Film Dichroism. III. Linearly-polarized Absorption Spectra of Highly Symmetric Triphenylmethane Dyes in the Stretched Poly(vinyl alcohol) Films

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The linear dichroic absorption spectra of Pararosaniline (PR), Crystal Violet (CV), and Ethyl Violet (EV) were measured in the UV and visible regions by the stretched film technique. Poly(vinyl alcohol) was used as the film matrix. A method, which is expressed in the forms of reduced dichroism and dichroic ratio, was proposed for the analysis of the linear dichroism of disk-like molecules. The dyes PR, CV, and EV were shown to behave like disks regarding their orientation in the polymer matrix. The isotropic absorption spectra of PR, CV, and EV were resolved into the in-plane and out-of-plane polarized components by the reduction procedure. In each isotropic spectrum the out-of-plane component was found to overlap with the intense in-plane component in the UV and visible wavelength regions.

Crystal Violet (CV) has attracted considerable attention in the last decade because it is a typical non-intercalative dye which binds to biopolymers.[1,2] Measurements of the optical rotatory dispersion[1] and linear flow dichroism[2,3] of CV bound to deoxyribonucleic acid (DNA) were carried out to elucidate the binding mode of the dye. In order to obtain useful information on the optical properties of the DNA–CV complexes, however, it is of utmost importance to know the polarization direction of the electronic absorption bands of CV itself in detail, as pointed out in a previous paper.[4] In the assignment of the polarization direction for the disk-like molecules which belong to a D_{nh} or C_{nv} ($n \geqq 3$) point symmetry, a transition polarized perpendicularly to the molecular plane (*i.e.*, out-of-plane transition) should not be ignored. Since CV is most likely to belong to the D_{3h} or C_{3v} point symmetry, the out-of-plane transition must be taken into account in the analysis of its dichroic data.

Recently, Yogev *et al.*[5] reported the expressions for the linear dichroism of disk-like molecules in some special cases and thereby resolved the isotropic absorption spectra of penta- and hexahelicenes into the in-plane and out-of-plane polarized absorption components. For the triphenylmethane dyes such as CV and Malachite Green, both the measurements of dichroic absorption spectra and the interpretations of the dichroic ratio have been carried out.[6,7] Tanizaki[6] first determined the relative directions of the transition moments of CV for the visible absorption bands. Nordén[7] measured the dichroic ratios of some triphenylmethane dyes in the visible region and explained them qualitatively. Both of these workers have suggested the possibility of the presence of an out-of-plane polarized absorption component in the isotropic spectrum of CV, but they have failed to show the location and band shape of the component.

The main objects of this paper are, first, to determine the in-plane and out-of-plane polarized absorption components (the reduced spectra) of CV from its dichroic absorption spectra by the *reduction procedure*;[8] second, to apply the same procedure to the dichroic spectra of Pararosaniline (PR) and Ethyl Violet (EV), which belong to the same point symmetry as CV (*i.e.*, D_{3h}[7,9] or C_{3v}[2,10]); and finally, to compare their reduced spectra. The three dyes are all derivatives of triphenylmethane differing only in the amino substitution and, therefore, are expected to have closely related spectral properties. The evaluation of the reduced spectra of those disk-like triphenylmethane dyes must differ from the previous case for the acridine dyes of C_{2v} point symmetry,[4] because PR, CV, and EV all lack the longest dimension in the molecular shape but possess several symmetrically distributed axes of equivalence. A new formalism of the linear dichroism of these disk-like molecules is necessary for the interpretation of the dichroic results.

The resultant reduced spectra of each dye show both the in-plane and out-of-plane polarized absorption components in the visible and UV regions. The presence of the out-of-plane component in the visible region indicates that the effective symmetry of PR, CV, and EV is not D_{3h} but rather C_{3v} or D_3 in the poly(vinyl alcohol) (PVA) film.

