Dichroism of Dyes in the Stretched PVA Sheet. II[1]. *The Relation between the Optical Density Ratio and the Stretch Ratio, and an Attempt to Analyse Relative Directions of Absorption Bands**

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Hitherto, dichroic properties have been mainly utilized to investigate dyeing mechanism[2] or the percentage orientation of fibres[3]. A conclusion derived from a number of experimental results shows that almost all dye molecules in dyed state should lie lengthwise along the cellulose chains[4]. In the previous paper[1], this conclusion was applied to presume the relative direction of transition moments of absorption bands of certain direct dyes in the stretched polyvinyl alcohol sheet from their dichroic properties. A similar attempt may not be applied to short molecules which show poor dichroism, and it is still more difficult, as it is not sure that such molecules are adsorbed on a fibre so as to orient parallel to the fibre axis. However, the fact that an observed optical density ratio (to be defined later) depends upon the stretch ratio of the sheet may give a key to analyse the direction of transition moment of the absorption band of the dye molecule. The purpose of this paper is to derive an expression for the density ratio as a function of the stretch ratio, to apply it to absorption bands of certain basic dyes, and to analyse their relative direction.

Experimental

Materials.—Polyvinyl alcohol (abbreviated to PVA) with the polymerization degree of about 1500 was used for preparing sheets by the method described in the previous paper[1].

Dyes used were crystal violet and auramine yellow which were recrystallized twice from ethanol, starting from the pure ones produced in the Laboratory of Hodogaya Kagaku Co., Ltd. The paper chromatography detected no colored impurities in these dyes.

PVA sheets, swollen fully in distilled water, were soaked in the aqueous dye solution at room temperature.

Measurements.—Measurements were carried out with a Shimadzu QB-50 spectrophotometer, in filter hole of which a sheet-polarizer of PVA-iodine[5] was set. To determine the correlation between the electric vector of polarized incident light and the stretching direction of the sample sheet, an apparatus shown in Fig. 1 was used. A colored and an uncolored PVA sheet were respectively pasted on a metal ring to be fixed in R_1 and R_2. The disk D graduated 0° to 360° on its circumference can be rotated at will in concentric with the toothed wheel G_1, and at the same time the rotation is transmitted through G_2, being used as a change gear, to R_1 and R_2. Gear ratios are all the same. This apparatus is set in the cell box of the spectrophotometer in place of

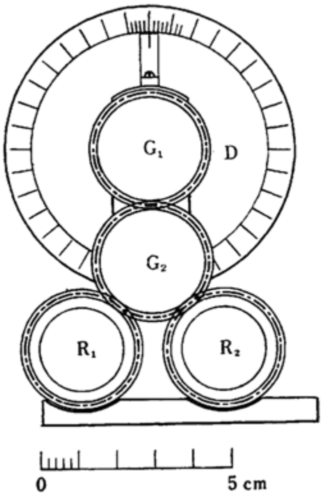

Fig. 1. Apparatus for rotating sample sheets.

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[1] Part I of this series, Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 542 (1957).

* Presented at 11th Annual Meeting of the Chemical Society of Japan, April 1958.

[2] T. H. Morton, *J. Soc. Dyers Col.*, **62**, 272 (1946); H. H. Summer, T. Vickerstaff and E. Waters, ibid., **69**, 181 (1953).

[3] J. M. Preston, ibid., **47**, 312 (1931); D. R. Morey, *Tex. Research*, **4**, 491 (1934); **5**, 105 (1935); J. M. Preston and P. C. Tsien, *J. Soc. Dyers Col.*, **62**, 368 (1946); **66**, 361 (1950); J. M. Preston and Y. F. Su, ibid., **66**, 357 (1950); D. R. Morey and E. V. Martin, *Tex. Research J.*, **21**, 607 (1951).

[4] T. Vickerstaff, "The Physical Chemistry of Dyeing", Second Edition, Oliver and Boyd, London (1954), p. 183.

[5] Y. Tanizaki, This Bulletin, **30**, 935 (1957).

the cell holder. Thus the correlation mentioned above was determined by means of the Malus' law.

Notations.—A circle drawn on the sheet before stretching is deformed into an ellipse after stretching. The ratio of the long axis of the ellipse to the short one is defined as the *stretch ratio* R_s[6]. $D_\parallel$ and $D_\perp$ are optical densities for completely and linerly polarized lights whose electric vectors are respectively parallel and perpendicular to the stretching direction. An *optical density ratio* R_d is then defined as $D_\parallel/D_\perp$.

