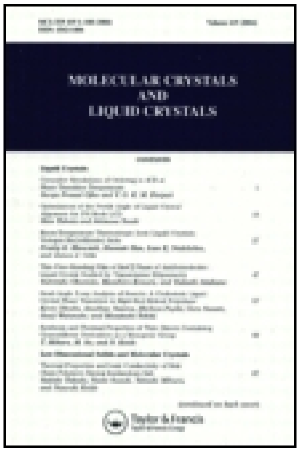

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Infrared Linear Dichroism of Nematic Solutions I. Orientation of Guest Molecules in Nematic Hosts

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Infrared Linear Dichroism of Nematic Solutions
I. Orientation of Guest Molecules in Nematic Hosts

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The orientational order and the biaxiality of some mono-substituted benzenes in nematic liquid crystals have been determined from infrared linear dichroism measurements. The experimental results are in good agreement with the theoretical predictions of the mean field theory.

Keywords: biaxial order, linear dichroism, I.R. spectroscopy

INTRODUCTION

Liquid crystals are valuable as anisotropic solvents in a variety of roles. The orientation of the solute molecules and the interaction between solute and solvent molecules have been extensively studied by NMR spectroscopy.[1] Although pure liquid crystals have been widely investigated by infrared dichroism measurements, molecules in solution have received less attention.[2,3,4,5] This is largely because infrared measurements suffer from the limitations that solvent bands often mask solute bands and that the solutes only show weak absorptions.

The nematic phases of cyclohexylcyclohexane derivatives which have recently become available[6] give a wider choice of suitable

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†Deceased.

solutes. The absorptions of the solutes which are mostly weak can then be measured with a high signal to noise ratio by means of FTIR spectroscopy because of the high radiation throughput. Infrared linear dichroism studies offer some advantages compared with other methods of determination of molecular orientation. They make it possible to determine the orientational order of both the solute and the solvent species at the same time and under the same conditions, there is no need for extensive computer programs to interpret the spectra and it is even possible to determine the orientation of different parts of a particular molecule. Furthermore one can investigate molecules of a certain conformation and also associations of molecules, e.g. pairs held together by hydrogen bonding. We have investigated the orientational behavior of some monosubstituted benzenes in the nematic solvent ZLI 1695 which is a mixture of cyanocyclohexylcyclohexane derivatives.

THEORY

The orientational order of nematic liquid crystals is in general described by an order matrix S_{ij} $(i, j = x, y, z)$.[7] This matrix can be diagonalized and then has only two independent elements because $S_{xx} + S_{yy} + S_{zz} = 0$. In pure liquid crystals one assumes rotational symmetry around the long molecular axis (z-axis). In this case $S_{xx} = S_{yy} = S_{zz}/2$ and only one order parameter $S = S_{zz} = \langle P_2 \rangle$ is left, which fully describes the orientational order.

For molecules, which do not have rotational symmetry about the z-axis, the order matrix has two independent diagonal elements. One takes

$$S = S_{zz} = 1 - \frac{3}{2}\overline{\sin^2\theta}$$

and

$$D = S_{xx} - S_{yy} = \frac{3}{2}\overline{\sin^2\theta \cos 2\varphi}\,.$$

S describes the mean deviation of the long molecular axis from the director of the nematic phase and D describes the difference in tendency of the two transverse molecular axes to align parallel to the director.

Luckhurst *et al.*[8] have developed the so called mean field theory to take into account the deviation from rotational symmetry. A measure of the deviation is then given by the biaxiality parameter λ and the variation of D with S is determined entirely by λ. The theory of Luckhurst *et al.* has been extended to deal with rigid molecules in solution by Emsley *et al.*[9] The value of the biaxiality parameter λ is dependent on the nature of both solute and solvent and λ is now a measure of the deviation of the solute molecules from cylindrical symmetry. The value of λ should be independent of the order of the solvent and of temperature.

The biaxiality parameter λ is related to any tensor property of a molecule,

$$\lambda = \frac{1}{4}\sqrt{6}\,\frac{\sigma_{yy} - \sigma_{xx}}{\sigma_{zz} - \frac{1}{2}\sigma_{yy} - \frac{1}{2}\sigma_{xx}}$$

where σ_{xx}, σ_{yy} and σ_{zz} are the components of the tensor after diagonalization.[10] The predictions of the theory were compared with experimental results for only one rigid molecule.[9] Herein we will compare the experimental results for several nonrigid molecules with the theoretical predictions.

