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Proposal of a new method to determine tilt angles of absorption transition moments in host-guest liquid crystal cells

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An idea for a method of experimental determination of tilt angles and order parameters of cylindrosymmetric transition moments of liquid crystals and of dyes in host-guest systems is described. Furthermore, first experimental hints are given. With freely rotating molecules, all transition moments result in an isotropic absorbance for UV/VIS-spectroscopy using polarized light. The resulting absorbance becomes anisotropic if the transition moment of the molecules is polarized, the molecules are aligned in a preferential direction, and the free rotation is suppressed. In this case, the measurement of A_{iso}, $A^{\perp}_{\mathrm{tilt}}$, and $A^{\parallel}_{\mathrm{tilt}}$ using polarized light is sufficient to calculate the related tilt angle Ψ, the order parameter S, and the absorbance $A_{\angle}$ as a function of the polarization angle. The local electric field and its influence on the dichroic ratio of an absorption band has not been considered. The precision of this method is still limited by the photometric accuracy of the spectrometer and the mechanical precision of the goniometric adjustment of the experimental apparatus.

1. Introduction

The order parameter S for liquid crystal molecules was first introduced by Zvetkoff [1]. According to his concept, S is defined as

$$S = \tfrac{1}{2}\langle 3\cos^2\Theta - 1\rangle, \qquad (1)$$

where the angular brackets denote an average and Θ is the angle between the molecular long axis and the macroscopic director **n**. Maier and Saupe [2–4] described the nematic behaviour of such systems in a molecular field theory approach assuming anisotropic dispersion forces between molecules. This concept, was subsequently developed further by Humphries, James, and Luckhurst [5]. Maier and Saupe [6] also proposed a variety of methods with which to measure S. One of them is based upon the measurement of the UV/VIS-absorbance with polarized light at the maximum of an absorption band. The band must belong either to a transition moment of the liquid crystal molecule or to a dichroic dye dissolved in the liquid crystal. In both cases, measurements give the order parameter S_{zz} for the transition dipole which is taken to be parallel to the z-axis [7]. A_{iso} is the absorbance for $S_{zz}=0$, i.e. for the isotropic case. These two parameters are related to $A_{\parallel}$ and $A_{\perp}$ as

$$S_{zz} = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + 2A_{\perp}}, \qquad (2)$$

$$A_{\mathrm{iso}} = \frac{A_{\parallel} + 2A_{\perp}}{3},$$

where $A_{\parallel}$ is the absorbance parallel and $A_{\perp}$ is the absorbance perpendicular to the macroscopic director **n**. These parameters can be rewritten as

$$A_{\parallel} = 3A_{\mathrm{iso}}\langle\cos^2\Theta\rangle, \qquad (4)$$

$$A_{\perp} = \tfrac{3}{2}A_{\mathrm{iso}}\langle 1 - \cos^2\Theta\rangle. \qquad (5)$$

2. Extension of the equations of absorbance to arbitrary tilt angles

By aligning the liquid crystal, for example by means of a rubbed alignment polymer [6], it is possible to induce a tilt angle Ψ between the laboratory axis W, i.e. the rubbing direction, and the director **n** which lies in the VW plane (figure 1). Equations (4) and (5) are valid only for a tilt angle of 0°, i.e. if **n** is parallel to W. Extending the equations to any tilt angle between 0° and 90°, the absorbances are labelled with the subscript 'tilt', which shows that Ψ is now arbitrary. In this case a measurement of $A^{\parallel}_{\mathrm{tilt}}$ and $A^{\perp}_{\mathrm{tilt}}$ yields the absorbances parallel and perpendicular to W. From geometrical

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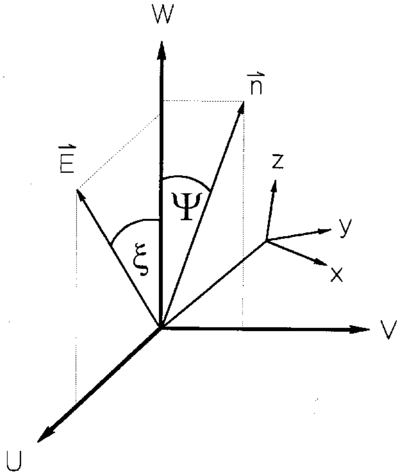

Figure 1. Relation between the molecular axes *x,y,z* and the laboratory axes *U, V, W*. The tilt angle Ψ is in the *VW* plane and the polarization angle ξ is in the *UW* plane.

