

# On the Determination of Transition-Moment Directions from Absorption Anisotropy Measurements\*

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Z. Naturforsch. **42a**, 617–621 (1987); received January 31, 1987

A formula is derived for the absorption anisotropy  $K = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$  (where  $A_{\parallel}$  and  $A_{\perp}$  are the absorbances parallel and perpendicular to the stretching direction of the polymer film, respectively) as a function of the stretch ratio,  $R_s$ , of the film and the angle  $\varphi$  between the absorption transition moment direction and the long axis of a prolate molecule. Employing this relation, absolute transition moment directions (the angles  $\varphi$ ) were determined experimentally for the following compounds: 1,8-diphenyloctatetraene (DPO), 1,6-diphenylhexatriene (DPH), 1,4-diphenylbutadiene (DPB), 4-dimethylamino-4'-nitrostilbene (DNS), 4-dimethylamino-4'-chlorostilbene (DCIS) and p-terphenyl (TP). The directions were found to be along the long molecular axis in the long-wave absorption band. Small deviations of the angles obtained from  $\varphi = 0^\circ$ , which were of the order of several degrees, are due to the incomplete linearity of the molecules under investigation.

## 1. Introduction

The knowledge of the electronic absorption and emission transition moment directions is of essential importance in the description of intra- and inter-molecular interactions, playing also an important role in the choice of appropriate fluorescent probes used for the investigation of the intramolecular properties of biologically active membranes and biomacromolecules. The effect of electrochromism of the absorption bands of liquid solutions depends to a considerable extent on the relative orientation of the electronic transition moment with respect to the electric dipole moment in the ground state (see [1–3]).

Spectroscopic measurements in polarized light have been extensively developed for systems displaying anisotropic distribution of the transition moments (e.g. in stretched polymer films, in liquid crystals). In such a case, a dependence of the absorption on the position of the polarization plane of the light with respect to a given direction of orientation has been observed [4, 5]. According to

Pringsheim [6], the dichroism

$$D = \frac{A_{\parallel} - A_{\perp}}{A_{\parallel} + A_{\perp}} = \frac{d - 1}{d + 1} \quad (1)$$

is a measure of this anisotropy, where

$$d = A_{\parallel} / A_{\perp} \quad (2)$$

has been termed the dichroic ratio.  $A_{\parallel}$  and  $A_{\perp}$  are the components of the absorbance ( $A = \varepsilon C l$ , where  $\varepsilon$  is the molar absorption coefficient in litres per mol · cm,  $C$  the concentration in mol/l, and  $l$  the length in cm) parallel and perpendicular to the distinguished Z-axis (e.g. to the stretching direction of the film). Recently also the concept of reduced linear dichroism has been used [7]:

$$\text{LD}^r = \frac{A_{\parallel} - A_{\perp}}{A_{\text{iso}}}, \quad (3)$$

where

$$A_{\text{iso}} = \frac{1}{3} (A_{\parallel} + 2A_{\perp}).$$

For reviews on linear dichroism spectroscopy including lists of the most important articles cf. [7–10].

The method of determining the angle between the directions of the absorption and emission transition moments in linear molecules embedded in uniaxially oriented polymer films has been reported in [11].

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\* This work was carried out under contract CPBP 01.06.

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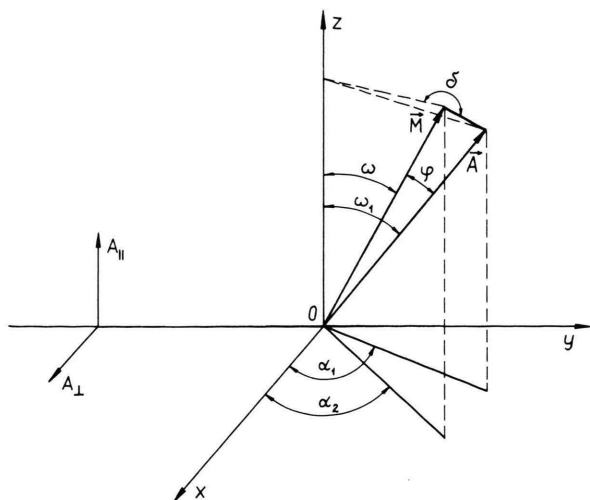


Fig. 1. Geometry of the system.

This method can be employed to measure the emission (fluorescence or phosphorescence) anisotropy as a function of the stretch ratio. In order to obtain complete information, the direction of the absorption transition moment with respect to a distinguished axis of the molecule under investigation must be known.