DETERMINATION OF ORDER PARAMETERS FROM LINEAR DICHROISM

As shown by Korte,[11] it is possible to determine the order parameters S and D from the infrared linear dichroism of two absorption bands having transition moments of different direction. Hence it is possible to determine the biaxiality of the solute molecules. The relation between the dichroic ratio $R = A_{\parallel}/A_{\perp}$ (A = Absorbance) and the order parameters S and D is given by,

$$\frac{R-1}{R+2} = S\left(1 - \frac{3}{2}\sin^2\alpha\right) - \frac{1}{2}D(\sin^2\alpha\cos 2\beta).$$

The angles α and β define the direction of the transition moment in the molecular frame (Figure 1). For a transition moment parallel to the principal axis z of the molecule ($\alpha = 0$) it follows that:

$$\frac{R-1}{R+2} = S.$$

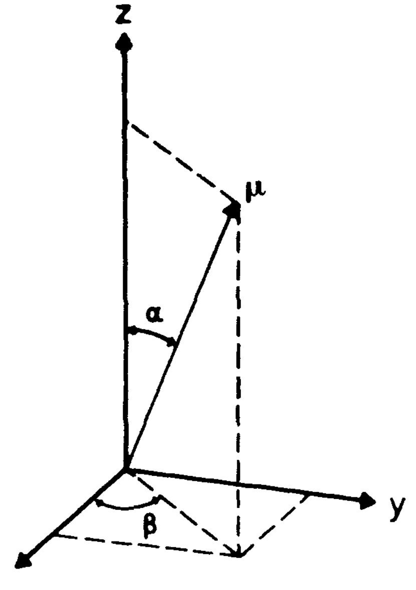

FIGURE 1 Definition of the angles used to specify the orientation of a transition moment μ in the molecular frame.

For any other orientation of the transition moment, a contribution from D appears. The strongest influence of D will be found for transition moments perpendicular to the principal axis ($\alpha = \pi/2$) i.e.

$$\frac{R-1}{R+2} = S + D\cos 2\beta .$$

If a transition moment is parallel to the x or y axes, we obtain $(S + D)$ and $(S - D)$, respectively.

The quantitative determination of the order parameters is influenced by the anisotropy of the internal field, which, in general, is not known exactly. However, the resulting errors can be minimized by choosing a liquid crystal host of low optical anisotropy.

EXPERIMENTAL

The infrared linear dichroism spectra were recorded with a computer controlled Fourier transform infrared spectrophotometer (NICOLET 7199) equipped with a wire grid polarizer (ORIEL). The sample was placed between two KBr plates. The spacing between the plates was adjusted to about 50 μm by a teflon spacer. To obtain a uniform planar director pattern, the KBr plates were polished in one direction before the measurements. The temperature of the samples was controlled by means of a thermostat with an accuracy of ±0.1°C. A ternary mixture of 4-*n*-alkyl-*trans*,*trans*-bicyclohexyl-4'-carbonitriles (i.e. Merck ZLI 1695) was used as the solvent. The solutions were prepared by mixing the components in the isotropic phase above the clearing point. The mole fractions were between 0.05 and 0.1.

RESULTS AND DISCUSSION

The molecules investigated have a phenyl ring as a common feature. This is the largest rigid part of the molecule and is the major factor determining the molecular shape and polarizability anisotropy. It would appear to be safe to assume that the phenyl ring exerts a strong influence on the orientation of the molecule and that the orientation of the ring may be taken as an indication of the orientation of the whole molecule.

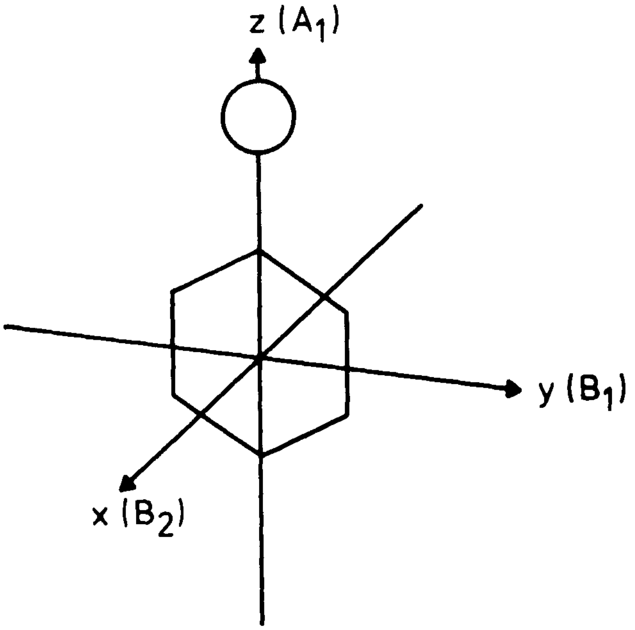

FIGURE 2 Molecular frame of monosubstituted benzenes with C_{2v} symmetry.