Experimental

Materials. Dyes used were all in the monocationic form, the anion being chloride. CV was purified as described before,[11] and PR and EV were purified by the method of preparative thin-layer chromatography. The powdered PVA sample with a nominal degree of polymerization of 1750 was obtained from Tokyo Kasei Co., Ltd. The concentration of each dye was *ca.* 20 μM ($1\ \mu\mathrm{M} = 1 \times 10^{-6}\ \mathrm{mol\ dm^{-3}}$) in the 9.1 w/w % aqueous PVA solution prior to casting. Both sample and reference films were prepared as described before.[4]

Apparatus. The linear dichroic absorption spectra ($A_{\parallel}$- and $A_{\perp}$-spectra) of PR, CV, and EV were measured on a Hitachi EPS-3T double beam recording spectrophotometer equipped with a mechanical stretcher designed and constructed in this laboratory.[12] The sample and reference films were stretched simultaneously in the cell compartment of the instrument at about 80 °C. The stretch ratio (S) was defined as described elsewhere.[4,6]

Evaluation of Reduced Spectra. All PR, CV, and EV belong to a D_{3h} or C_{3v} point symmetry and possess no uniquely defined axis of orientation (the longest axis). However, they have several axes equally distributed in the molecular plane, according to the definitions of the axes for the disk-like molecule given in Ref. 8 (see Fig. 3). The experimental fact is that each dye in the stretched PVA film can be oriented; the orientation should be ascribed to the redistribution of the "circular"plane from its random distribution before stretching. Therefore, the orienting property of all those dyes may be represented by the behavior of a disk molecule. When the in-plane or the out-of-plane polarized transitions are assumed in the isotropic spectrum of the disk-like molecule, the reduction procedure for the molecule will be employed to evaluate the reduced spectra, namely, the (A_y+A_z)-spectrum for the in-plane polarized absorption component of the isotropic spectrum and the A_x-spectrum for the out-of-plane polarized component.

If the disk-like molecules are oriented unidirectionally in the PVA film, the formulas necessary for the procedure are as follows:[8]

$$A_\perp - \frac{1}{d}A_\parallel = \frac{d-1}{d}A_x \tag{1}$$

$$A_\parallel - d_x A_\perp = \frac{d-1}{d}(A_y+A_z) \tag{2}$$

where d_x and d ($d=d_y=d_z$ for the disk-like molecule) are the *reduction factors*[8] which should be determined by the procedure. The *orientation factors*[8] K_x and K ($K=K_y=K_z$) are given by

$$K_x = \frac{d_x}{2+d_x} \quad \text{and} \quad K = \frac{d}{2+d} \tag{3}$$

Results and Discussion

Isotropic, Dichroic, and R_d-Spectra.[4] Figures 1a—1c show two kinds of isotropic spectra, *i.e.*, $\bar{k}\times A_0(S=1)$ (open circles) and $A=(A_\parallel+2A_\perp)/3$ (solid curve), for PR, CV, and EV in the PVA film at an S value of 3.7. A good agreement between these two isotropic spectra in each case suggests that the dye molecules are oriented unidirectionally in the stretched film. The observed isotropic spectrum of each dye in the film was similar to the spectrum in the corresponding aqueous PVA solution, except that the film spectrum was slightly shifted toward the long-wavelength side. There appear three peaks (designated as **A**, **C**, and **D**), shoulder(s) in the 340—400 nm region, and a shoulder (designated as **B**) in each film spectrum. These apparent wavelength positions are given for PR, CV, and EV in Table 1.

PR: Figure 2a shows the dichroic, $\Delta A/A$, and R_d-spectra of PR in the UV and visible regions. The $A_\parallel$-spectrum is always more intense than the $A_\perp$-spectrum over the entire wavelength. The R_d-spectrum decreases slightly on the long-wavelength side of the visible peak, but changes irregularly in the UV region. The R_d-spectrum becomes highest near the shoulder band at *ca.* 510 nm and the UV peak at 294 nm.

