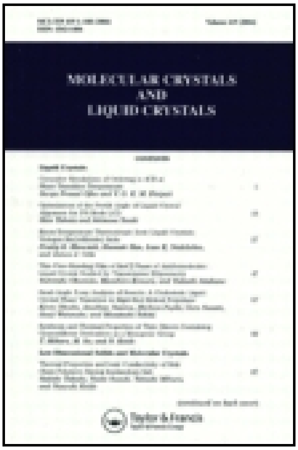

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Influence of the Order Parameter *D* on the Linear Dichroism of Nematic Liquid Crystals

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When a uniaxial nematic phase is formed by biaxial molecules, in addition to S the order parameter D is necessary to describe the molecular order. It is shown here that D effects the dichroic ratio whenever the orientation of the transition moment differs from the molecular axis defining the director. The evaluation of experimental results with respect to D and its interpretation are discussed.

INTRODUCTION

The orientational order of nematic liquid crystals is usually characterized by the order parameter $S \equiv 1 - (3/2)\overline{\sin^2\theta}$ where θ denotes the angle between the principal axis of the molecule and the director, the upper bar indicates the ensemble average. A convenient way to determine S experimentally is by linear dichroism measurements. In general, several isolated and pronounced bands, for which the orientation of the related linear transition moment with respect to the molecular geometry is known, are available in the ultraviolet or infrared spectrum. The relation between S and the dichroic ratio has been derived by Maier and Saupe assuming the molecules constituting the nematic phase to be cylindrically symmetric.[1]

In such a case, no other parameter is necessary to describe the order of an optically uniaxial phase. In reality however, the molecules will deviate from this shape so that the two transverse axes are distinguishable and hence, their difference has to be taken into account.

The relevant order parameter D was introduced by Alben, McColl, and Shih[2] as the difference in the tendencies of the transverse axes to project on the nematic axis (difference between the elements S_{22} and S_{33} of the order tensor **S**). Other definitions of this parameter based on Euler angles[3] and Wigner coefficients[4] differ in simple numerical factors only. As Straley pointed out,[3] the parameters S and D are sufficient to characterize the order of a uniaxial phase even if it consists of biaxial particles. The contribution of D to the dichroic ratio will be outlined here, which in turn allows its experimental determination.

CALCULATION

Maier and Saupe derived the relation between the dichroic ratio and the order parameter S using Euler angles to describe the actual orientation of a molecule with respect to a laboratory frame.[1] The same approach will be used here, however, the simplification for cylindrically symmetric molecules is discarded.

Let a single molecule be represented by its axes x', y', and z', where z' is the principal axis. The average orientation of z' defines the

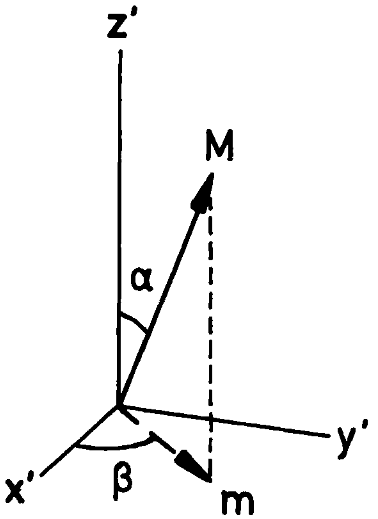

FIGURE 1 Definition of the angles used to specify the orientation of a transition moment M with respect to the molecular axes x', y', and z' (m is the projection of M on the $x'y'$ plane).

director which is taken to be parallel to the z axis of the laboratory frame x, y, z. In the latter frame the orientations of the molecular axes are described by the Euler angles θ denoting the angle between z and z', ψ being the nutation angle, and ϕ giving the pure rotation.[5]

We consider a transition moment which forms an angle α with z' and whose projection on the $x'y'$ plane forms an angle β with the x' axis of the molecule (Figure 1). The components of the oscillator strength f (being proportional to the square of the transition moment) effective parallel to x', y', and z', respectively, are

$$\begin{aligned} f_{x'} &= f\sin^2\alpha\cos^2\beta \\ f_{y'} &= f\sin^2\alpha\sin^2\beta \\ f_{z'} &= f\cos^2\alpha \end{aligned} \tag{1}$$

