Directions of the Electronic Transition Moments in Dioxido-p-terphenyl *

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The directions of the absorption, fluorescence and phosphorescence transition moments of dioxido-p-terphenyl are determined from measurements of the absorption and emission anisotropies as functions of the dichroic ratio in stretched PVA films.

The knowledge of the electronic transition moment directions in absorption, fluorescence and phosphorescence is of particular importance when explaining the photophysical properties and intramolecular processes in complex molecules. Dioxido-p-terphenyl is a very interesting scintillating molecule with high fluorescence quantum yield and, simultaneously, unusually high phosphorescence quantum yield ($\varphi_{\mathrm{Ph}} \approx 0.1$) at room temperature in polyvinyl alcohol (PVA) films. Blocking of the movement of the benzene rings in p-terphenyl by using oxygen as bridging element leads to coplanarity of all rings [1]. Highly resolved vibronic spectra were obtained for this molecule in n-hexane at 77 K [2].

The PVA films with embedded dioxido-p-terphenyl molecules were prepared as reported previously [3]. The emission anisotropy was measured by means of an apparatus described elsewhere [4, 5]. A pulse nitrogen laser was employed for the phosphorescence measurements. Figure 1 shows for the molecule investigated in a 5-fold stretched PVA film the absorbance components parallel, $A_{\|}$, and perpendicular, $A_{\perp}$, to the direction of the film stretching and the dichroic ratio

$$R_{\mathrm{d}} = A_{\|}/A_{\perp} \tag{1}$$

in the wavenumber region from 28 kK to 40 kK. The direction of the electronic absorption transition moment for the longwave absorption band was determined from the measured absorption anisotropy, employing the relation (10) given in [6]. The angle φ thus obtained between the long molecular axis and the direction of the electronic transition moment amounts to about 24°. Since the molecule investigated is not exactly linear, the effectiveness of the orientation in the stretched PVA film should be lower than that predicted by the theoretical model, thus affecting significantly the obtained value of the angle φ (different from zero).

Figure 2 shows the fluorescence and phosphorescence spectra of dioxido-p-terphenyl in an isotropic PVA film at room temperature. The limiting fluorescence and phosphorescence anisotropies in isotropic PVA films for $\lambda_{\mathrm{exc}} = 338$ nm amount at 0.3 and -0.15, respectively. Figure 3 shows the measured fluorescence and phosphorescence anisotropies as functions of the measured dichroic ratio, R_{d}, in the stretched PVA film, and the theoretical dependences calculated by means of the relation [7]

$$r(\beta, R_{\mathrm{d}}) = \left\{\frac{3}{2}\,\frac{(a^2-1)^{1/2} + 2a^2(a^2-1)^{-1/2} - 3a^2 \arcsin\dfrac{1}{a}}{2(a^2-1)^{-1/2} - 2\arcsin\dfrac{1}{a}} - \frac{1}{2}\right\}\left(\frac{3}{2}\cos^2\beta - \frac{1}{2}\right), \tag{2}$$

where

$$a^2 = \frac{(0.8\,R_{\mathrm{d}} + 0.2)^2}{(0.8\,R_{\mathrm{d}} + 0.2)^2 - 1} \quad \text{for} \quad R_{\mathrm{d}} > 1\,.$$

β is the angle between the absorption and emission transition moments.

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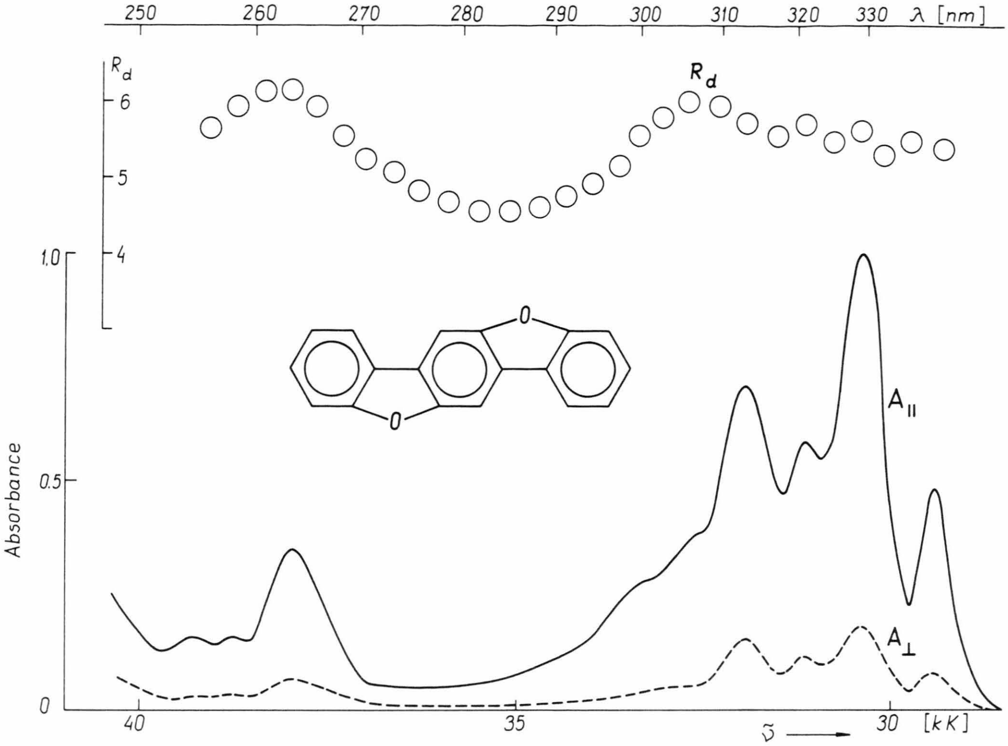

