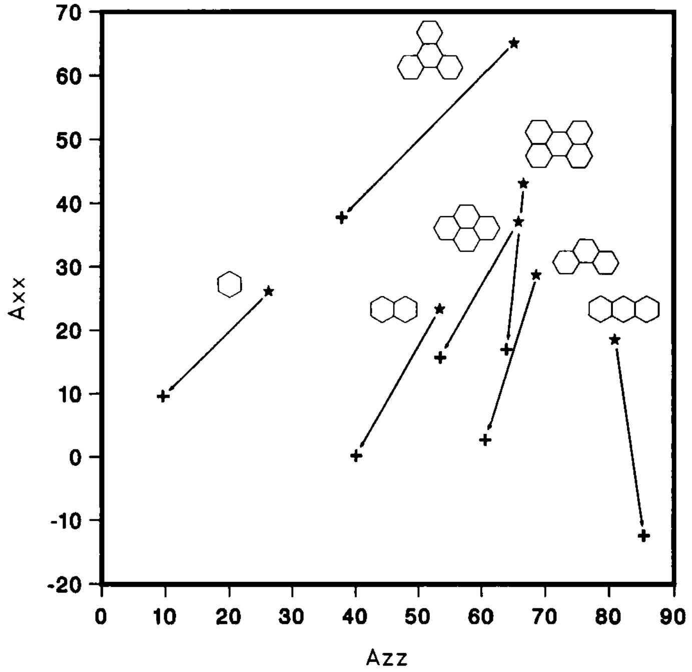

FIGURE 2 Measured interaction tensor elements A_{xx} vs. A_{zz} in 10^{-22}J of polycyclic aromatic ring systems at 305K ($T^* = T/T_{NI} = 0.88$). Comparison of the solvents ZLI 1132 (★) and EBBA (+).

TABLE III

Calculated molecular order and interaction tensor elements in 10^{-22}J based on the bond interaction tensor of anthracene (deviation from measured values in brackets).

solute in ZLI 1132	S_{xx}	S_{zz}	A_{xx}	A_{zz}
benzene	0.098 (−0.035)	0.098 (−0.035)	16.8 (−9.4)	16.8 (−9.4)
naphthalene	−0.007 (−0.013)	0.316 (−0.009)	17.6 (−5.8)	48.8 (−4.6)
anthracene	−0.132 (0.000)	0.504 (0.000)	18.6 (0.0)	80.9 (0.0)
triphenylene	0.198 (0.002)	0.198 (0.001)	66.0 (0.9)	66.0 (0.9)
phenanthrene	0.010 (0.044)	0.355 (−0.043)	34.0 (5.2)	65.2 (−3.4)
pyrene	0.017 (−0.008)	0.372 (0.022)	44.8 (7.6)	76.0 (10.2)
perylene	0.205 (0.150)	0.205 (−0.117)	76.8 (33.6)	76.8 (10.2)
solute in EBBA	S_{xx}	S_{zz}	A_{xx}	A_{zz}
benzene	0.057 (0.005)	0.057 (−0.005)	8.7 (−0.9)	8.7 (−0.9)
naphthalene	−0.100 (−0.031)	0.358 (0.054)	−1.8 (2.0)	47.1 (7.0)
anthracene	−0.246 (0.000)	0.596 (0.000)	−12.4 (0.0)	85.4 (0.0)
triphenylene	0.182 (0.020)	0.182 (0.020)	50.6 (12.8)	50.6 (12.8)
phenanthrene	−0.083 (0.041)	0.412 (−0.024)	12.2 (9.5)	61.0 (0.4)
pyrene	−0.076 (−0.039)	0.440 (0.086)	23.2 (7.5)	72.1 (18.6)
perylene	0.194 (0.266)	0.194 (−0.220)	61.6 (44.6)	61.6 (−2.3)

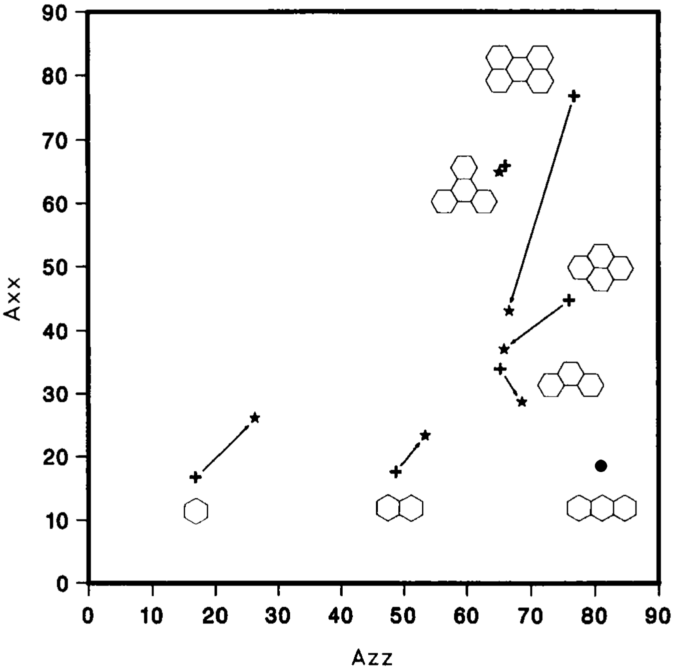

FIGURE 3 Interaction tensor elements A_{xx} vs. A_{zz} in 10^{-22}J of polycyclic aromatic ring systems dissolved in ZLI 1132. The deviations between the values measured (★) and calculated (+) on the basis of anthracene are marked by arrows.