considerations it follows that $A^{\perp}_{\text{tilt}}$ is independent of Ψ:

$$A^{\perp}_{\text{tilt}} = A_{\perp}. \tag{6}$$

For homogeneous alignment, the tilt angle Ψ is 0° and **n** is parallel to *W* (figure 2(*a*)). The absorbance parallel to *W* is given by

$$A^{\parallel}_{\text{tilt}} = A_{\parallel}. \tag{7}$$

For homeotropic alignment, the tilt angle $\Psi = 90°$ and **n** is perpendicular to *W* (figure 2(*b*)). Accordingly the absorbance parallel to *W* is

$$A^{\parallel}_{\text{tilt}} = A^{\perp}_{\text{tilt}} = A_{\perp}. \tag{8}$$

If Ψ is arbitrary, i.e. the most general case (figure 2(*c*)), $A^{\parallel}_{\text{tilt}}$ as a function of Ψ is given by:

$$A^{\parallel}_{\text{tilt}} = A_{\parallel}\cos^2\Psi + A_{\perp}\sin^2\Psi. \tag{9}$$

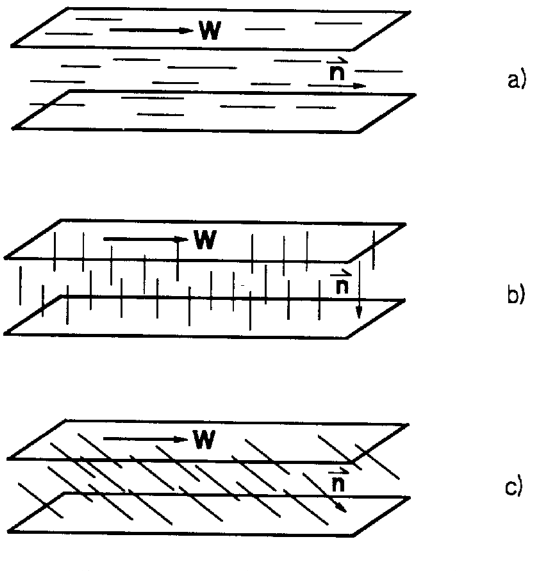

Figure 2. Alignments: (*a*) homogeneous, (*b*) homeotropic, (*c*) with tilt angle.

With equations (4) and (5) it follows that for arbitrary Ψ and arbitrary S_{zz}

$$A^{\parallel}_{\text{tilt}} = \tfrac{3}{2}A_{\text{iso}}(2\langle\cos^2\Theta\rangle\cos^2\Psi + \sin^2\Psi - \langle\cos^2\Theta\rangle\sin^2\Psi), \tag{10}$$

$$A^{\perp}_{\text{tilt}} = \tfrac{3}{2}A_{\text{iso}}\langle 1 - \cos^2\Theta\rangle \equiv A_{\perp}. \tag{11}$$

This dependence is illustrated in figure 3. Equation (10) turns into the well known equations (4) and (5), if Ψ is set to 0° or 90°. Curves (*d*) and (*e*) in figure 3 describe a system with negative dichroism, i.e. $A^{\parallel}_{\text{tilt}}$ is smaller than $A^{\perp}_{\text{tilt}}$, as for example for the distribution of the transition moments in an azobenzene containing isotropic polymer after irradiation with linearly polarized light [8]. The tilt angle Ψ and $\langle\cos^2\Theta\rangle$ can be calculated using equations (10) and (11). Initially, the parameters A_{iso}, $A^{\parallel}_{\text{tilt}}$, and $A^{\perp}_{\text{tilt}}$ have to be determined experimentally using polarized light. Equation (11) yields $\langle\cos^2\Theta\rangle$, which gives the order parameter S_{zz},

$$\langle\cos^2\Theta\rangle = \frac{-2A^{\perp}_{\text{tilt}}}{3A_{\text{iso}}} + 1. \tag{12}$$

The value of $\langle\cos^2\Theta\rangle$ determined in this way makes it possible to calculate Ψ, using equation (10), namely

$$\sin^2\Psi = \frac{-2A^{\parallel}_{\text{tilt}} + 6A_{\text{iso}}\langle\cos^2\Theta\rangle}{3A_{\text{iso}}(\langle 3\cos^2\Theta - 1\rangle)}. \tag{13}$$

