# Directions of the Electronic Absorption Transition Moments in ω-Substituted 4-Dimethylamino-trans-Styrenes

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Absorption transition moment directions of the diphenylphosphinyl (**2a**) and methylsulphonyl (**3a**) ω-substtuted in 4-dimethylamino-trans-styrenes were determined in stretched poylvinyl alcohol (PVA) films based on measurements of the absorption anisotropies. It has been found that the long-wave absorption spectrum consists of two bands corresponding to differently directed transition moments. The transition moment of the intensive long-wave $^1L_a$ band is lies along the long axis of these molecules whereas that of the short-wave $^1L_b$ band is oriented at $\varphi = 38°$ for **2a** and $\varphi = 35°$ for **3a** relative to the transition moment direction of the $^1L_a$ band.

## 1. Introduction

As follows from quantum mechanical calculations, the longest-wave absorption band of 4-dimethylamino-ω-diphenylphosphinyl-trans-styrene (**2a**) and 4-dimethylamino-ω-methylsulphonyl-trans-styrene (**3a**) (Fig. 1) consists of two electronic transitions [1]. In the unsubstituted styrene these transitions were found at 40 300 $cm^{-1}$ (high intensity, $^1L_a$-band) and 35 400 $cm^{-1}$ (lower intensity, $^1L_b$-band) [2]. This marked separation between the $S_0-S_2$ and $S_0-S_1$ transitions disappears upon the introduction of electron-effective substituents in positions ω and p, causing the $S_0-S_2$ transition to be strongly bathochromically shifted [1, 3–5]. As evidenced by calculations [1] and experiments [3, 5], the more intensive $^1L_a$ band is for **2a** and **3a** located at longer wavelengths.

In the present paper, experimental investigations on the absorption transition moment directions of molecules **2a** and **3a** are reported.

## 2. Experimental

### 2.1. Samples and Methods

Isotropic films were prepared from a 15% aqueous solution of polyvinyl alcohol (PVA) in which the molecules of **2a** and **3a** were embedded by methanol. The method of obtaining the films was described earlier [6–8]. The PVA films were stretched at about 350 K, the rate stretching being under control. The quality of the films obtaind was found to be significantly affected by temperature and the stretching rate. The most homogeneous films were selected for the measurements.

The polarized absorption measurements were carried out with a single beam Beckman model 25 spectrophotometer. The use of a parallel light beam and the Glan prism enabled a high degree of polarization to be attained ($P > 0.98$).

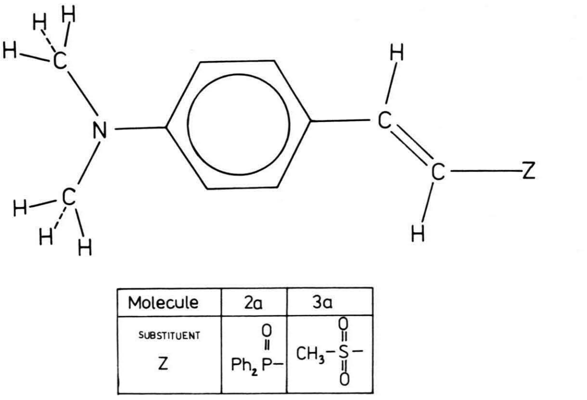

Fig. 1. Structural formula of 4-dimethylamino-ω-diphenylphosphinyl-trans-styrene (**2a**) and 4-dimethylamino-ω-methylsulphonyl-trans-styrene (**3a**).

