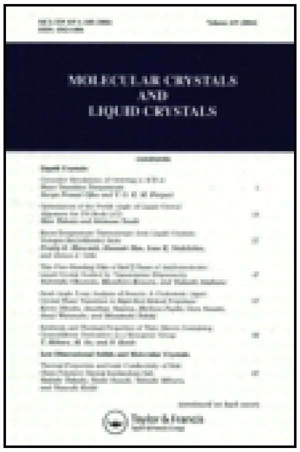

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Infrared Linear Dichroism of Nematic Solutions II. Correlation of Biaxiality with Molecular Properties

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Infrared Linear Dichroism of Nematic Solutions
II. Correlation of Biaxiality with Molecular Properties

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The biaxial ordering of some monosubstituted benzenes was determined from the infrared linear dichroism of solutions in the nematic host phase ZLI 1695. A correlation was found between the biaxiality and the anisotropy of the molecular shape. The orientational order of the solutes in this solvent appears to be determined entirely by dispersion forces but in other nematic solvents additional types of intermolecular forces are involved.

Keywords: nematic solutions, infrared dichroism, biaxiality

INTRODUCTION

Liquid crystals are widely used as anisotropic solvents giving systems of homogeneously oriented solute molecules and hence enabling spectroscopic studies to be carried out of the anisotropy of physical molecular properties. It has been shown that for some nematic molecules a correlation exists between the orientational order and the anisotropy of the polarizability.[1,2,3]

In a previous paper[4] we showed that the molecular biaxiality can be determined from infrared linear dichroism measurements. Now we examine the relationship between the biaxiality and the anisotropy of molecular dimensions for a series of monosubstituted benzenes.

The liquid crystalline order is, in general, discussed in terms of anisotropic dispersion interactions. The dispersion forces are corre-

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†Deceased.

lated with the polarizabilities of the molecules. The polarizability values are known for only a few molecules. LeFevre and LeFevre have shown, that in many cases the ratios of the polarizabilities, $\alpha_{zz} : \alpha_{yy} : \alpha_{xx}$ correspond to the ratios of molecular dimensions $l_z : l_y : l_x$.[5] The molecular dimensions can be calculated from bond lengths and van der Waals radii. We will therefore examine the relationship between the biaxiality λ and the molecular dimensions of solute molecules.

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_{zz}, σ_{yy} and σ_{xx} are the components of the tensor after it is diagonalized.[6] We use the molecular dimensions l_i as the tensor properties σ_{ii}.

The biaxiality parameter λ vanishes for cylindrical molecules, $\lambda = 0$, if the z-axis is chosen parallel to the long molecular axis. This also occurs for disc-like molecules, if the z-axis is perpendicular to the disc. If for a disc-like molecule one defines a cartesian frame with the z-axis in the plane, λ has its maximum value of $(3/2)^{1/2}$.

EXPERIMENTAL

The experimental details of the preparation of the solutions and the measurement of the infrared linear dichroism were described in our previous paper.[4]

As liquid crystalline solvent ZLI 1695 (Merck), a ternary mixture of 4-*n*-alkyl-*trans*,*trans*-bicyclohexyl-4′-carbonitriles, was used. The mole fractions of the solutes were between 0.05 and 0.10.

The measurements were performed at 23°C, a temperature appreciably below the clearing point of the solutions (T_c = 65–70°C).

RESULTS AND DISCUSSION

We have determined the biaxiality parameter λ for benzene $\underline{1}$, fluorobenzene $\underline{2}$, chlorobenzene $\underline{3}$, bromobenzene $\underline{4}$, iodobenzene $\underline{5}$, benzonitrile $\underline{6}$, phenylacetylene $\underline{7}$, phenylisocyanate $\underline{8}$, phenylisothiocyanate $\underline{9}$, toluene $\underline{10}$ and nitrobenzene $\underline{11}$ in the nematic phase ZLI 1695.

The order parameters S and D were determined from the dichroic ratios of the absorption bands at 1485 cm^{-1} (δ_{CC}) and 672 cm^{-1} (Γ_{CC}). The transition moments of these vibrations are in the plane and perpendicular to the plane, respectively. From the order parameters we have determined the biaxiality parameter using graphs of D vs. S as given by Emsley et al.[7]

The molecular dimensions were calculated from bond lengths and van der Waals radii.[8,9]

Figure 1 shows the relationship between the values of the biaxiality parameter λ_{cal}, calculated from molecular dimensions and the experimental values.

It is apparent that there is a correlation between λ_{exp}, and λ_{cal}. The sequence λ(PhF) > λ(PhCl) > λ(PhBr) > λ(PhI), inferred from molecular dimensions, is verified by the experimental data. Chlorobenzene and toluene, which possess identical dimensions, have virtually identical values of the biaxiality parameter λ_{exp}.