Theoretical

Let us suppose that an imaginary sphere in substrate of PVA sheet is deformed, being kept at a constant volume by stretching into a spheroid. If the optical property around the stretching direction were isotropic and any unit vector with an angle θ_0 against the stretching direction in the sphere were transformed into a unit vector with θ in the spheroid, the distribution of vectors after stretching, $f(\theta)$, would be determined in the following way,

$$f(\theta)=\int_0^{\pi/2} G(\theta,\theta_0)F(\theta_0)\mathrm{d}\theta_0 \tag{1}$$

where $F(\theta_0)$ means a function of distribution before stretching, and $G(\theta,\theta_0)$ is a function of transformation which makes θ_0 transform to θ by stretching. Since it is natural to consider that the distribution of vectors before stretching is quite at random, then $F(\theta_0)$ may be expressed as follows,

$$F(\theta_0)=\sin\theta_0$$

$$\text{or}\qquad =\frac{\tan\theta_0}{\sqrt{1+\tan^2\theta_0}} \tag{2}$$

On the basis of the assumption that the deformation takes place under a constant volume, the relation between θ_0 and θ is expressed as follows,

$$\tan\theta_0=R_s\tan\theta$$

where R_s is the axial ratio of the ellipsoid and is equal to the stretch ratio mentioned above. Then the transformation function may be written as follows

$$G(\theta,\theta_0)=\delta(\tan^{-1}(R_s\tan\theta)-\theta_0)\rho(\theta_0) \tag{3}$$

where δ is a delta-function and ρ is a surface element, namely

$$\rho(\theta_0)=R_s\frac{\sin\theta_0\cos^2\theta_0}{\sin\theta\cos^2\theta} \tag{4}$$

By the combination of Eqs. 1, 2, 3 and 4,

$$f(\theta)=\int_0^{\pi/2}\delta(\tan^{-1}(R_s\tan\theta)-\theta_0)\times\frac{R_s}{\sin\theta\cos^2\theta}\frac{\tan^2\theta_0\,\mathrm{d}\theta_0}{(1+\tan^2\theta_0)^2}$$

The interval of this integration involves zero. So that, according to the nature of δ-function[7], this integration becomes equal to the integrand excluding δ-function, in which θ_0 is replaced by $\tan^{-1}(R_s\tan\theta)$, that is,

$$f(\theta)=\frac{R_s^3\tan^2\theta}{\sin\theta\cos^2\theta(1+R_s^2\tan^2\theta)^2}$$

$$\text{or}\qquad f(\theta)=\frac{R_s^3\sin\theta}{\{1+(R_s^2-1)\sin^2\theta\}^2} \tag{5}$$

where $R_s\geq1$ and $0\leq\theta\leq\pi/2$. Determining $N(R_s)$ so as to make the integration with respect to θ unity, namely,

$$\int_0^{\pi/2}N(R_s)f(\theta)\mathrm{d}\theta=1$$

$N(R_s)f(\theta)$ for several values of R_s provides the curves shown in Fig. 2. This figure indicates that for large R_s values, that is, when the PVA sheet is stretched to a high degree, the greater part of vectors becomes able to meet the stretching direction. This

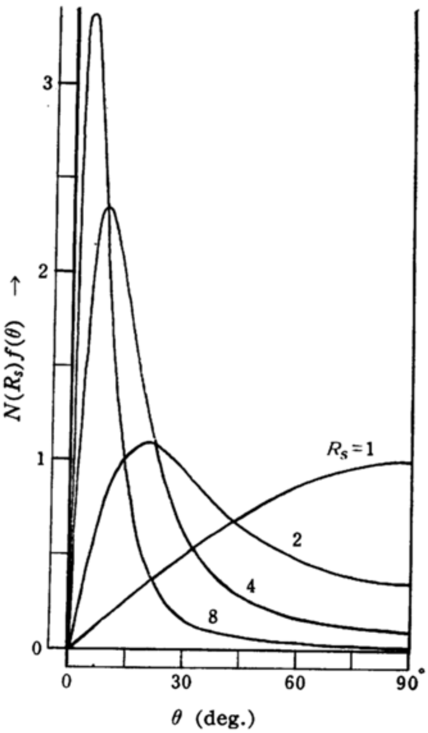

Fig. 2. Distribution curves, $N(R_s)f(\theta)$, for several values of the stretch ratio, R_s.