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### 2.2. Absorption Spectra in Isotropic PVA Films

The absorption spectra of **2a** and **3a** measured in isotropic (unstretched) PVA films are shown in Figs. 2 and 3. As in liquid solutions, the longwave absorption bands have irregular shapes [9]. The absorption bands of **2a** and **3a** should be analyzed as a superposition of two bands, each corresponding to an individual transition. The absorption spectrum was recovered from these two component bands by a computer simulation in which the band envelope $A_i(\tilde{\nu})$ of the $i$-th component band was assumed to have the conventional form of a Gaussian error function at a given wavenumber $\tilde{\nu}$ [10]:

$$A_i(\tilde{\nu}) = A_{i,\max} \cdot \exp\left\{-\frac{(\tilde{\nu} - \nu_{i,\max})^2}{2\delta_i}\right\}, \qquad (1)$$

where $\tilde{\nu}_{i,\max}$, $A_{i,\max}$ and $\delta_i$ are the peak position, the maximum intensity of the optical density at $\tilde{\nu}_{i,\max}$ and the corresponding halfwidth of the $i$-th band, respectively.

Figures 2 and 3 show the absorption spectra of **2a** and **3a** resolved into two Gaussian bands. Table 1 summarizes the Gaussian parameters of the two bands. The fit by one Gaussian component proved unsatisfactory (a large value of $\chi^2_R$).

### 2.3. Absorption anisotropy Measurements in Anisotropic PVA Films

The following expression was obtained, based on simple geometrical considerations for the absorption anisotropy of uniaxial polymer films with axially symmetric long luminescent molecules (LM) [11]:

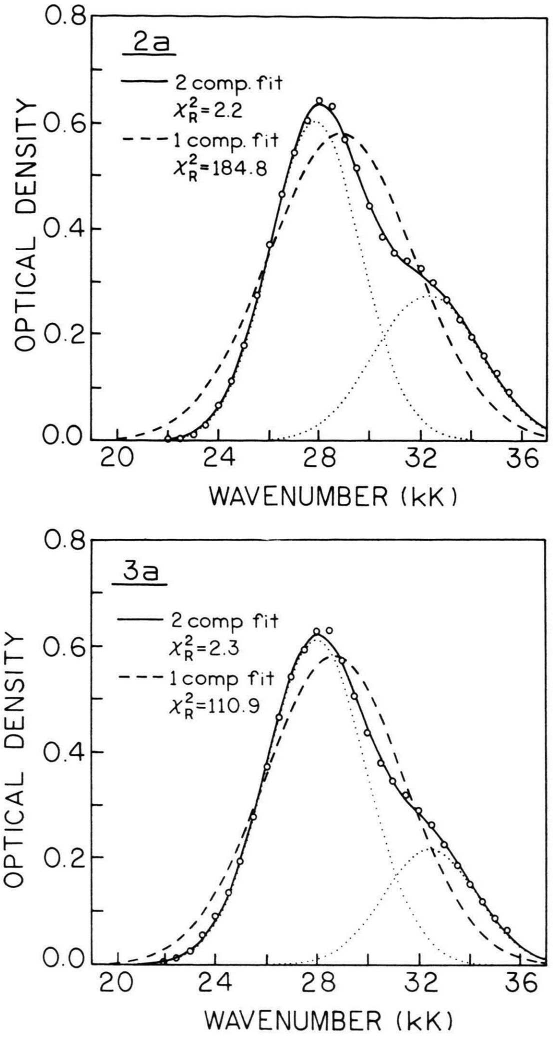
$$K(R_s, \varphi) = \frac{A_\parallel - A_\perp}{A_\parallel + 2A_\perp} \qquad (2)$$

$$= \left\{\tfrac{3}{2}\, a^2\left[1 - (a^2-1)^{1/2} \arcsin\frac{1}{a}\right] - \tfrac{1}{2}\right\}\left(\tfrac{3}{2}\cos^2\varphi - \tfrac{1}{2}\right),$$

where

$$a^2 = \frac{R_s^2}{R_s^2 - 1} \quad \text{for} \quad R_s > 1. \qquad (3)$$

$\varphi$ denotes the angle between the long molecular axis and the direction of the absorption transition moment, $R_s$ is the stretch ratio, $A_\parallel$ and $A_\perp$ are the components of absorbance, $A = \varepsilon\, c\, l$, parallel and perpendicular to the stretching direction (the $Z$-axis) of the polymer film ($\varepsilon$ is the molar absorption coefficient in litres per



Figs. 2 and 3. Absorption spectra of **2a** and **3a** in isotropic PVA film at room temperature. The measured values are given by circles and the two component fit by continuous lines.