The present paper reports a very simple method of determining the direction of the absorption transition moment of prolate molecules.

## 2. Theory

Let us consider a prolate molecule, the direction of the long axis,  $\vec{OM}$ , of which and the absorption transition moment direction,  $\vec{A}$ , make angles  $\omega$  and  $\omega_1$  with the Z-axis (the stretching direction of the polymer film), respectively. Let  $\varphi$  denote the angle between  $\vec{OM}$  and  $\vec{A}$ .  $A_{||}$  and  $A_{\perp}$  are the absorbances parallel and perpendicular to the stretching direction, respectively, as observed along the Y-axis (Figure 1). The angles  $\omega$ ,  $\omega_1$ ,  $\varphi$  and  $\delta$  meet the relation

$$\cos \omega_1 = \cos \omega \cos \varphi + \sin \omega \sin \varphi \cos \delta. \quad (4)$$

For ellipsoidal molecules, the distribution with respect to the angle  $\delta$  is isotropic. On squaring (4) and averaging  $\cos^2 \omega_1$  over  $\delta$  we obtain

$$\begin{aligned} \langle \cos^2 \omega_1 \rangle &= \cos^2 \omega \cos^2 \varphi + \frac{1}{2} \sin^2 \omega \sin^2 \varphi \\ &= \left( \frac{3}{2} \cos^2 \omega - \frac{1}{2} \right) \left( \cos^2 \varphi - \frac{1}{3} \right) + \frac{1}{3}. \end{aligned} \quad (5)$$

The angle  $\varphi$  between the long molecular axis,  $\vec{OM}$ , and the transition moment direction,  $\vec{A}$ , is constant for a given transition in an absorbing molecule. The orientation is uniaxial and the molecular distribution about the orientation direction (the Z-axis) is isotropic. The final averaging of  $\cos^2 \omega_1$  over all angles  $\omega$  ( $0 \leq \omega \leq \pi/2$ ) is denoted by  $\langle \cos^2 \omega_1 \rangle$ . We introduce the following definition of the absorption anisotropy (similar to that of the emission anisotropy) \*

$$\begin{aligned} K(\omega_1) &= \frac{A_{||} - A_{\perp}}{A_{||} + 2A_{\perp}} = \frac{3}{2} \frac{A_{||}}{A} - \frac{1}{2} \\ &= \frac{3}{2} \langle \cos^2 \omega_1 \rangle - \frac{1}{2}, \end{aligned} \quad (6)$$

where  $A = A_{||} + 2A_{\perp}$  is the total absorbance.

Substitution of (5) into (6) yields

$$K(\omega, \varphi) = \left( \frac{3}{2} \langle \cos^2 \omega \rangle - \frac{1}{2} \right) \left( \frac{3}{2} \cos^2 \varphi - \frac{1}{2} \right), \quad (7)$$

where

$$\langle \cos^2 \omega \rangle = \frac{\int_0^{\pi/2} \cos^2 \omega \cdot f(\omega) d\omega}{\int_0^{\pi/2} f(\omega) d\omega}, \quad (8)$$

and  $f(\omega)$  is the distribution function of the long molecular axis,  $\vec{OM}$ , relative to the orientation direction (the Z-axis).

Tanizaki [14] derived the following distribution function of oriented rods with respect to the stretching direction (the Z-axis) in the ground state:

$$f(\omega) = R_s^2 \sin \omega \{1 + (R_s^2 - 1) \sin^2 \omega\}^{-3/2}, \quad (9)$$

where  $R_s$  is the stretch ratio of a polymer, expressing the ratio of the major to minor axes of a spheroid formed from a sphere as a result of polymer stretching. For an isotropic distribution, i.e. when complete disordering occurs (unstretched polymer films),  $R_s = 1$ ,  $f(\omega) = \sin \omega$  from (9), and  $\langle \cos^2 \omega \rangle = 1/3$  from (8), which, according to (7), yields  $K(\omega, \varphi) = 0$ .

For  $R_s > 1$ , and based on (7), (8) and (9) we obtain

$$\begin{aligned} K(R_s, \varphi) &= \left\{ \frac{3}{2} a^2 \left[ 1 - (a^2 - 1)^{1/2} \arcsin \frac{1}{a} \right] - \frac{1}{2} \right\} \\ &\quad \cdot \left( \frac{3}{2} \cos^2 \varphi - \frac{1}{2} \right), \end{aligned} \quad (10)$$

\* A similar expression, the so-called "director" (the orientation parameter), characterizing the average direction of the orientation of a huge molecular ensemble was introduced by Maier and Saupe [12, 13] for liquid crystals.