Because of the proportionality between molecular dimensions and

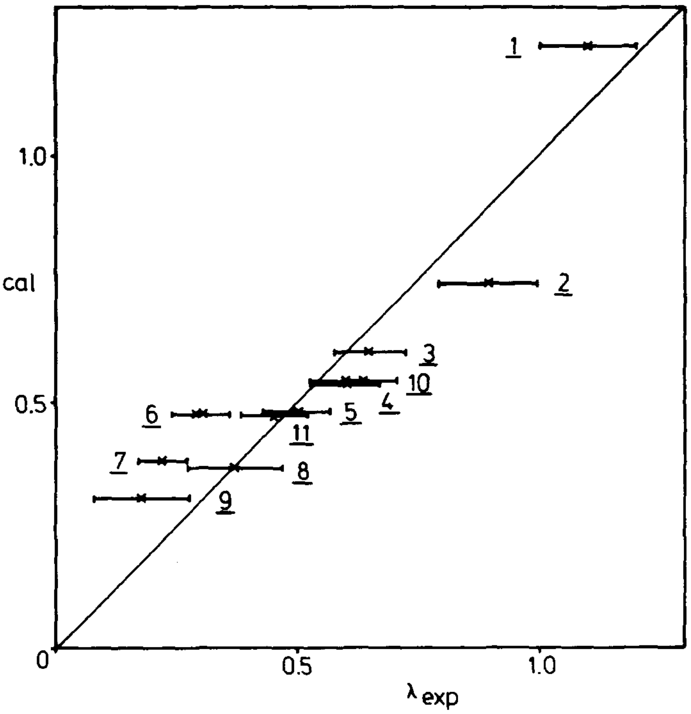

FIGURE 1 Correlation between calculated (λ_{cal}) and experimental biaxiality parameters (λ_{exp}).

polarizabilities, it appears that the orientation of these molecules in the nematic phase of ZLI 1695 is determined only by anisotropic dispersion forces between guest and host molecules.

Deviations from the correlation line are found for benzonitrile 6, phenylacetylene 7 and phenylisothiocyanate 9. The orientation of 6 and 7 has been discussed in a previous paper.[4] These molecules show specific guest/host interactions. The molecular dimensions of phenylisocyanate 8 and phenylisothiocyanate 9 were calculated for a linear configuration. However, microwave spectroscopic investigations have shown, that 8 is not in fact linear and the substituent is not parallel to the 1,4-axis of the ring.[10] Phenylisothiocyanate 9 presumably, has also a nonlinear structure. This molecule is therefore shorter and the calculated biaxiality parameter is too large.

The orientations of some monosubstituted benzenes in nematic solvents have been measured by NMR spectroscopy.[11-18] The values of the order parameters S and D, determined from infrared linear dichroism, show a similar dependence on structure as the order

TABLE I

Comparison of the orientational orders from NMR and infrared linear dichroism measurements for fluorobenzene 2, chlorobenzene 3, bromobenzene 4, iodobenzene 5 and benzonitrile 6

Compound	Solvent	$\frac{T}{°C}$	S	D	λ	Ref.
2	Licristal IV	30	0.1215	0.1339	0.56	11
	ZLI 1167		0.0726	0.1725	1.1	12
	ZLI 1695	23	0.10	0.18	0.90	[a]
3	Licristal IV	30	0.1630	0.1272	0.43	11
	ZLI 1167		0.1147	0.1411	0.61	15
	ZLI 1695	23	0.22	0.23	0.65	[a]
4	Licristal IV	30	0.1554	0.1146	0.41	11
	ZLI 1167	32	0.11425	0.12121	0.54	16
	ZLI 1695	23	0.21	0.20	0.60	[a]
5	Licristal IV	30	0.1533	0.1121	0.40	11
	ZLI 1167		0.1245	0.1007	0.42	13
	ZLI 1695	23	0.21	0.18	0.50	[a]
6	Licristal IV	30	0.2054	0.1226	0.37	11
	Licristal IV	28	0.159	0.098	0.34	14
	EBBA	25	0.1696	0.0592	0.20	17
	NP 1565 TNC	25	0.2313	0.1614	0.45	17
	ZLI 1167	25	0.1494	0.1078	0.40	17
	HOAB	80	0.197	0.129	0.40	18
	ZLI 1695	23	0.31	0.12	0.30	[a]

[a] This work.

parameters determined from NMR measurements (Table I). The absolute values of the order parameters are not comparable, because the experimental conditions were different.

The orientational order of the solutes is strongly dependent on temperature. The biaxiality parameter λ should be independent of temperature.[7] The biaxiality parameter of the solute molecules is influenced by the nature of the solvent. The orientational order of guest molecules in different liquid crystals is not solely determined by dispersion forces.

CONCLUSION

A correlation was found between the orientational order of some monosubstituted benzenes in ZLI 1695 and the anisotropy of the molecular shape. The orientation of these molecules in this particular solvent appears to be determined only by anisotropic dispersion forces.

A comparison of the orientational behavior of some molecules in different nematic solvents shows, that contributions to the intermolecular potential other than dispersion forces are important.

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