Table 1. Parameters of the Gaussian bands corresponding to the resolved absorption spectra (mean standard deviations for individual parameters are given in parentheses).

| Compound | 1st component | | | 2nd component | | |
|---|---|---|---|---|---|---|
| | $A_{\max}$ | $\tilde{\nu}_{\max}$ [kK] * | $\sigma$ [kK] | $A_{\max}$ | $\tilde{\nu}_{\max}$ [kK] | $\sigma$ [kK] |
| **2a** | 0.605<br>(0.012) | 27.84<br>(0.06) | 1.81<br>(0.03) | 0.274<br>(0.007) | 32.31<br>(0.14) | 2.11<br>(0.11) |
| **3a** | 0.613<br>(0.007) | 27.97<br>(0.05) | 1.97<br>(0.04) | 0.217<br>(0.008) | 32.46<br>(0.14) | 1.82<br>(0.10) |

* 1 kK = $10^3$ cm$^{-1}$.

mole · cm, $c$ is the concentration in mole/litre, and $l$ is the length in cm).

For the molecules investigated, the value of the absorption anisotropy, $K$, measured experimentally for the longwave part of the spectrum, attains a relatively high value for the maximum 5.25-fold stretching ($R_s=(5.25)^{3/2}=12$ [12]): 0.61 for **2a** and 0.59 for **3a** (Figs. 4 and 5). Both this fact and the molecular shape and symmetry permit to put forward the idea that the absorption transition moment direction, $\boldsymbol{A}$, is parallel or very close to that of the long orientation axis of the LM ($\varphi_{\nu<25\,\mathrm{kK}}\approx 0°$).

Setting $\varphi=0°$ in (2) one obtains

$$K_0=\tfrac{3}{2}a^2\left[1-(a^2-1)^{1/2}\arcsin\frac{1}{a}\right]-\tfrac{1}{2}=\tfrac{3}{2}u-\tfrac{1}{2}, \qquad (4)$$

where

$$u=a^2\left[1-(a^2-1)^{1/2}\arcsin\frac{1}{a}\right] \qquad (5)$$

is the degree of orientation of the long axes of the LM in the stretched film.

In our case, the maximum stretch is considered. Formula (4) for the orientation degree implies that

$$u=\tfrac{2}{3}K_0+\tfrac{1}{3}. \qquad (6)$$

$K_0$ is the maximum value of the measured absorption anisotropy at a fixed stretch degree, $R_s^{\max}$.

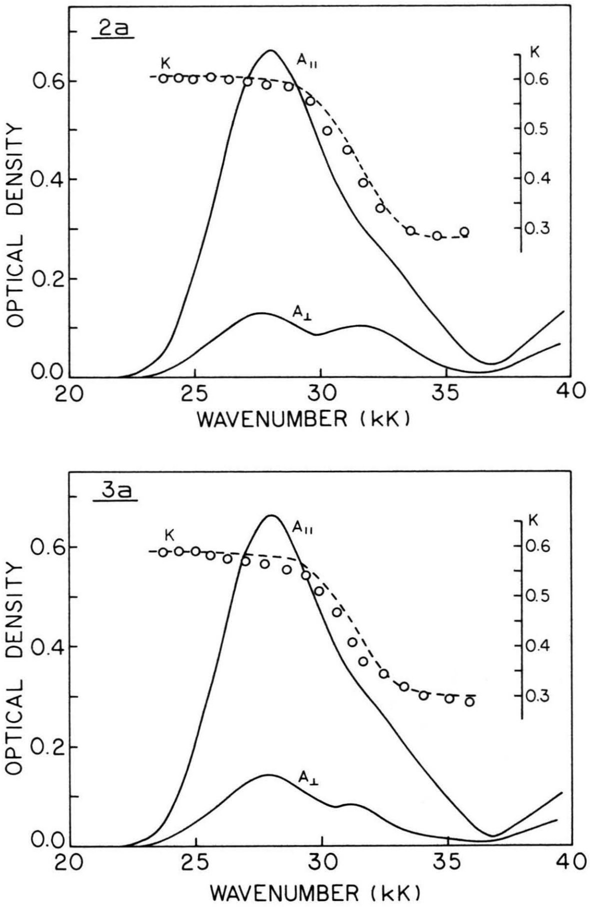
For any other transition at the same stretch ratio, $R_s^{\max}$, according to (2) one obtains