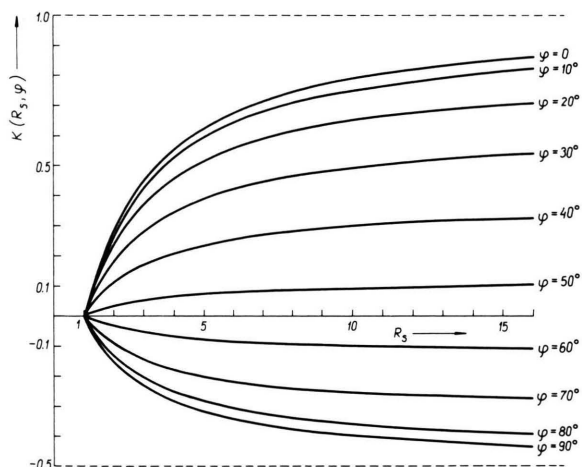


Fig. 2. Theoretical dependence of  $K(R_s, \varphi)$  on the stretch ratio  $R_s$  for various values of  $\varphi$ .

where

$$a^2 = R_s^2 / (R_s^2 - 1). \quad (11)$$

Formula (10) expresses the theoretical dependence of the absorption anisotropy,  $K(R_s, \varphi)$ , upon the stretch ratio  $R_s$  and the angle  $\varphi$  between the transition moment direction,  $\vec{A}$ , and the long molecular axis,  $\vec{OM}$ . By plotting  $K(R_s, \varphi)$  versus  $R_s$  for various values of  $\varphi$  ( $0 \leq \varphi \leq \pi/2$ ), a family of curves representing (10) is obtained, as shown in Figure 2.

The limiting values of the absorption anisotropy are:

1. For  $R_s \rightarrow 1$  (isotropic distribution),  $K(R_s, \varphi) \rightarrow 0$  irrespective of the angle  $\varphi$ .
2. For  $R_s \rightarrow \infty$  (complete orientation),  $K(R_s, \varphi) \rightarrow (\frac{3}{2} \cos^2 \varphi - \frac{1}{2})$ , and  $K(R_s, 0) = 1$  with  $\varphi = 0$ ,  $K(R_s, \pi/2) = -\frac{1}{2}$  with  $\varphi = \pi/2$ .

#### Order parameters in other theories

Based on (10) and the following expression in the diagonal reference system obtained by Matsuoka and Nordén [15, 16] for reduced linear dichroism,  $LD^r$  (cf. (3)), as a function of the orientation parameter  $S_{ii}$  ( $i = x, y, z$ ) and the angle  $\varphi$  between the long molecular axis and the transition moment vector:

$$LD^r = 3(S_{yy} \sin^2 \varphi + S_{zz} \cos^2 \varphi), \quad (12)$$

the relation between the orientation parameter,  $S_{zz}$ , and the stretch ratio,  $R_s$ , of a polymer can be found. For the group of linear molecules considered,  $S_{xx} = S_{yy}$  and, owing to  $S_{xx} + S_{yy} + S_{zz} = 0$ , we

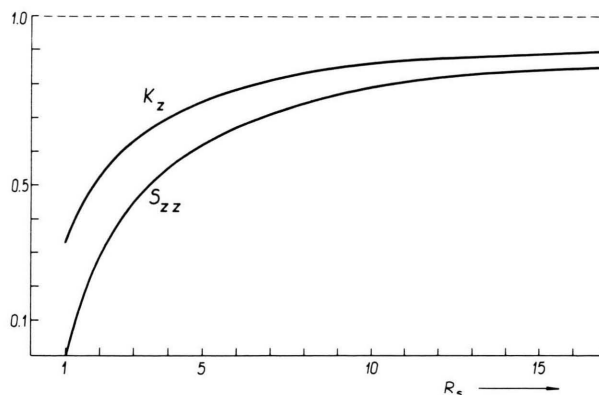


Fig. 3. Dependence of the orientation parameters  $S_{zz}$  and  $K_z$  upon the stretch ratio  $R_s$ .

obtain

$$S_{yy} = S_{xx} = -\frac{1}{2} S_{zz}. \quad (13)$$

Hence, upon introducing (13) into (12) we have

$$\frac{LD^r}{3} = S_{zz} \left( \frac{3}{2} \cos^2 \varphi - \frac{1}{2} \right). \quad (14)$$

By comparing (10) and (14), and since  $K(R_s, \varphi) = LD^r/3$ , one obtains the equation

$$S_{zz} = \frac{3}{2} a^2 \left[ 1 - (a^2 - 1)^{1/2} \arcsin \frac{1}{a} \right] - \frac{1}{2}, \quad (15)$$

which expresses the orientation parameter of rod molecules as a function of the stretch ratio,  $R_s$ , of the polymer film. For  $R_s \rightarrow \infty$ ,  $S_{zz} \rightarrow 1$ .