CV: Figure 2b shows the dichroic, $\Delta A/A$, and R_d-spectra of CV in the UV and visible regions. The $A_\parallel$-spectrum is more intense than the $A_\perp$-spectrum except in the 280 nm region. There are two peaks in the 340—400 nm region, which were obscure in the dichroic spectra of PR. In spite of the simple profile of the isotropic absorption spectrum in the visible and UV regions, the R_d-spectrum is not flat but changes irregularly. The R_d-spectrum gives the highest value near the shoulder band at *ca.* 556 nm and the lowest value near 280 nm. A gradual decrease of the R_d-spectrum is noted near the principal peak in the visible region (570—670 nm). Those apparent dichroic features in the visible region are in excellent agreement with previous reports.[6,7]

EV: Figure 2c shows the dichroic, $\Delta A/A$, and R_d-spectra of EV. The $A_\parallel$-spectrum is always more intense than the $A_\perp$-spectrum in the UV and visible regions. The R_d-spectrum of EV behaves very much

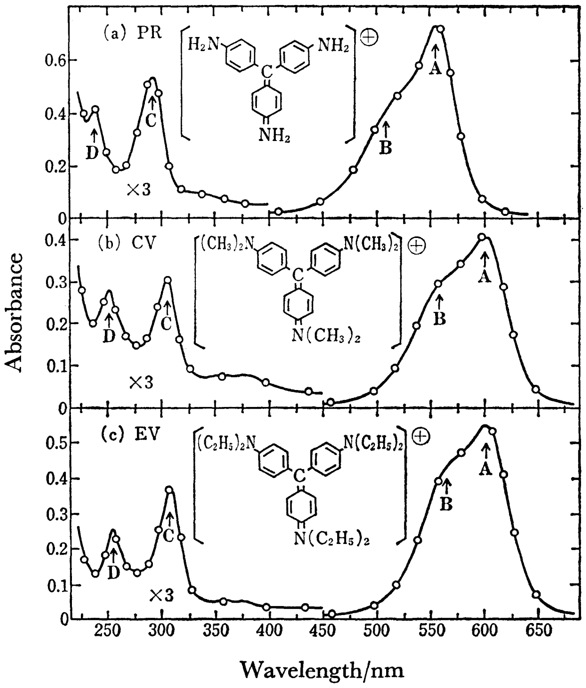

Fig. 1. Isotropic spectra of PR, CV, and EV in the stretched PVA film at $S=3.7$. The solid line (——) is the isotropic spectrum calculated from $A_\parallel$ and $A_\perp$ by the use of the relation, $A=(A_\parallel+2A_\perp)/3$. Circles (-o-o-) are the normalized isotropic absorbance calculated from $\bar{k}\times A_0(S=1)$. For the definition of these quantities, see Ref. 4. The values of $\bar{k}$ were 0.65 for PR and 0.61 for CV and EV. Letters **A** to **D** indicate the apparent peak or shoulder positions in each isotropic spectrum.

TABLE 1. THE APPARENT BAND POSITIONS (**A**—**D**) IN THE ISOTROPIC SPECTRA AND THE TRANSITION MOMENT ANGLES (θ_A–θ_C) AT THE CORRESPONDING BAND POSITIONS OF PR, CV, AND EV

Dyes	Apparent positions[a)] (nm)				Angles (deg)		
	A	**B**	**C**	**D**	θ_A	θ_B	θ_C
PR	557(549)	510(500)	294	241	48±1	48±1	49±1
CV	600(594)	560(550)	308(304)	252(251)	48±1	46±1	49±1
EV	603(601)	565(555)	310(308)	256(254)	49±1	47±1	47±1

a) The values in the parentheses are the corresponding positions in the aqueous PVA solution.