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[6] E. H. Land, *J. Opt. Soc. Am.*, **41**, 957 (1951).

[7] P. A. M. Dirac, "Quantum Mechanics", Third Edition, Oxford (1947), p. 58.

will correspond to a distribution of a characteristic direction, which is regarded as a vector and is called hereafter an *orientation axis*, of the molecular species. So that, when the direction of the transition moment corresponding to an absorption band is on the orientation axis, the problem is rather easy to be dealt with. For the present purpose, however, it is necessary to consider a general case where transition-directions of dye molecules do not always coincide with orientation axes. Therefore, it will be convenient to introduce here an imaginary plane made of an orientation axis and a direction of transition moment. This plane does not necessarily coincide with the usual molecular plane, and is temporarily called a *light absorption-plane*. The transition moment μ of an absorption band can be decomposed into two components within the light absorption-plane, one of which is normal and the other parallel to the orientation axis, namely μ_b and μ_a respectively. Consequently, if the value of $|\mu_a/\mu_b|=r$ can be obtained, $\cot^{-1}r$ will give the angle of a direction of transition against the orientation axis of a molecule.

Now, if we imagine rectangular coordinates in the PVA substrate, so as to run the Z axis parallel with the stretching direction (see Fig. 3), and if the angle between Z and μ_a is θ, then three components of μ_a can be written as follows,

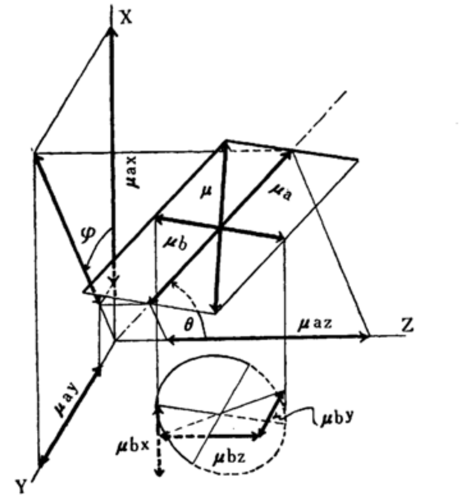

Fig. 3. Rectangular coordinates in the PVA substrate, of which the Z axis is taken parallel to the stretch direction of the PVA sheet. A transition moment μ of a dye molecule is decomposed to a parallel component μ_a and a normal μ_b to the orientation axis in the light absorption-plane.

$$\begin{cases} \mu_{aX}=\mu_a\sin\theta\cos\varphi \\ \mu_{aY}=\mu_a\sin\theta\sin\varphi \\ \mu_{aZ}=\mu_a\cos\theta \end{cases} \tag{6}$$

where φ is the angle between X and the projection of μ_a on the XY-plane. Similarly, corresponding ones for μ_b can be represented by

$$\begin{cases} \mu_{bX}=\mu_b(\cos^2\theta+\sin^2\theta\sin^2\varphi)^{1/2}\cos\phi \\ \mu_{bY}=\mu_b\left(\dfrac{\sin^4\theta\sin^2\varphi\cos^2\varphi\cos^2\phi+\cos^2\theta\sin^2\phi}{\cos^2\theta+\sin^2\theta\sin^2\varphi}\right)^{1/2} \\ \mu_{bZ}= \\ \mu_b\left(\dfrac{\sin^2\theta\cos^2\theta\cos^2\varphi\cos^2\phi+\sin^2\theta\sin^2\varphi\sin^2\phi}{\cos^2\theta+\sin^2\theta\sin^2\varphi}\right)^{1/2} \end{cases} \tag{7}$$

where φ is the angle between the X axis-orientation axis-plane and the light absorption-plane. The angle θ takes values of zero to $\pi/2$, and φ and ϕ values of zero to 2π. Integration with respect to φ and ϕ must be averaged for the region. Thus the components of μ for the X, Y and Z directions should be of the form

$$\begin{cases} \mu_X{}^2=\displaystyle\int_{\theta=0}^{\pi/2}\frac{1}{2\pi}\int_{\varphi=0}^{2\pi}\frac{1}{2\pi}\int_{\phi=0}^{2\pi} \\ \qquad\times(\mu_{aX}{}^2+\mu_{bX}{}^2)N(R_s)f(\theta)\,\mathrm{d}\phi\,\mathrm{d}\varphi\,\mathrm{d}\theta \\ \text{etc.} \end{cases} \tag{8}$$