The change of the absorbance due to the rotation of the

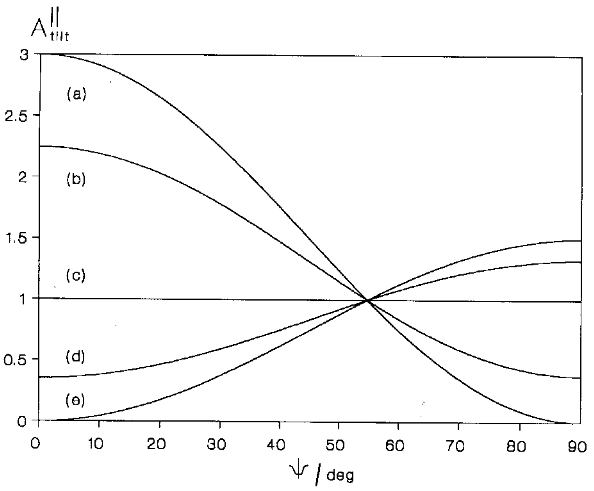

Figure 3. $A^{\parallel}_{\text{tilt}}$ as a function of Ψ; the values are calculated for $A_{\text{iso}} = 1$. The *x*-axis reflects the tilt angle Ψ; the *y*-axis shows $A^{\parallel}_{\text{tilt}}$; for $\Psi = 90°$, the *y*-axis shows $A^{\perp}_{\text{tilt}}$. (*a*) Curve for $S_{zz} = 1$, (*b*) curve for $S_{zz} = 0{\cdot}625$, (*c*) curve for $S_{zz} = 0$ (isotropic phase, magic angle), (*d*) curve for $S_{zz} = -0{\cdot}325$, (*e*) curve for $S_{zz} = -0{\cdot}5$.

cell or of the polarizer by the angle ξ (figure 1) yields $A_{\angle}$. Whereas the light propagates in the V direction and is polarized in the VW plane if $\xi=0°$, it is polarized in the UV plane if $\xi=90°$. The equation for $A_{\angle}$ is

$$A_{\angle}=A^{\parallel}_{\mathrm{tilt}}-(A^{\parallel}_{\mathrm{tilt}}-A^{\perp}_{\mathrm{tilt}})\sin^2\xi. \qquad (14)$$

It is sufficient to vary ξ between 0° and 90° to determine the dependence of the absorbance on the angle of the incident polarized light (figure 4). Figure 5 shows $A_{\angle}$ as a function of the polarization angle ξ at constant S_{zz} and variable tilt angle Ψ. Such a rotation of the director **n** or of the optical axis of the cylindrosymmetrical transition moment, respectively, occurs for example in azobenzene-containing liquid crystal polymers when irradiating the system with linearly polarized light [8–10].

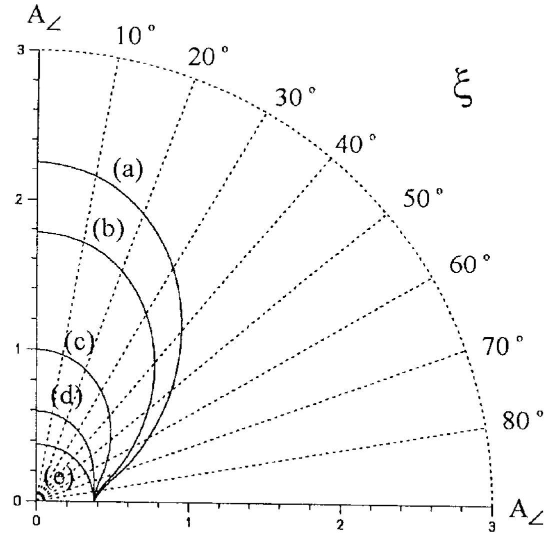

Figure 5. $A_{\angle}$ as a function of the polarization angle ξ at constant S_{zz} and variable tilt angle Ψ; the values are calculated for $A_{\mathrm{iso}}=1$ and $S_{zz}=0{\cdot}625$. The values of the x-axis and y-axis refer to $A^{\parallel}_{\mathrm{tilt}}$; the quarter circle shows the dependence of the absorbances on the polarization angle ξ. (*a*) Curve for $\Psi=0°$, (*b*) curve for $\Psi=30°$, (*c*) curve for $\Psi=54{\cdot}73°$ (isotropic phase, magic angle), (*d*) curve for $\Psi=70°$, (*e*) curve for $\Psi=90°$.