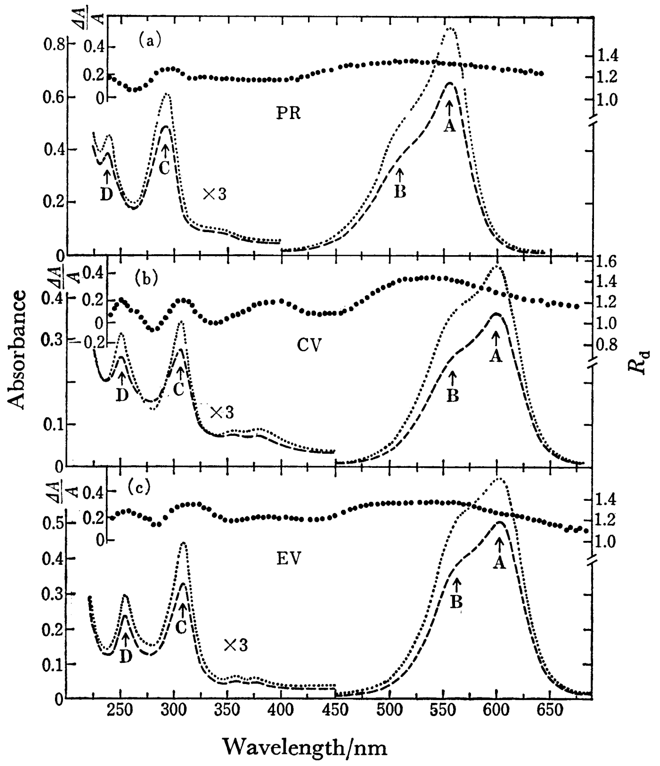

Fig. 2. Dichroic spectra and R_d-spectra of PR, CV, and EV in the stretched PVA film at $S=3.7$. The R_d-value can be converted into the reduced dichroism, $\Delta A/A$, which is referred to the left ordinate of each figure, by the use of Eq. 6 in Ref. 4. Symbols are: the parallel $A_{\parallel}$ (·········) and perpendicular $A_{\perp}$ (———) polarized spectra, and $\Delta A/A$ or R_d-spectrum (••••••). Letters **A** to **D** are the same as in Fig. 1.

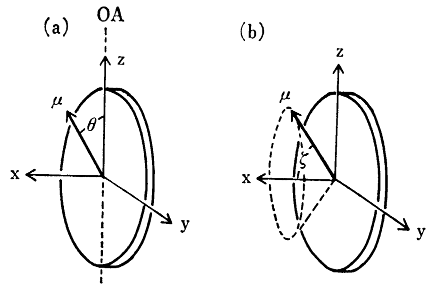

Fig. 3. Schematic illustration of the perfect orientation of a disk-like molecule in the stretched PVA film. The molecule has a transition dipole moment μ taking an arbitrary direction. The molecular coordinates are the y- and z-axes (in-plane) and the x-axis (out-of-plane), where the z-axis is tentatively taken along the stretching direction. (a) The direction of μ is measured by an angle θ relative to an orientation axis (OA) in the molecular plane. (b) The direction of μ is measured by an angle ζ with respect to the out-of-plane x-axis.

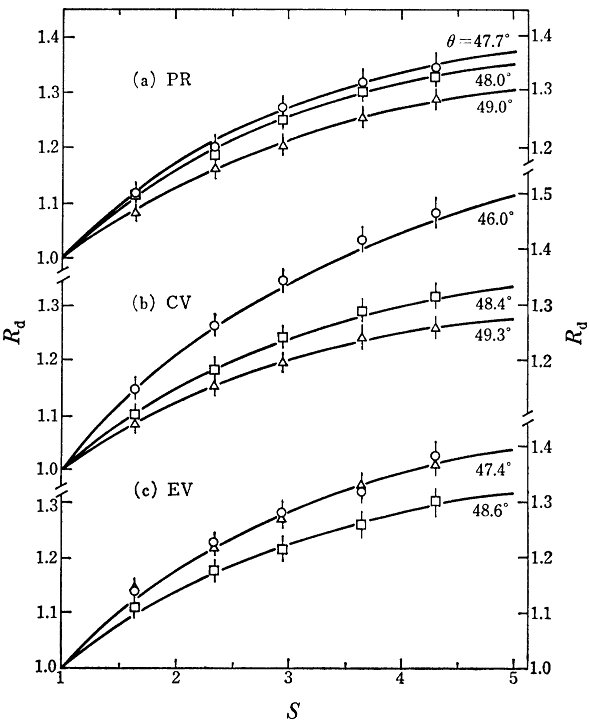

Fig. 4. Dependence of R_d on S for PR, CV, and EV. Symbols (□, ○, and △) denote the R_d-values at the wavelength positions of **A**, **B**, and **C** at five different S-values. Each solid curve is a theoretical one which fits best to those observed points. The value of the angle θ specifying each curve was determined by the method of Tanizaki.

like that of CV, although the R_d-values of EV at the UV peaks (**C** and **D**) are larger than those of CV at the corresponding positions.