Substitution of Eqs. 6 and 7 for Eq. 8, and integrations with respect to φ and ϕ, give

$$\begin{cases} \mu_X{}^2=\mu_Y{}^2=\dfrac{1}{4}\displaystyle\int_0^{\pi/2}\{2\mu_a{}^2\sin^2\theta \\ \qquad+\mu_b{}^2(1+\cos^2\theta)\}N(R_s)f(\theta)\,\mathrm{d}\theta \\ \mu_Z{}^2=\dfrac{1}{2}\displaystyle\int_0^{\pi/2}(2\mu_a{}^2\cos^2\theta \\ \qquad+\mu_b{}^2\sin^2\theta)N(R_s)f(\theta)\,\mathrm{d}\theta \end{cases} \tag{9}$$

Since the optical density D is proportional to μ^2, it may be possible to write

$$R_d\equiv\frac{D_\parallel}{D_\perp}=\frac{\mu_Z{}^2}{\frac{1}{2}(\mu_X{}^2+\mu_Y{}^2)}=\frac{\mu_Z{}^2}{\mu_X{}^2} \tag{10}$$

For non-stretched state, i. e. $R_s=1$, integration of Eq. 9 gives $\mu_X{}^2=\mu_Y{}^2=\mu_Z{}^2=\mu^2/3$. Hence the following relation can be obtained by the aid of Eq. 10,

$$R_d=1 \quad (R_s=1)$$

For $R_s>1$, combination of Eqs. 9 and 10, and integration with respect to θ give

$$R_d=\frac{2+2(2r^2-1)T(R_s)}{(2r^2+1)-(2r^2-1)T(R_s)} \tag{11}$$

where

$$T(R_s)=\frac{R_s^2}{R_s^2-1}\left\{1-\frac{N(R_s)}{\sqrt{R_s^2-1}}\log(R_s+\sqrt{R_s^2+1})\right\}$$

$$N(R_s)=2\left\{\frac{1}{\sqrt{R_s^2-1}}\log(R_s+\sqrt{R_s^2-1})+R_s\right\}^{-1}$$

and $R_s>1$.

This is the final expression. Plotting R_d against R_s for various values of a parameter r curves representing Eq. 11 are obtained as shown in Fig. 4.

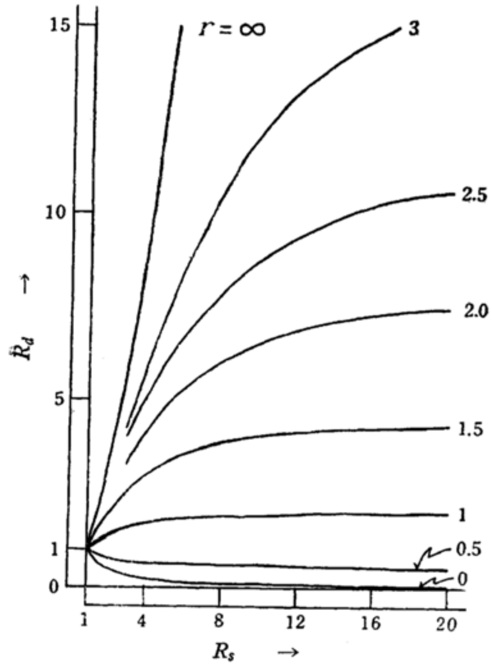

Fig. 4. Relation between R_d and R_s for various values of r.

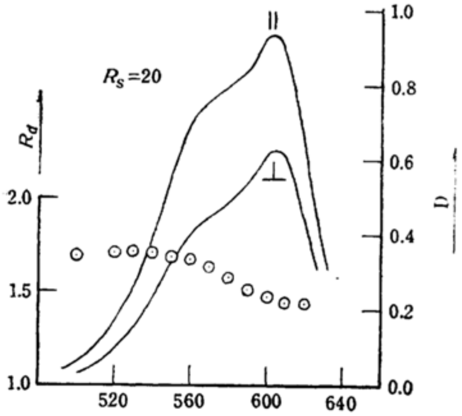

Fig. 5. Absorption spectra by polarized light of the crystal violet ion in the stretched PVA sheet. ‖ means the absorption curve when the electric vector of incident light is parallel and ⊥ means when the vector is normal to the stretch direction. Circles indicate the optical density ratio, R_d.