Similarly, for the model of Thulstrup, Michl and Eggers [17, 18], the orientation parameter  $K_z$  assumes the form

$$K_z = a^2 \left[ 1 - (a^2 - 1)^{1/2} \arcsin \frac{1}{a} \right]. \quad (16)$$

For  $R_s \rightarrow \infty$ ,  $K_z \rightarrow 1$ . Figure 3 shows parameters  $S_{zz}$  and  $K_z$  as functions of the stretch ratio  $R_s$ .

It is worth mentioning that, based on (6), Fraser's formula [19]

$$K(\omega) = \frac{d-1}{d+2} \quad (17)$$

can be readily obtained, where

$$d = \frac{A_{\parallel}}{A_{\perp}} = 2 \langle \text{ctg}^2 \omega \rangle = 2 \frac{\langle \cos^2 \omega \rangle}{1 - \langle \cos^2 \omega \rangle} \quad (18)$$

if  $\varphi = 0$ , i.e.  $\omega$  is the angle between the transition moment vector,  $\vec{A}$ , and the stretching direction of a polymer film. With (8) and (9), (16) becomes

$$\langle \cos^2 \omega \rangle = K_z,$$

where  $a^2$  is expressed by (11). Thus, the stretch ratio,  $R_s$ , can be taken into account also in Fraser's formula.

### 3. Experimental

#### 3.1. Samples and Methods

In order to determine the absolute directions of the absorption transition moments (with respect to the long molecular axis) of prolate molecules, (10) was employed to investigate chemical substances which have already been examined previously [11], and also three new substances, the chemical formulas of which are shown in Figure 4. The compounds investigated were: 1,8-diphenyloctatetraene (DPO), 1,6-diphenylhexatriene (DPH), 1,4-diphenylbutadiene (DPB), 4-dimethylamino-4'-nitrostilbene (DNS), 4-dimethylamino-4'-chlorostilbene (DCIS) and p-terphenyl (TP). Isotropic films were made of a 15% aqueous solution of polyvinyl alcohol (PVA) in which the luminescent molecules were set up by methanol. The method of obtaining the PVA films was analogical to that described by Tanizaki et al. [20]. The PVA films were stretched at about 350 K,

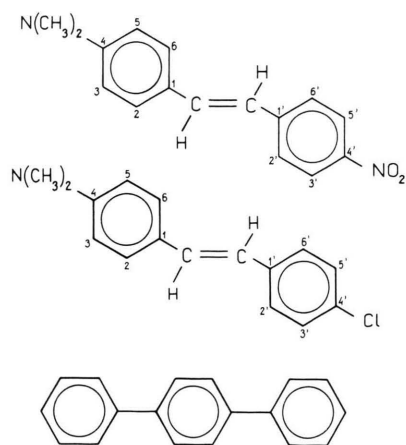


Fig. 4. Structural formulas of DNS, DCIS and TP. The structural formulas for DPO, DPH and DPB have been given in [11].

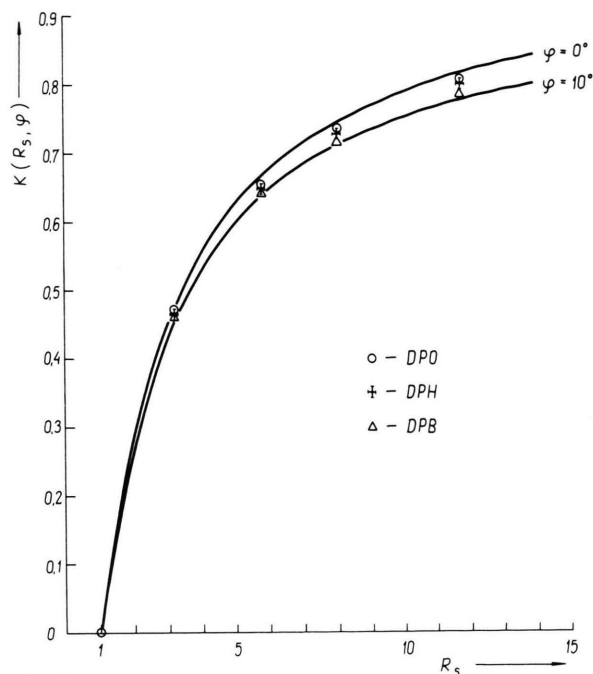


Fig. 5.