$$K(\varphi)=(\tfrac{3}{2}u-\tfrac{1}{2})(\tfrac{3}{2}\cos^2\varphi-\tfrac{1}{2})=K_0(\tfrac{3}{2}\cos^2\varphi-\tfrac{1}{2}). \qquad (7)$$

Hence for an optionally directed transition moment, (7) gives

$$\varphi=\arccos\left[\left(\frac{2}{3}\,\frac{K(\varphi)}{K_0}+\frac{1}{3}\right)^{1/2}\right]. \qquad (8)$$

Based on the absorption spectra of **2a** and **3a**, resolved into the Gaussian components (Fig. 2 and 3), it can be assumed that the region above 34 kK corresponds to an almost pure electronic (shortwave) transition. A certain stability of the absorption anisotropy, $K$, at the level of the lowest value can also be observed in this region (0.27 for **2a** and 0.30 for **3a**). From (8) it can be calculated for the model assumed that the orientation of this electronic transition relative to the long axis is: $\varphi=38°$ for **2a** and $\varphi=35°$ for **3a**.



Figs. 4 and 5. Absorbance (optical density) components, $A_\parallel$ and $A_\perp$, and absorption anisotropy, $K=(A_\parallel-A_\perp)/(A_\parallel+2A_\perp)$, as functions of the wavenumber, $\tilde{\nu}$, for **2a** and **3a** in a stretched PVA film. The dashed curve was calculated according to (9).

Employing the definition of the absorption anisotropy, $K$, [11] and the relative transition intensities recovered from the Gaussian distribution (Figs. 2 and 3), the values of $K$ can be calculated for various wavenumbers $\tilde{\nu}$. It can be shown by resolving both transitions into the absorbance components, $A_\parallel$ and $A_\perp$, that owing to additivity the resultant absorption anisotropy, $K(\tilde{\nu})$, is a linear combination of the anisotropies of the two transitions:

$$K(\tilde{\nu})=\alpha_0(\tilde{\nu})\,K_0+\alpha_1(\tilde{\nu})\,K_1, \qquad (9)$$

where $K_0$ and $K_1$ are the absorption anisotropies for the first (the maximum value) and the second (the minimum value) transition, respectively, and $\alpha_0(\tilde{\nu})$ and $\alpha_1(\tilde{\nu})$ are the relative contributions of the Gaussian bands to the absorption spectra for a given wavenumber $\tilde{\nu}$ ($\alpha_0(\tilde{\nu})+\alpha_1(\tilde{\nu})=1$ for each $\tilde{\nu}$ in the case of both transitions).

Figures 4 and 5 show the experimental values of the absorption anisotropy (o) along with $K(\tilde{\nu})$ calculated (broken lines) from (9) with the use of the Gaussian distribution presented in Figs. 2 and 3. A good accordance of the results has been observed.

## 3. Conclusion

The longwave absorption specrum of molecules **2a** and **3a** consists of two bands with different transition moment directions. The transition moment of the more intensive $^1L_a$ band is directed along the long molecular axis, whereas those of th short wave $^1L_b$-band of **2a** and **3a** lie at angles $\varphi = 38°$ and $\varphi = 35°$, respectively, relative to the $^1L_a$-band transition moment.

### *Acknowledgements*

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