The resulting components parallel to x, y, z (laboratory frame) are obtained by applying the Euler transformations[5]

$$\begin{aligned} f_x &= f\Big[(\cos\psi\cos\phi - \cos\theta\sin\psi\sin\phi)^2\sin^2\alpha\cos^2\beta \\ &\quad + (\cos\psi\sin\phi + \cos\theta\sin\psi\cos\phi)^2\sin^2\alpha\sin^2\beta \\ &\quad + \sin^2\theta\sin^2\psi\cos^2\alpha\Big] \\ f_y &= f\Big[(\sin\psi\cos\phi + \cos\theta\cos\psi\sin\phi)^2\sin^2\alpha\cos^2\beta \\ &\quad + (\sin\psi\sin\phi - \cos\theta\cos\psi\cos\phi)^2\sin^2\alpha\sin^2\beta \\ &\quad + \sin^2\theta\cos^2\psi\cos^2\alpha\Big] \\ f_z &= f\Big[\sin^2\theta\sin^2\phi\sin^2\alpha\cos^2\beta \\ &\quad + \sin^2\theta\cos^2\phi\sin^2\alpha\sin^2\beta + \cos^2\theta\cos^2\alpha\Big] \end{aligned} \tag{2}$$

By simple trigonometric manipulations and formal introduction of the ensemble average we arrive at

$$\begin{aligned} \overline{f_x} &= f\Big[\tfrac{1}{2}\sin^2\alpha + \tfrac{1}{2}\big(1 - \tfrac{3}{2}\sin^2\alpha\big)\big(\overline{\sin^2\theta} - \bar{t}\big) \\ &\quad + \tfrac{1}{4}\sin^2\alpha\cos 2\beta\big(\overline{\sin^2\theta\cos 2\phi} + 2\bar{v}\big)\Big] \\ \overline{f_y} &= f\Big[\tfrac{1}{2}\sin^2\alpha + \tfrac{1}{2}\big(1 - \tfrac{3}{2}\sin^2\alpha\big)\big(\overline{\sin^2\theta} + \bar{t}\big) \\ &\quad + \tfrac{1}{4}\sin^2\alpha\cos 2\beta\big(\overline{\sin^2\theta\cos 2\phi} - 2\bar{v}\big)\Big] \\ \overline{f_z} &= f\Big[1 - \sin^2\alpha - \big(1 - \tfrac{3}{2}\sin^2\alpha\big)\overline{\sin^2\theta} \\ &\quad - \tfrac{1}{2}\overline{\sin^2\theta\cos 2\phi}\sin^2\alpha\cos 2\beta\Big] \end{aligned} \tag{3}$$

where

$$t = \sin^2\theta \cos 2\psi$$
$$v = (1 + \cos^2\theta)\cos 2\psi \cos 2\phi - 2\cos\theta \sin 2\psi \sin 2\phi$$

For a uniaxial phase $\overline{f_x}$ and $\overline{f_y}$ have to be equal, i.e. $\bar{t}$ and $\bar{v}$ vanish as derived by Straley.[3] He pointed out also that $\overline{\sin^2\theta \cos 2\phi}$ is the additional order parameter necessary for biaxial molecules and that this is related to D by

$$D = \tfrac{3}{2}\overline{\sin^2\theta \cos 2\phi} \tag{4a}$$

After substitution of the averaged values by the order parameters S and D, Eqs. (3) can be rewritten as

$$\begin{aligned} \overline{f_x} = \overline{f_y} &= \tfrac{1}{3}f\left[1 - S\left(1 - \tfrac{3}{2}\sin^2\alpha\right) + \tfrac{1}{2}D\sin^2\alpha\cos 2\beta\right] \\ \overline{f_z} &= \tfrac{1}{3}f\left[1 + 2S\left(1 - \tfrac{3}{2}\sin^2\alpha\right) - D\sin^2\alpha\cos 2\beta\right] \end{aligned} \tag{4b}$$