Determination of Transition Moment Angles. In a previous paper we have dealt with the acridine dyes of C_{2v} point symmetry, each of which has a unique axis of orientation in the molecular plane (*i.e.*, the orientation axis). In that treatment the transition moment angles relative to the orientation axis were determined by the method of Tanizaki.[6] However, in the case of the disk-like molecule, such an orientation axis can not be assigned uniquely in the molecular plane because of its possible distribution in any direction. Nevertheless, if we presume an orientation axis (OA) in the molecular plane of the disk-like molecule, we can estimate the direction of a transition moment μ as the angle θ relative to the OA (Fig. 3a) by the method of Tanizaki. However, since this value of θ results from the averaging over μ around the out-of-plane axis (x-axis), it is only an apparent angle.

In the radially symmetrical molecules such as PR, CV, and EV, all in-plane polarized transitions will show a constant dichroic ratio at a given value of S.[5] Moreover, in the absence of the out-of-plane polarized transitions, the values of θ for the in-plane transitions of the disk-like molecule will become 45°.[5–7] In order to determine the values of θ, the dependence of R_d on S was examined at the positions of **A**, **B**, and **C** for PR, CV, and EV. The results are shown in Fig. 4, where the values of θ were determined by the method of Tanizaki.[4,6] The observed values of R_d appear to fall on the respective theoretical curves indicated by the angle θ within experimental errors. As shown in Fig. 4, Tanizaki's method is applicable for the molecules which give rise to a small dichroic ratio. All values of θ for

PR, CV, and EV are given in Table 1. It should be noted that each θ is determined relative to an arbitrary and unspecified axis in the molecular plane and, hence, that the angle θ is only apparent. It is now clear that the values of θ are not equal to, but always larger than, 45° at the positions of **A**, **B**, and **C**, and that they differ from each other. These results are indeed strong and direct evidence that the apparent bands **A**, **B**, and **C** each contain not only the in-plane but also the out-of-plane transitions. The presence of the out-of-plane polarized transition(s) in those wavelength positions will be shown below.

The in-plane polarized transitions of the disk-like molecule can not be divided uniquely into the so-called y- and z-axis polarized components[4)] because of the flatness of the R_d-spectrum. However, the isotropic spectrum should be divided into the in-plane and the out-of-plane polarized absorption components, as carried out by Yogev *et al.*[5)] In order to determine these absorption components, it is necessary to differentiate the out-of-plane polarized transition from the in-plane polarized one in the same overlapping wavelength region in the isotropic spectrum. For this purpose, Yogev *et al.* have attempted to determine the direction of the out-of-plane transition moment by two angles of α and β relative to two particular axes in the molecular plane.[5)] However, this determination of the direction is not well suited for the disk-like molecule of high symmetry, because the out-of-plane transition moment vector is generally distributed equally and evenly around the x-axis when the molecules are oriented unidirectionally. In order to find the in-plane and out-of-plane polarized transitions more convincingly, a new analysis of the linear dichroism for a disk-like molecule will be presented in the next section.