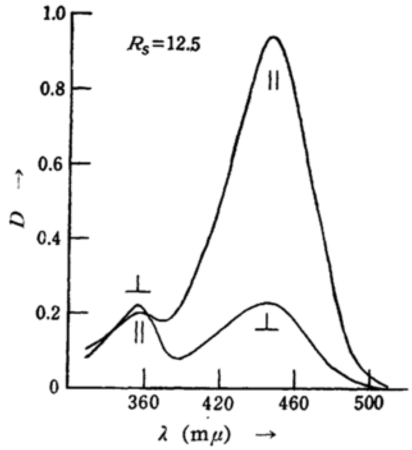

Fig. 6. Absorption spectra by polarized light of the auramine yellow ion in the stretched PVA sheet. The meaning of ‖ and ⊥ is the same as in Fig. 5.

Results

Absorption spectra by polarized light of the crystal violet and the auramine yellow ion in stretched PVA sheets are shown in Figs. 5 and 6, respectively. Fig. 5 shows that the crystal violet ion has an absorption maximum at about 605 mμ and a shoulder at about 560 mμ, and that R_d values near the shoulder are larger than that at the absorption maximum. Fig. 6 shows that the auramine yellow ion has the first (445 mμ) and the second (~375 mμ) band whose dichroic properties are different from each other. This means that transition moments corresponding to these absorption bands have different directions.

Observed and calculated relations between R_d and R_s of each absorption band are shown in Figs. 7 and 8. Fig. 7 shows the case of the crystal violet ion; the observed values at 605 mμ are represented by the white circles and those of 560 mμ by the half solid circles, and the full lines are the curves obtained from Eq. 11 putting $r=0.86$ for the 605 mμ band and $r=0.90$ and 0.92 for the 560 mμ band. Similarly, Fig. 8 shows the result of the auramine yellow ion; the observed values for the first band are indicated by the white circles and for the second band (375 mμ) by the half solid circles, and the corresponding full lines are calculated by Eq. 11 putting $r=1.55$ and 1.60 for the first band and $r=0.60$, 0.65 and 0.70 for the second band, respectively. In Fig. 8 it is noticed that, in the small region of R_s, the observed value of R_d are smaller for the first band and larger for the second band than the calculated ones represented by the full lines. This fact may be simply interpreted as the effect due to the overlap of both bands. That is to say, on account of the mutual superposition of the bands the first band with large R_d may apparently increase the small R_d value of the second band and the converse would hold good. For the large R_s value, however, the observed R_d values roughly run along the respective calculated lines. In the case of crystal violet (Fig. 7), the observed R_d values for small R_s values are smaller than the calculated ones, and these differences are larger at 560 mμ than at 605mμ.

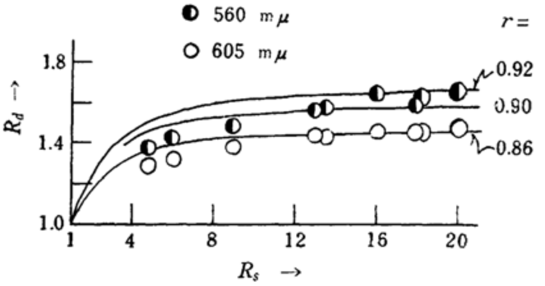

Fig. 7. Observed and calculated relations between R_d and R_s of the crystal violet ion in the stretched PVA sheet.

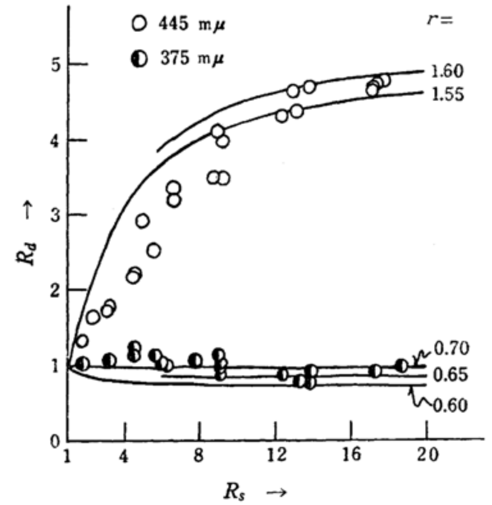

Fig. 8. Observed and calculated relationships between R_d and R_s of the auramine yellow ion in the stretched PVA sheet.

Thus, it can be said that Eq. 11 explains the experimental relation between R_d and R_s except for the smaller region of R_s and accordingly that Eq. 5 represents approximately well the nature of the distribution of such short molecules as the crystal violet ion in the stretched PVA substrate.