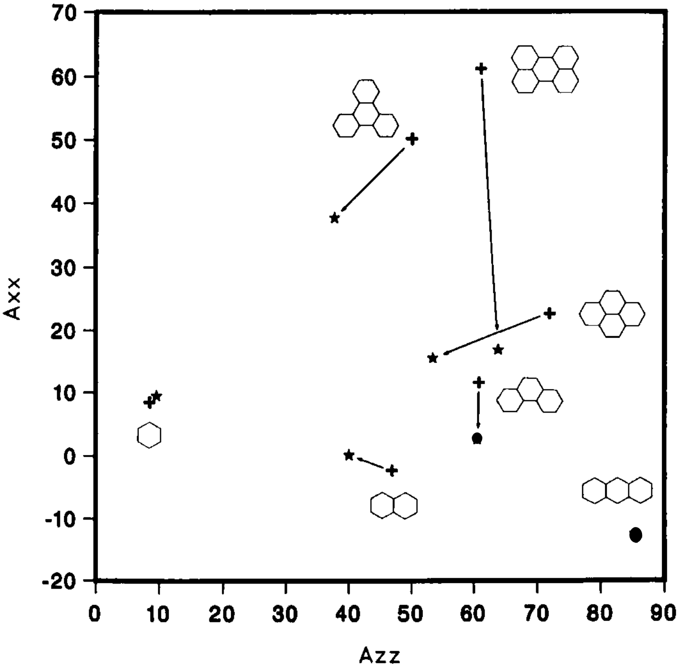

FIGURE 4 Interaction tensor elements A_{xx} vs. A_{zz} in 10^{-22}J of polycyclic aromatic ring systems dissolved in EBBA. The deviations between the values measured (★) and calculated (+) on the basis of anthracene are marked by arrows.

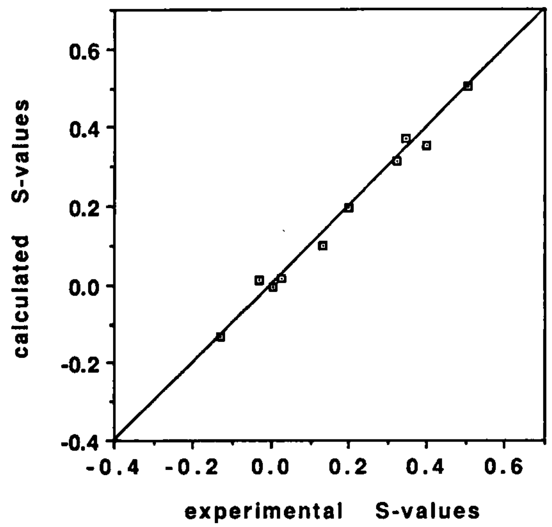

FIGURE 5 S-values calculated on the basis of anthracene vs. measured S-values in the solvent ZLI 1132 at 305K ($T^* = T/T_{NI} = 0.88$).

CONSIDERATION OF MOLECULAR SHAPE

Our earlier studies on the degrees of order of chlorobenzenes dissolved in liquid crystals have demonstrated that an approach which considers molecular size and shape[7] and assumes that a restoring force of the liquid crystal proportional to the circumference $c(\Omega)$ of the solute leads to an interaction energy proportional to $kc^2(\Omega)/2$, where k is an elastic Hooke's law force constant, allows a prediction of

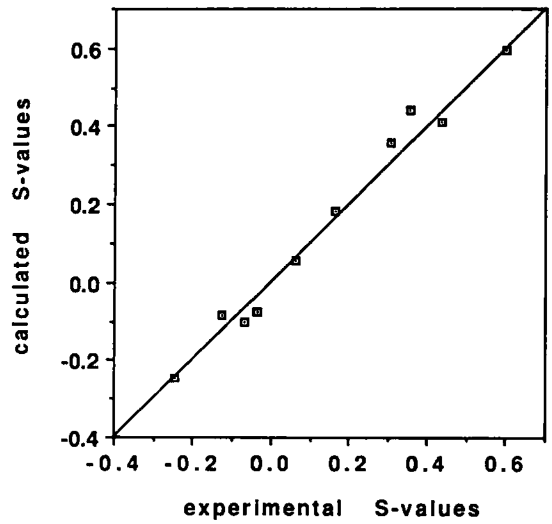

FIGURE 6 S-values calculated on the basis of anthracene vs. measured S-values in solvent EBBA at 305K ($T^* = T/T_{NI} = 0.88$).