The order parameters were determined from the dichroic ratios of the absorption bands at 1500 cm^{-1} (ν_{CC}) and 700 cm^{-1} (Γ_{CC}) of the phenyl ring. Under the condition of local C_{2v} symmetry of the ring, the transition moments of these vibrations are in the *z* and *x* direction of the molecular frame (Figure 2). In order to test the theory we determined the local order parameters *S* and *D* of the phenyl ring for the molecules 2-phenylpropanole 1, 2-phenylpropanal 2, 1-phenylethylamine 3, 2-phenylbutanole 4, 1-phenylethanole 5, phenylacetylene 6 and benzonitrile 7 at several temperatures in the nematic phase of ZLI 1695. The variation of the order parameter *D* with the order parameter *S* is shown in Figures 3–5.

Compounds 1 to 5 show a good agreement of the experimental data with the theoretical predictions (Figures 3 and 4). The values of the biaxiality parameter λ have little or no dependence on temperature. No influence of the hydrogen bonds between guest and host molecules on the orientational order of the phenyl ring is perceptible. The theory of Emsley *et al.* therefore means to be applicable, not

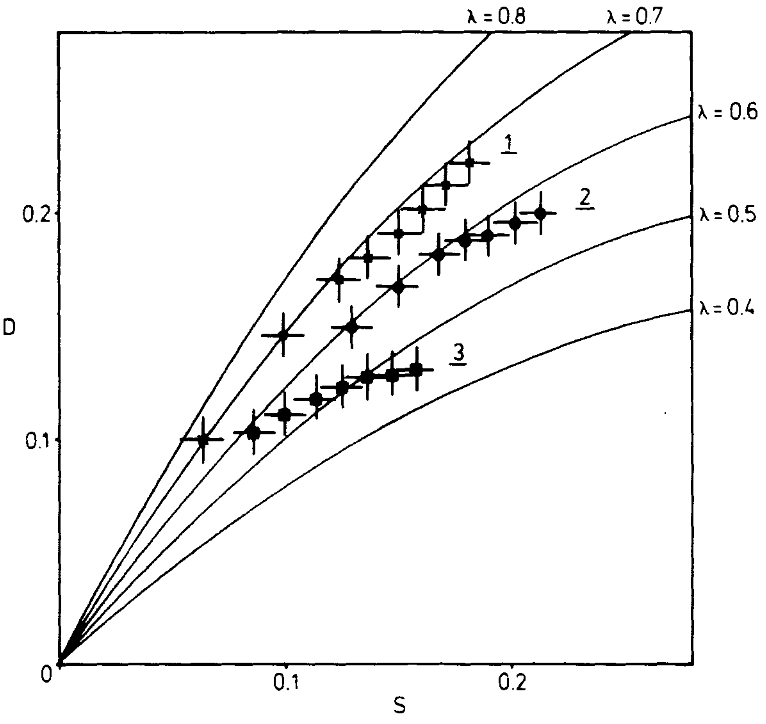

FIGURE 3 Dependence of *D* on *S* for 2-phenylpropanole 1, 2-phenylpropanal 2 and 1-phenylethylamine 3 in ZLI 1695 (mole fraction 0.07).

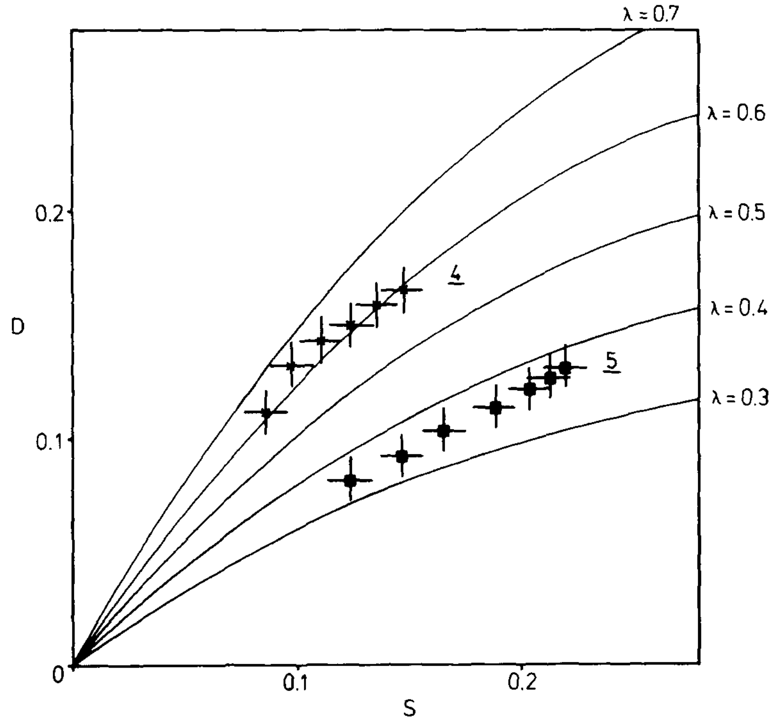

FIGURE 4 Dependence of *D* on *S* for 2-phenylbutanole 4 and 1-phenylethanole 5 in ZLI 1695 (mole fraction 0.07).

only to rigid molecules, but also to molecules with some flexible parts.