Fig. 1. Absorbance components, $A_{\parallel}$ and $A_{\perp}$, and the dichroic ratio, R_d, as function of the wavenumber, $\tilde{\nu}$, for dioxido-p-terphenyl in PVA films.

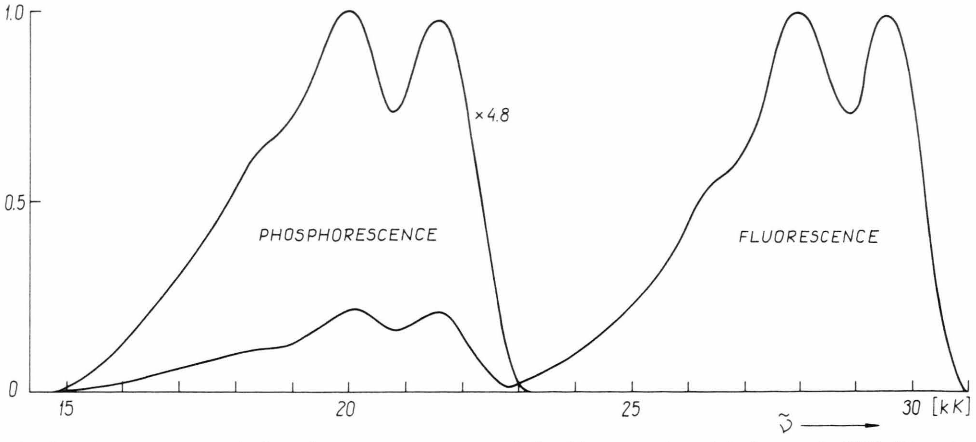

Fig. 2. Fluorescence and phosphorescence spectra of dioxido-p-terphenyl in isotropic PVA film at room temperature.

The angle β determined for fluorescence from (2) (see Fig. 3) amounts to about 15°. This relatively high value, as compared to those obtained for other linear molecules [7], results from the fact that the direction of the absorption transition moment makes a certain small angle φ different from zero relative to the long molecular axis. The results of the phosphorescence anisotropy are in good agreement with the theoretical predictions (Fig. 3) and, according to (2), yield for the angle β a value close to 90° ($\beta = 83°$). Thus, the transition moment of the phsophorescence of dioxido-p-terphenyl is polarized perpendicularly to the molecular plane.

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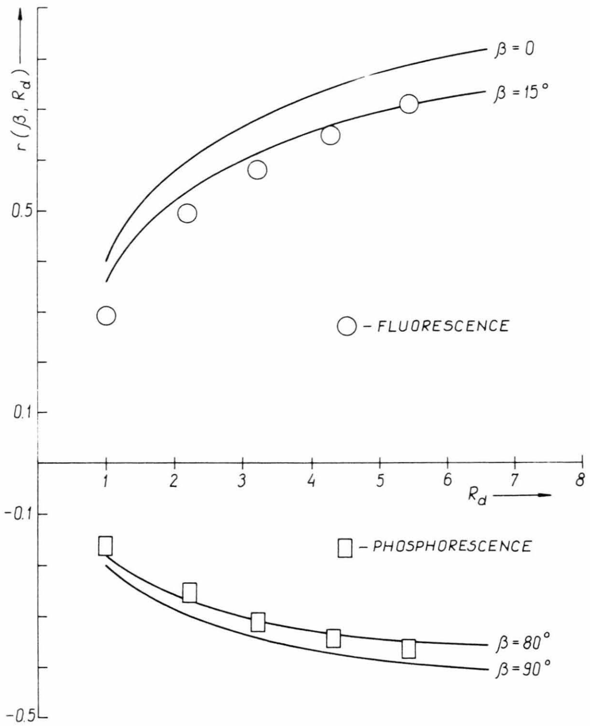

Fig. 3. Dependence of $r(\beta, R_d)$ on the dichroic ratio R_d for dioxido-p-terphenyl in stretched PVA film. Full lines represent the theoretical curves obtained according to (2).

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