TABLE IV

Order parameters calculated from an elastic deformation according to maximum circumference model[7] and resulting force constants k in mdyne/Å (deviation from measured values in brackets).

solute in ZLI 1132	S_{xx}	S_{zz}	k
benzene	0.133 (0.000)	0.133 (0.000)	7.83
naphthalene	−0.007 (−0.012)	0.324 (0.001)	5.68
anthracene	−0.139 (−0.008)	0.498 (−0.006)	4.76
triphenylene	0.197 (0.000)	0.197 (0.000)	6.47
phenanthrene	−0.051 (−0.017)	0.394 (−0.004)	4.76
pyrene	0.022 (−0.003)	0.344 (0.000)	5.33
perylene	0.039 (−0.016)	0.319 (−0.002)	4.16

solute in EBBA	S_{xx}	S_{zz}	k
benzene	0.062 (0.000)	0.062 (0.000)	2.04
naphthalene	0.005 (0.074)	0.294 (−0.010)	5.05
anthracene	−0.224 (0.022)	0.621 (0.025)	6.60
triphenylene	0.162 (0.000)	0.162 (0.000)	3.78
phenantrhene	−0.086 (0.038)	0.453 (0.017)	5.73
pyrene	0.012 (0.049)	0.363 (0.009)	5.81
perylene	−0.034 (0.039)	0.439 (0.025)	6.34

S-values which is more precise than the one based on transferability of bond contributions.

We have applied this approach to our selection of aromatic molecules. The results for the two liquid crystal solvents are summarized in Table IV.

They show that the average S-error is now 0.007 in ZLI 1132 and 0.03 in EBBA so that with the exception of perylene the improvement is very moderate. In both solvents the resulting elastic constants k are found to vary considerably with the solute molecule (Table IV), however, we detect an interesting linear relation between the k-values of the same solutes in the two different solvents as shown in Figure 7.

Because of the negative slope $m = \Delta k(\mathrm{EBBA})/\Delta k(\mathrm{ZLI\ 1132}) = -1.27$ (with correlation coefficient 0.97) there exists a mixture of the two solvents in which k is practically independent of the solute. The resulting mixture of 55% ZLI 1132 and 45% EBBA agrees with the one which was used for the earlier measurements on chlorobenzenes because a minimal contribution for this mixture of the solute quadrupolar moment to the orienting energy had been predicted.[7]

CONCLUSIONS

The present studies show that in polycyclic aromatic molecules the transferability of bond contributions to the molecular orienting energy (i.e. degree of order) is fulfilled better than in chlorobenzenes. The reason seems to be that the deviations from transferability in the interaction tensor elements of the order of $10 \cdot 10^{-22}$J

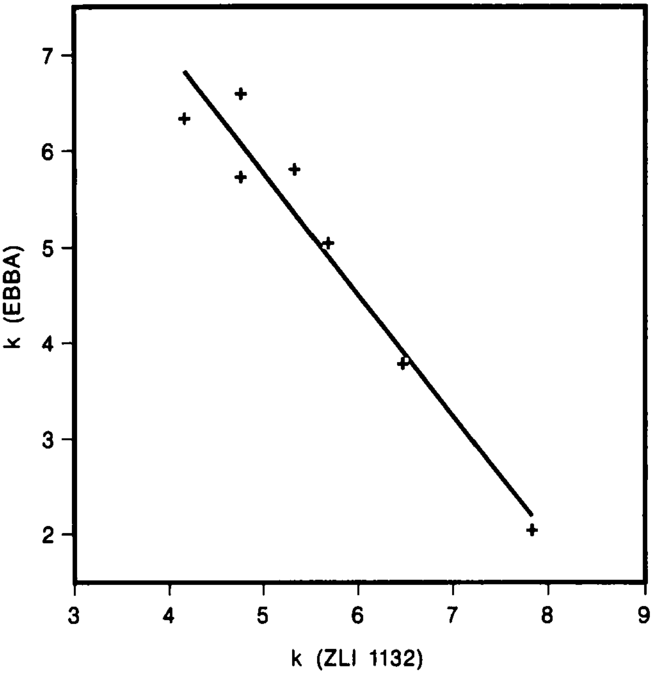

FIGURE 7 Elastic Hooke's law force constant k in mdyne/Å derived from degrees of order of solutes in the solvent EBBA vs. values in the solvent ZLI 1132. See Table IV.

are similar in both groups of molecules but the elements are considerably larger in the polycyclic systems ($60 \cdot 10^{-22}$J) than in the chlorobenzenes ($30 \cdot 10^{-22}$J). Consequently it is possible to predict degrees of order of aromatic ring systems on the basis of measured bond contributions with an accuracy of approximately 0.04. This is true as long as there is no contradiction between the symmetry of the molecule based on number and direction of bonds and the symmetry based on position of bonds or molecular shape, as e.g. in perylene.

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