Analysis of Linear Dichroism for Disk-like Molecules. As a representative disk-like molecule, CV is chosen for illustration of procedures. Since CV does not possess a defined axis of orientation lying in the molecular plane, it will orient itself in the stretched PVA film preferentially with its plane parallel to the stretching direction. The definition of the molecular axes x, y, and z is shown in Fig. 3b, where a transition moment μ of the molecule is directed along an arbitrary direction. The direction of the moment is measured with the angle ζ relative to the x-axis. According to this scheme, the reduced dichroism and the dichroic ratio ($\Delta A/A$ and R_d) for an assembly of like molecules are represented by Eqs. 4 and 5, respectively, by analogy with the case for the rod-like molecules:[13)]

$$\frac{\Delta A}{A} = \frac{3(A_{\parallel} - A_{\perp})}{A_{\parallel} + 2A_{\perp}} = \frac{3}{2}(3\cos^2\zeta - 1)\Phi \tag{4}$$

and

$$R_d = \frac{A_{\parallel}}{A_{\perp}} = \frac{2+2(3\cos^2\zeta - 1)\Phi}{2-(3\cos^2\zeta - 1)\Phi} \tag{5}$$

where Φ is the orientation function[14)] and takes any value between 0 and −0.5 depending on the orientability of a particular kind of dye embedded in the PVA film. The detailed discussion will be given later.[13)] A very closely related orientation function has already been derived for the disk-shaped molecule in the study of electric dichroism.[15)] The function Φ may be connected to the degree of orientation, f ($0 \leqq f \leqq 1$), of the assembly of dye molecules in such a way that $f = -2\Phi$. The value of f then represents a hypothetical fraction of the disk-like molecules having their planes in the direction of stretch at a given S. It should be noted that, at the limiting stretch ratio ($S \rightarrow \infty$), Φ takes a value of −0.5 if the orientation is such that the y- or z-axis is parallel to the stretching direction, but it takes a value of 1 if the orientation is such that the x-axis is parallel to the stretching direction. (The latter is the case of a cylindrical molecule for which the x-axis is the longest.) Thus the general behavior of Φ for the disk-like molecule differs from that for the rod-like molecule.[13)]

On the basis of Eqs. 4 and 5, the analysis of the linear dichroism for the disk-like molecule will be shown below in order to differentiate the out-of-plane polarized transition from the in-plane polarized one. When dichroic absorption spectra are measured for a disk-like molecule, they should show that a transition moment with $\zeta = 0°$ will preferentially absorb the light polarized perpendicularly to the direction of stretch. (In this case a negative linear dichroism should be observed.) If all molecules are oriented with their molecular plane perfectly parallel to the stretching direction (*i.e.*, $\Phi = -0.5$ or $f = 1$), the reduced dichroism, $\Delta A/A$, and the dichroic ratio, R_d, for the transition moment with $\zeta = 0°$ would have the limiting values of −1.5 and 0 in Eqs. 4 and 5, respectively. If the molecules are partially oriented, the reduced dichroism and the dichroic ratio for the same transition moment would be a function of Φ or f only and may be obtained from Eqs. 4 and 5 by substituting $\zeta = 0°$:

$$\frac{\Delta A}{A} = 3\Phi = -\frac{3}{2}f \tag{6}$$

$$R_d = \frac{1+2\Phi}{1-\Phi} = \frac{2(1-f)}{2+f} \tag{7}$$

Since Φ varies between 0 and −0.5 (f varies between 0 and 1), $-1.5 \leqq \Delta A/A \leqq 0$ and $0 \leqq R_d \leqq 1$. On the other hand, the reduced dichroism and the dichroic ratio due to a transition moment polarized in the molecular plane may be given by substituting $\zeta = 90°$ into Eqs. 4 and 5:

$$\frac{\Delta A}{A} = -\frac{3}{2}\Phi = \frac{3}{4}f \tag{8}$$

$$R_d = \frac{2-2\Phi}{2+\Phi} = \frac{4+2f}{4-f} \tag{9}$$

In this special case, $0 \leqq \Delta A/A \leqq 3/4$ and $1 \leqq R_d \leqq 2$. Equations 7 and 9 are now reduced to the same expressions which have been derived by Yogev *et al.* (Eqs. 2 and 9 in Ref. 5). Thus, Eqs. 4 and 5 are more general and appropriate to the analysis of the dichroic spectra containing both the in-plane and out-of-plane polarized transitions.