Discussion

The crystal violet ion. — Lewis and his coworkers[8] considered that the absorption band in the visible region of the crystal violet ion consists of those of isomers A and B. According to their consideration, the isomer A has a structure like a propeller with three blades (i. e. three benzene rings) and the isomer B has a similar form in which one blade is turned in the opposite direction from the others. As regards the absorption band here discussed, the main band belongs to the A isomer and the shoulder indicates the superposition of two bands A and B. In radially symmetrical molecules such as crystal violet, so-called x and y bands, which are both in the molecular plane[9], coincide with each other. In such a case, the transition moment is equal in all directions of the plane. This should be indeed the case of the A isomer. Furthermore, if we assume that the orientation axis is in the molecular plane, we should expect the value of r to be unity; that is, the angle of the direction of the transition moment against the orientation axis is expected to be 45°. According to our result, however, r equals to 0.86 and the corresponding orientation angle is $\cot^{-1} r=$ 49°. On the other hand, though the B isomer has not the same symmetry as the A isomer, the apparent moment would be regarded to be still equal in all directions of the molecular plane of the B isomer in the statistical sense, because the spacial extent, which may be one principal factor to govern the orientation of the molecule, seems to be passably symmetrical considering its solid thickness. So that, also in the case of the B isomer the angle mentioned above would be expected again to be 45°. But the present result indicates that r equals $0.92\sim0.90$, hence $\cot^{-1} r$ equals to $47.5°\sim48°$.

Fig. 5 indicates that the R_d values near the absorption maximum are always

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8) G. N. Lewis, T. T. Magel and D. Lipkin, *J. Am. Chem. Soc.*, **64**, 1774 (1942).

9) G. N. Lewis and J. Bigeleisen, ibid., **65**, 2102 (1943).

smaller than that of the shoulder. According to resolution of the observed band into those of isomers made by Lewis and his coworkers[8], the maximum corresponding to the isomer A is scarcely overlapped by the band of the isomer B, while the slope of the former almost covers the latter. This implies that the observed R_d value at the maximum wavelength gives the true R_d value for the A isomer, but the observed one at the shoulder, gives the smaller than the true value for the B isomer. Accordingly, it is considered that the absorption corresponding to the B isomer has the possibility of taking the r value of unity (i. e. the corresponding angle is 45°). From this fact we should be led to the conclusion that the orientation axis of the molecule deviates from its plane in the A isomer rather than in the B isomer. This seems indeed to be improbable from the point of view of their geometrical shapes. Therefore it seems wise to discard the abovementioned explanation and to adopt the alternative[10] that both bands originate from only one species. That is to say, the light absorption bands originate from two kinds of transition in one molecular species, one of which lies on the molecular plane and the other of which has two components parallel and normal to the plane. The former may correspond to the 560 mμ band and the latter to 605 mμ. Thus we can explain the experimental facts that the 560 mμ band has always the greater R_d value than that at 605 mμ, and the R_d value of the former has the possibility to take the r value of unity.

The auramine yellow ion.—For the first band of the auramine yellow ion, the corresponding r value is 1.55~1.60 (see Fig. 8). Accordingly the angle of the transition-direction against the orientation axis is 32.5°~32°. Similarly, since the most probable value of r for the second band is 0.65, the corresponding angle is obtained as 57°. Since the mutual correlation of the absorption planes of both bands is unfortunately unknown, the angle between two directions of the corresponding transition moments can not be decided directly. Nevertheless, when it is supposed that the absorption planes coincide with each other, namely when both transitions are on the same molecular plane, the angle just mentioned would be $57°+32°=89°$ or $57°-32°=25°$. Here the former value approximates to a right angle. This fact is of interest, because, in such a molecule as the auramine yellow ion, there may exist the x and y bands which are on the molecular plane and at right angles to each other[9].

Summary

1) An expression for the optical density ratio was derived as a function of the stretch ratio.

2) Dichroism of the crystal violet and auramine yellow ion in stretched PVA sheets was observed, and the relation of the optical density ratio to the stretch ratio was plotted. It was shown that the theoretical expression derived here could explain rather well the experimental relation between these two quantities.

3) The analytical results were as follows. The main absorption band and the shoulder of the crystal violet ion did not orginate from the two isomers but were perhaps due to one species. For the auramine yellow ion the angle between the transition directions corresponding to the first and the second band might be approximately a right angle provided that the *absorption-planes* were in a same plane.

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[10] Y. Mori, Presented at the Symposium of Electronic State, Nagoya, Oct. 1956.