The absorbance (peak or, more precise, integral values) of a given sample for radiation linearly polarized parallel to x, y, and z is proportional to $\overline{f_x}$, $\overline{f_y}$, and $\overline{f_z}$, respectively.[1] Experimental parameters as well as the oscillator strength f itself (but not the correction factor for the internal field[1]) are eliminated if the dichroic ratio $R = \overline{f_z}/\overline{f_y}$ is employed. Using Eqs. (4), the well known expression $(R - 1)/(R + 2)$ becomes

$$\frac{R-1}{R+2} = S\left(1 - \tfrac{3}{2}\sin^2\alpha\right) - \tfrac{1}{2}D\sin^2\alpha\cos 2\beta \tag{5}$$

In comparison with the Maier Saupe treatment we have obtained an additional term proportional to the order parameter D which comes into play whenever the constituting molecules differ from cylindrical symmetry.

DISCUSSION

Before discussing Eq. (5), some remarks on D itself shall be made. The function $\sin^2\theta \cos 2\phi$, the ensemble average of which defines D, depends on the deviation (θ) of the molecular long axis from the director as well as on the angle of pure rotation (ϕ). Starting from coinciding axes (x, x'; y, y'; z, z') an arbitrary orientation of the molecule is obtained by rotation around the z axis and subsequent pivoting on an axis in the x, y plane. By definition[5] ϕ is measured from the intersection of the xy plane with the $x'y'$ plane (which is the pivoting axis) to the molecular axis x'. If the pivoting axis happens to coincide with x' the contribution of this orientation to D is positive. On the other hand, pivoting on the y' axis leads to a maximal negative contribution.

On the whole, the order parameter D may adopt positive, negative, or zero values. Positive values will occur if the molecules tend to pivot on the x' axis more often or with larger amplitudes than on the y' axis. Furthermore, the product $D\cos 2\beta$ is positive if the transition moment projects more on the x' axis, provided this is the preferred pivoting axis. If for any reason the molecular frame has been chosen in such a way that the preferred pivoting axis has been called y', the order parameter D will be negative. For a transition moment parallel to this axis, however, the angle β equals $\pi/2$ and hence $\cos 2\beta$ is negative also.

Consequently, a positive product $D\cos 2\beta$ indicates that the absorption band under consideration is due to a transition moment which projects predominantly on the preferred pivoting axis. The opposite case is indicated by a negative value of $D\cos 2\beta$. This product is zero if the transition moment projects equally on both the x' and the y' axis ($\beta = \pi/4$) or if D itself vanishes which happens when none of the two axes is preferred, e.g. for a cylindrically symmetric molecule.

Equation (5) differs from the result obtained by Maier and Saupe[1] for cylindrically symmetric molecules only by the term depending on D. Therefore, for a transition moment parallel to the principal axis z' of the molecule ($\alpha = 0$) both calculations give

$$(R-1)/(R+2) = S \tag{6a}$$

However, if the molecules are biaxial, a contribution from D appears for any other orientation of the transition moment: The result is not S alone but a superimposition of S and D depending contributions. The strongest influence of D will be found for transition moments perpendicular to the principal axis ($\alpha = \pi/2$), for which Eq. (5) reads

$$2(1-R)/(2+R) = S + D\cos 2\beta \tag{6b}$$

If additionally a transition moment is strictly parallel either to the x' or to the y' axis, we obtain $(S + D)$ or $(S - D)$, respectively, from Eqs. (6).

The contributions from S and D cannot be distinguished from a single experiment. To obtain S separately, a suitable transition moment parallel to the principal axis of the molecule must be chosen. A direct measurement of D is possibly only if the factor of S in Eq. (5) vanishes, i.e. if a transition moment exists whose orientation matches exactly the condition $\sin^2\alpha = 2/3$.

On principle, S and D can be determined from the dichroic ratios of any two bands for which the orientations of the related linear transition moments relative to the molecular axes are different and known. However, the experimental results have to be corrected for the internal field, which usually is not known precisely. If the correction is omitted in the evaluation of the dichroic ratio of a 'parallel band' and the one of a 'perpendicular band' by application of Eq. (6a) and Eq. (6b), respectively, different results do not necessarily indicate an influence by D: even for cylindrically symmetric molecules and provided that the internal field changes both dichroic ratios by the same factor (dispersion neglected), the different evaluation leads to different results.