The dependence of $\Delta A/A$ or R_d on wavelength makes it possible to distinguish between the in-plane and the out-of-plane transitions of the disk-like molecule. If only the in-plane or the out-of-plane polarized transitions are present in the observed wavelength region, the wavelength dependence of $\Delta A/A$ or R_d becomes flat throughout the region concerned at a given value of S. The absolute values of $\Delta A/A$ or R_d depend only on the degree of orientation, as indicated by Eqs. 6 and 7 for the out-of-plane transition or by Eqs. 8 and 9 for the in-plane transition. If both the in-plane and the out-of-plane transitions are overlapped, the wavelength dependence is not constant any longer in a particular wavelength region, the former being located in the region with the large $\Delta A/A$ or R_d-value and the latter being located in the region with the small $\Delta A/A$ or R_d-value. This is because the values of $\Delta A/A$ and R_d of the out-of-plane transition should be smaller than those of the in-plane transition at a given value of S (for the details, see the next section).

Reduced Spectra of PR, CV, and EV. The following analysis is based on the assumption that the dyes PR, CV, and EV in the PVA film can be treated as disk-like molecules oriented with their molecular planes parallel to the stretching direction (see Fig. 3b). Since the structure of those dyes belong to a D_{3h} or C_{3v} point symmetry, the assumption is probably quite appropriate. Their absorption spectra then consist of the transitions which are allowed in the plane (yz-plane) perpendicular to the three-fold symmetry axis and possibly along the three-fold symmetry axis (x-axis), *i.e.*, the out-of-plane polarized transitions. The in-plane polarized transitions may lie along either the y- or z-axis. From the changes in each $\Delta A/A$ or R_d-curve of PR, CV, and EV (Figs. 2a—2c), the absorption band near the **B** position appears to be mainly composed of the in-plane transition because of the largest $\Delta A/A$ or R_d-value, whereas the absorption band near the **A** position appears to be composed of the intense in-plane and weak out-of-plane transitions because of the smaller $\Delta A/A$ or R_d-value.

On the basis of the apparent spectral features, the reduction procedure was applied to the dichroic absorption spectra of PR, CV, and EV measured at $S=3.7$. The reduction factors d_x and d in Eqs. 1 and 2 were sought out by means of the trial-and-error reduction search.[8] The best values are given in Table 2, together with the values of the orientation factors K_x and K calculated from Eq. 3. The resultant reduced spectra of those dyes are shown in Figs. 5a—5c. As expected from the R_d data in Figs. 2a—2c, an out-of-plane polarized transition is clearly unmasked in the visible band at *ca.* 577 nm for PR, 608 nm for CV, and 613 nm for EV in each A_x-spectrum (solid curve). The in-plane polarized transitions, probably y- and z-axis polarized, are dominant in the visible region, as indicated by the (A_y+A_z)-spectrum (dotted curve).

The isotropic spectrum of each dye in the visible region may contain three different electronic transitions: two lie in the molecular plane (the A_y- or A_z-component near the **B** position and the A_z- or A_y-component near the **A** position) and one lies out of the molecular plane (the A_x-component near the **A** position). The present analysis for CV is in good agreement with the qualitative interpretation proposed by Tanizaki[6] and Nordén.[2,7] Hidden in the isotropic spectrum in the visible region, the out-of-plane polarized transition is responsible for the decrease in the R_d-values near the principal band at **A** position (Figs. 2a—2c). The weak isotropic band in the 340—420 nm region mostly consists of the in-plane transitions, while the bands in the 220—340 nm region contain both the out-of-plane and intense in-plane transitions (see Fig. 5). Thus, the isotropic spectra of the highly symmetric triphenylmethane dyes such as PR, CV, and EV could now be resolved into their in-plane and out-of-plane components by the reduction procedure. The presence of the out-of-plane component may give a key for elucidating the configuration of triphenylmethane dyes[16] and, consequently, the metachromatic changes caused by interaction with various polyelectrolytes and biopolymers.[11,17,18]

Table 2. The average values of the reduction factors (d_x and d) and the orientation factors (K_x and K) of PR, CV, and EV at $S=3.7$