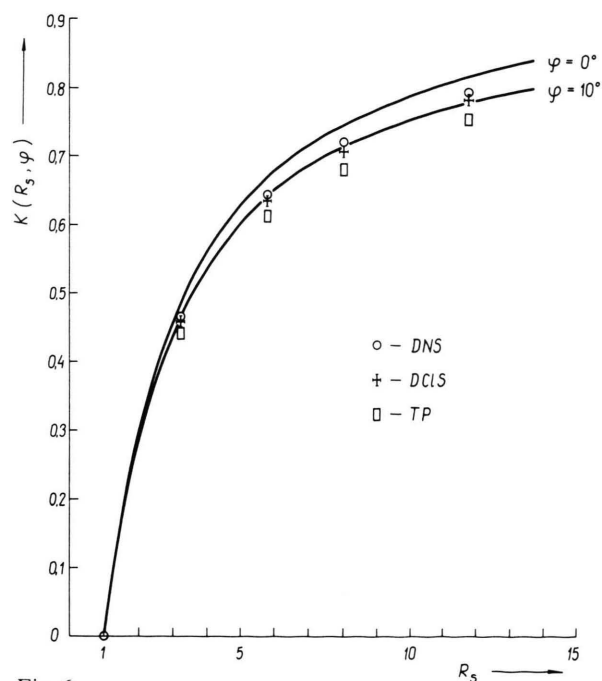


Fig. 6.

Figs. 5 and 6. Dependence of  $K(R_s, \varphi)$  on the stretch ratio  $R_s$  for DPO, DPH, DPB, DNS, DCIS and TP. Points: experimental values; solid lines: theoretical curves obtained according to (10) for  $\varphi = 0^\circ$  and  $\varphi = 10^\circ$ .

the rate of stretching being controlled. The quality of the obtained films was found to be essentially affected by the temperature and the stretching rate. The most homogeneous films were selected for the measurements.

The absorption measurements were carried out using a single-beam VSU-2P spectrophotometer (Carl Zeiss). The employment of a parallel light beam and the use of a Glan prism enabled a high polarization degree of the incident light to be achieved ( $P > 0.98$ ).

### 3.2. Results and Discussion

For the measured components  $A_{\parallel}$  and  $A_{\perp}$  of the absorption spectra of the compounds investigated in PVA as a function of the wavenumber,  $\tilde{\nu}$ , it was found that in the long-wave absorption bands for DPO (22 000–30 000  $\text{cm}^{-1}$ ), DPH (24 000–32 000  $\text{cm}^{-1}$ ), DPB (26 000–34 000  $\text{cm}^{-1}$ ), DNS (18 000–25 000  $\text{cm}^{-1}$ ), DCIS (24 000–30 000  $\text{cm}^{-1}$ ) and TP (30 000–40 000  $\text{cm}^{-1}$ ), the absorption anisotropy,  $K = (A_{\parallel} - A_{\perp}) / (A_{\parallel} + 2A_{\perp})$ , remained constant.

The measured absorption anisotropies,  $K$ , as functions of the stretch ratio,  $R_s$ , for the PVA films with DPO, DPH and DPB are given in Fig. 5, and those with DNS, DCIS and TP in Figure 6. The measured values lie between the curves  $K(R_s, \varphi)$  calculated according to (10) for the angles  $\varphi = 0^\circ$  and  $10^\circ$ , which evidences that the transition moments of the molecules investigated are directed along the long molecular axes when exciting in the long-wave absorption band. Slight differences between the obtained angles  $\varphi$  and  $\varphi = 0^\circ$  are due to incomplete linearity of the molecules under study. From a comparison of the values found for the angle  $\varphi$  ( $\varphi \approx 4.5^\circ$  for DPO,  $\varphi \approx 5^\circ$  for DPH,  $\varphi \approx 7^\circ$  for DPB,  $\varphi \approx 5.5^\circ$  for DNS,  $\varphi \approx 8^\circ$  for DCIS and  $\varphi \approx 11^\circ$  for TP) with the molecular length it can be concluded that the length of the molecules influences considerably the effectiveness of their orientation in the stretched PVA film\*.

\* Note added in proof: In the previous paper [11]  $a^2 = R_s^2 / (R_s^2 - 1)$  should have also been printed.

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