This obstacle can be removed by choosing two bands for which the same evaluation applies, for instance those due to transition moments parallel to the two transverse axes x' and y'. The results agree when D vanishes, a difference proves D to be different from zero as far as the dispersion can be neglected. The quantitative determination of S and D (when different from zero) is affected in any case by disregarding the internal field. The resulting errors can be minimized by choosing a compound of low optical anisotropy and by measuring in the infrared range, where additionally the dispersion is usually negligible.

Largest values of D are to be expected for planar molecules. Since nematogenic molecules in most cases comprise several planar but not necessarily coplanar parts, a nonmesogenic compound dissolved in a nematic liquid crystal was chosen as a first example. Obviously, Eqs. (5) and (6) apply for this case as well. A condition for the selection of the solute was the existence of strong and isolated bands in the infrared range due to transition moments having the required orientations.

9-Fluorenone was found to be suitable, assuming its largest extension to be aligned parallel to the director of the solvent. The transition moment of the ν(CO) vibration (at about 1715 cm^{-1}) and of the γ(CH) vibration (out of plane) of the six-membered rings (at about

738 cm^{-1}) are perpendicular to it ($\alpha = \pi/2$); the former lies within the molecular plane, the latter perpendicular to it.

For a solution of 9-fluorenone (mole fraction 0.07) in an equimolar mixture of EBBA and MBBA at 20 °C (clearing temperature $T_c \simeq$ 42 °C) the following dichroic ratios were found

$$R_{\gamma(\mathrm{CH})} = 0.504$$

$$R_{\nu(\mathrm{CO})} = 0.876$$

when no correction for the internal field has been made. If the direction of the γ(CH) transition moment is identified with x', Eq. (6b) gives for this vibration ($\beta = 0$)

$$S + D = 0.396$$

and (with $\beta = \pi/2$) for the ν(CO) band

$$S - D = 0.088$$

These values allow to calculate the order parameters separately resulting in $S \simeq 0.24$ and $D \simeq 0.15$ for the solute.

As obvious from the definitions D is correlated with S. The mutual relation has been derived by Luckhurst *et al.*[4] from a molecular field theory where the influence of the molecular structure is taken into account by a parameter λ. This has been explained by Van der Meer and Vertogen[6] in terms of that molecular property σ which governs the nematic alignment

$$\lambda = \frac{1}{4}\sqrt{6}\,\frac{\sigma_2 - \sigma_1}{\sigma_3 - \frac{1}{2}\sigma_2 - \frac{1}{2}\sigma_1} \tag{7}$$

Assuming σ to be represented by the shape of the molecule,[6] the geometrical measures of a model can be used to estimate λ. In the case of 9-fluorenone this leads to $\lambda \simeq 0.5$.

Figure 2 shows D versus S, calculated from the formulae given by Luckhurst *et al.*[4] for different values of λ. Couples of S and D values obtained in the same way and for the same sample as before from measurements at various temperatures between 20 °C and 41 °C are given therein also. For $S > 0.11$ the agreement of the experimental results with the theoretical calculations for $\lambda = 0.4$ is unexpectedly good. It must be kept in mind, that the influence of the internal field was disregarded. A correction might shift the results to smaller S and larger D values, i.e. to a somewhat larger value of λ. As to the results with $S < 0.11$, one should consider that they were obtained as differences between small values determined at $T/T_c > 0.99$.

The value $\lambda = 0.5$ has been derived from the maximal extensions of the molecule; smaller values are obtained when averaging over the protruding atoms. Therefore, $\lambda = 0.4$ as taken from Figure 2 seems to be within the limits of the applied model. On the whole, the influence of the order parameter D on the dichroic ratio and its comparatively large values found for 9-fluorenone in a nematic solvent seem to be supported by these theoretical considerations.

It is hoped that in the described way information on the actual orientation and conformation or — upon scanning the temperature or other parameters— on conformational changes of the molecules in a liquid crystal can be gathered.