3. Experimental hints

Initially, the parameter-triplet A_{iso}, $A^{\perp}_{\mathrm{tilt}}$, and $A^{\parallel}_{\mathrm{tilt}}$ has to be determined experimentally using linearly polarized light [11]. Sources of errors are the photometric accuracy of the spectrometer, and especially the precision of the positioning of the polarizers, cell-holders etc. To avoid the consequences of flickering in the nematic phase near the clearing-point, i.e. fluctuating values of absorption, it is advantageous to average the output of the spectrometer over some seconds. For very small and large angles Ψ, it is useful to introduce a cell tilt angle of about 20° by means of the cell-holder in the spectrometer, because in this way the differences in the values of the triplet of absorbances become larger. If a cell tilt angle is adjusted, the reference beam should be attenuated and thereby balanced using a suprasil plate in order to equalize the intensities, altered through reflections. In this case, if $\Psi<10°$, the calculated angle ψ is $\psi=20°+\Psi$ or $\psi=20°-\Psi$. If $\Psi>80°$, the calculated ψ is $\psi=70°+(90°-\Psi)$ or $\psi=70°-(90°-\Psi)$. The correct value is obtained by rotating the cell about 180° around the U-axis. In this case an A_{iso} with a cell tilt angle is obtained. But here the absolute optical path length and absorbance in the cell do not matter, because the relative triplet of absorbances contains the desired information. Therefore it is possible and useful to normalize the three parameters measured such that $A_{\mathrm{iso}}=1$ by dividing the triplet of absorbances by A_{iso}. This facilitates the comparison of the absorbances of different cells. Indeed A_{iso} has to be corrected, taking into consideration the thermal expansion of the cell and the coefficient of thermal expansion, including phase transitions of the liquid crystal. The measurement of $A_{\angle}$ at different temperatures, i.e. order parameters, in the same mesophase, yields A_{iso} from the intersection of the graphs in figure 4. A_{iso} also results from a measurement at the magic angle. If the cell parameters and the host–guest mixtures are very well defined, A_{iso} can be calculated using the Beer–Lambert law.

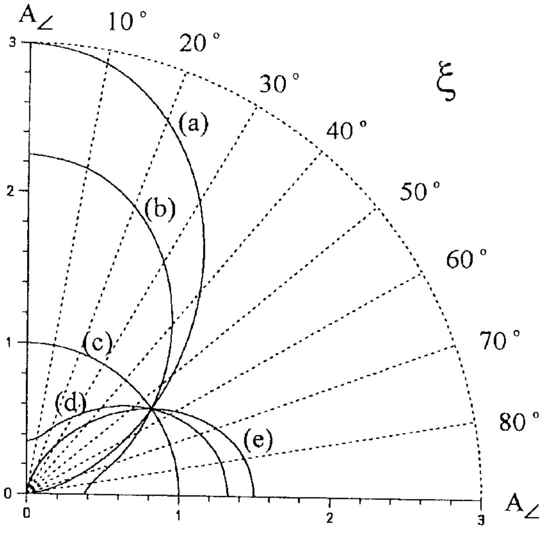

Figure 4. $A_{\angle}$ as a function of the polarization angle ξ at constant Ψ and variable order parameter S_{zz}; the values are calculated for $A_{\mathrm{iso}}=1$ and $\Psi=0°$. The values of the x-axis and y-axis refer to $A^{\parallel}_{\mathrm{tilt}}$; the quarter circle shows the absorbances as a function of the polarization angle ξ. (*a*) Curve for $S_{zz}=1$, (*b*) curve for $S_{zz}=0{\cdot}625$, (*c*) curve for $S_{zz}=0$ (isotropic phase, magic angle), (*d*) curve for $S_{zz}=-0{\cdot}325$, (*e*) curve for $S_{zz}=-0{\cdot}5$.

The local electric field and its influence on the intensity of an absorption band [6, 11, 12] has not been considered. Bicyclohexyl derivatives with small Δn and Bis (octylamino)azobenzenes have been used exclusively in a promising first assay [13].

4. Application of the method

The method is useful in the determination of Ψ and $A_{\angle}$ for cylindrosymmetric transition moments. There is no difference between the determination of the tilt angle of the transition moment and the determination of a cell tilt angle via the cell-holder in the spectrometer. The method is especially favorable for host-guest liquid crystal cells with small Δn. The corresponding values of Ψ and S_{zz} for the cylindrosymmetric transition moment of the dye can be determined exactly in this way. For the liquid crystal itself, Ψ can be determined exactly, as well as the value of S_{zz}, as a function of the interaction between the dye and the LC [14]. The order parameter S_{M} of a molecule can deviate from the order parameter S_{T} of the transition moment [6, 15], if the transition moment is not polarized parallel to the molecular long axis. For pure liquid crystals, the absorbances may of course be too high, and furthermore the absorption bands of transition moments which are not polarized parallel, may overlap [16]. If the cell tilt angle is 0° and $\Psi \neq 0°$, a measurement of $A^{\parallel}_{\mathrm{tilt}}$ and $A^{\perp}_{\mathrm{tilt}}$ yields, by neglecting the tilt angle, with equation (2) an order parameter in the direction of W, which is called S_W. It is possible to transpose this S_W into S_{ii} or A_{ii} [17]. Yang *et al.* [18] have reviewed a variety of additional methods to measure tilt angles.

5. Conclusion and outlook

The idea is sound, the method is very simple and both will have an impact on the LC-discipline because it is essentially a consequence of Maier–Saupe theory. Therefore my invitation to all experimentalists is to try to understand and calculate using their own triplets of A_{iso}, $A_{\perp}$, and $A_{\parallel}$. We hope that the method is also attractive to other experimentalists so that they may find ways of putting the idea to wider use.

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