Dyes	d_x	$d=d_y=d_z$	K_x	$K=K_y=K_z$
PR	0.48	1.35	0.194	0.403
CV	0.30	1.54	0.130	0.435
EV	0.38	1.45	0.160	0.420

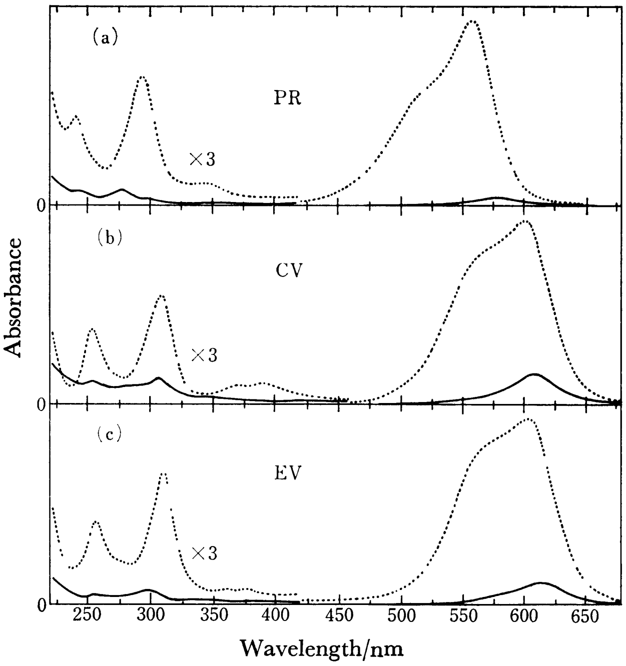

Fig. 5. The reduced (A_y+A_z)- and A_x-spectra of PR, CV, and EV. The in-plane (yz-plane) and the out-of-plane (x-axis) polarized absorbances (arbitrary units) are shown by the dotted and the solid curves, respectively.

If triphenylmethane has a triangular and planar configuration with three benzene rings toward the corners (D_{3h} point symmetry), the resolved out-of-plane component may have to be attributed to n-π^* transitions. However, the presence of numbers of n-π^* transitions is unrealistic in the visible and near UV regions. The structure of the triphenylmethane skelton is probably distorted in such a way that the central carbon-phenyl ring bonds either form a pyramidal structure (C_{3v} point symmetry), remain co-planar with three phenyl rings being tilted (D_3 point symmetry), or a pyramidal structure with the tilted rings (C_3 point symmetry). In order to discuss the configuration of the triphenylmethane dyes more in detail, a complete assignment of each absorption band may be necessary by taking into account both the in-plane and out-of-plane polarized transitions. Nevertheless, the optical properties now available for biologically important triphenylmethane dyes will facilitate the structural studies of the complexes between biopolymers and these dyes.[1,2,18–20]

Conclusions

Since the R_d-values of triphenylmethane dyes PR, CV, and EV were not large as compared with those of acridine dyes,[4] the values of the transition moment angles θ at the absorption band centers of each dye could be evaluated by the method of Tanizaki.[6] However, these values give rise to only the apparent angles for disk-like triphenylmethane dyes. The orientation of those highly symmetric dyes originates from a mechanism which differs from that of acridine dyes. To evaluate the reduced spectra of the disk-like molecule, a new analysis of the linear dichroism was presented (Eqs. 4 and 5). In this analysis the transition moment angle is measured relative to the x-axis, which is perpendicular to the molecular plane. This method differs from the one proposed by Yogev *et al.*[5] The major findings in this work are as follows: (1) In the isotropic spectra of PR, CV, and EV, both the out-of-plane and in-plane polarized electronic transitions are present and overlap each other in the UV and visible regions. In particular, the intense visible band is a composite of one out-of-plane and two in-plane transitions. (2) The behavior of the orientation function Φ for the disk-like molecule can be related to the degree of orientation f by $f=-2\Phi$, which differs from the relation $f=\Phi$ for the rod-like molecule.

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14) This quantity will be represented by the orientation factors K_i (i=x, y, z) as $\Phi=(3K_x-1)/2=1-3K_y=1-3K_z$.

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