The compounds 6 and 7 are rigid. They show a similar orientational behaviour. The variation of *D* with *S* is not in accordance with the theoretical predictions (Figure 5) and the biaxiality parameter λ shows a strong dependence on temperature (Figure 6). Phenylacetylene 6 possesses an acidic hydrogen atom, which can act as a donor in a hydrogen bond with the nitrile group of the host. In solution there is a temperature dependent equilibrium between the hydrogen bonded and the free species. The absorption bands of the phenyl ring which were studied show no dependence of the frequency on the bound state of the methine group. The dichroic ratios of the absorption bands are functions of the orientational orders of both species. Considering the change in concentration with temperature, the temperature dependence of λ is the superposition of the temperature dependencies of the orientational orders of the two species (weighted according to their concentrations).

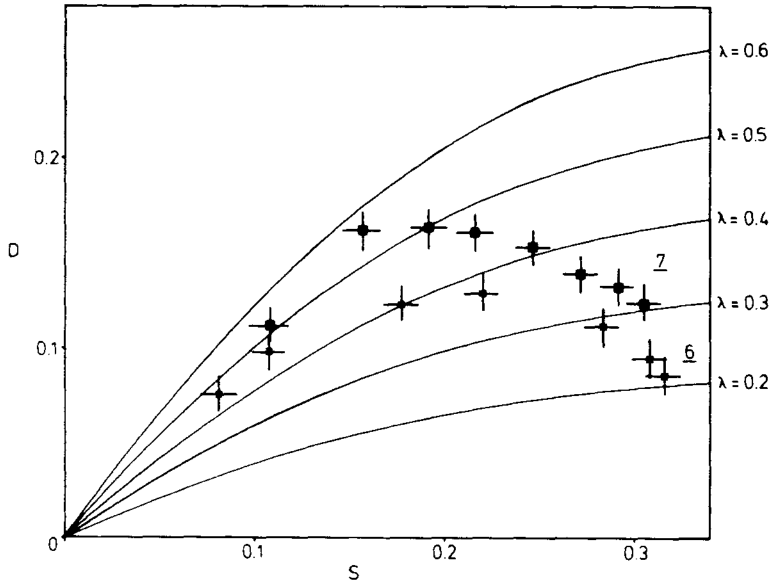

FIGURE 5 Dependence of D on S for phenylacetylene 6 and benzonitrile 7 in ZLI 1695 (more fraction 0.10).

Benzonitrile 7 has a nitrile group and a strong dipole moment, like the host molecules. Here we can assume an equilibrium between free molecules and guest-host associates, which originate from dipole–dipole correlation. This fully explains the observed orientational order. For the molecules 6 and 7 we must assume a set of order parameters for each species in solution.

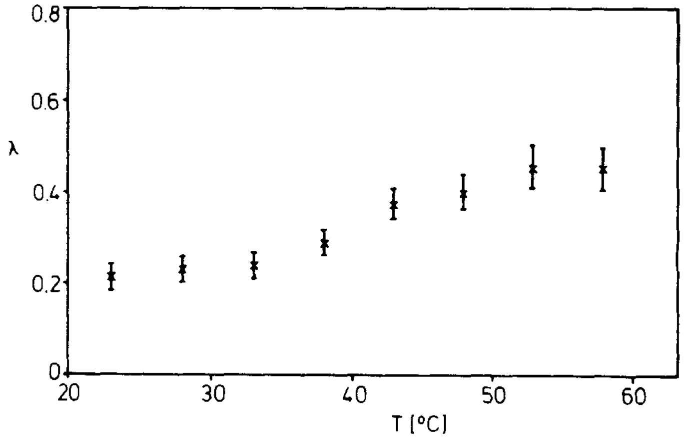

FIGURE 6 Dependence of the biaxiality parameter λ on temperature for phenylacetylene in ZLI 1695 (mole fraction 0.10).

CONCLUSION

The measurement of infrared linear dichroism is a valuable tool for the investigation of guest molecules in nematic solvents. The orientational order of the investigated guest molecules can be described by the theory of Emsley *et al.* This theory is applicable to both rigid and flexible molecules. If a compound exists as different molecular species in solution, each species must be described by its own set of order parameters. The correlation of orientational order with molecular properties will be the subject of a forthcoming paper.

Acknowledgments

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