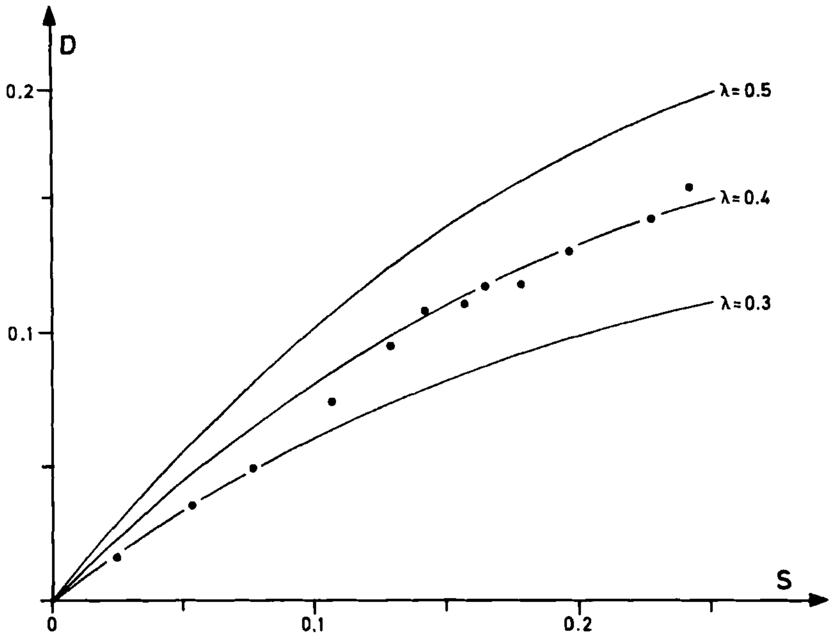

FIGURE 2 Dependence of D on S according Luckhurst *et al.*[4] for different values of λ and experimental results for 9-fluorenone dissolved in EBBA/MBBA (mole fraction 0.07).

After completion of the manuscript I became aware of the paper by Clark and Saunders,[7] who use an expression equivalent to Eq. (5) of this paper, which they had derived elsewhere.[8] The additional factor $\sqrt{3}$ in their equation is due to a slightly different definition of D. If D is determined from other molecular properties[9] this factor appears explicitly also. The different sign of the term depending on D means no discrepancy since Clark and Saunders choose the x' axis to lie in the molecular plane.

In both cases the order parameters of a nonmesogenic compound dissolved in a nematic liquid crystal are determined from dichroic ratios. However, Clark and Saunders evaluate two bands in the visible range (one of the related transition moments being parallel to z'). Their results show a tendency different from what was predicted theoretically by Luckhurst *et al.*[4] This might be due to the particular solute; on the other hand, in both papers the influence of the internal field is not taken into account quantitatively and hence the accuracy of the data presented is not precisely known.

The agreement of finding remarkably large values of D suggests that even for molecules deviating from planar shape this order parameter cannot be neglected a priori.

Acknowledgments

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References

1. A. Saupe and W. Maier, *Z. Naturforsch.*, **16a**, 816 (1961).
2. R. Alben, J. R. McColl and C. S. Shih, *Solid State Communications*, **11**, 1081 (1972).
3. J. P. Straley, *Phys. Rev. A*, **10**, 1881 (1974).
4. G. R. Luckhurst, C. Zannoni, P. L. Nordio and U. Segre, *Molecular Physics*, **30**, 1345 (1975).
5. I. Bronstein and K. Semendjajew, *Taschenbuch der Mathematik*, Verlag H. Deutsch, Frankfurt, 1964.
6. B. W. Van der Meer and G. Vertogen, *Physics Letters A*, **59**, 279 (1976).
7. M. G. Clark, F. C. Saunders, *Mol. Cryst. Liq. Cryst.* **82** (*Letters*), 267 (1982).
8. F. C. Saunders, L. Wright, M. G. Clark, in '*Liquid Crystals and Ordered Fluids*', vol. 4, J. F. Johnson, A. C. Griffin, Eds., Plenum, New York, in press.
9. E. H. Korte, *Mol. Cryst. Liq. Cryst.* (*Letters*), in press.