

*Dichroism of Dyes in the Stretched PVA Sheet. III¹⁾.
Direction of Absorption of Pinacyanol Iodide^{*1}*

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In the previous paper¹⁾, a theoretical expression was derived concerning the relation between the optical density ratio $R_d (=D_{\parallel}/D_{\perp})$ and the stretch ratio R_s of the sample sheet, for the analysis of the relative absorption direction of dye molecules in the stretched PVA (polyvinyl alcohol) sheet. It was also proved experimentally that the adopted assumption in the derivation of the distribution function and accordingly the above R_d expression are adequate²⁾. A parameter r in the R_d expression, which determines the $R_d - R_s$ curve practically, is a particular one to each absorption band. Also this r -value determines the angle between the transition direction and the orientation axis of the molecule. Therefore, the greater the number of the absorption band in the observable region, the easier would be the discussion on the correspondence between

the relative transition direction and the molecular structure.

In this paper, turning our attention to the fact that the pinacyanol cation reveals a number of absorption bands from the visible to the near ultraviolet region, we determined the relative transition direction of some absorptions from the quantitative analysis. We also deduced the directions of other absorptions.

Experimental

The pinacyanol iodide used was synthesised and purified in the Laboratory of Fuji Photo Film Co., Ltd.

The experiment was carried out in the same way as before^{1,3)}. When a quantitative test is required, the correction of absorption and reflection by the substrate of the sheet becomes important, especially in the ultraviolet region.

Resultant optical density D from the absorption and/or the reflection of the PVA sheet itself in the visible region is as small as less than 0.05, almost

1) Part II of this series, Y. Tanizaki, This Bulletin, **32**, 75 (1959).

*1 Presented at the 12th Annual Meeting of the Chemical Society of Japan, Kyoto, April, 1959.

2) Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, **32**, 1362 (1959).

3) Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec. (Nippon Kagaku Zasshi)*, **78**, 542 (1957).

independent of the stretch ratio R_s , and the difference of D_{\parallel} and D_{\perp} is negligible because it is of the order of 0.001. In the near ultraviolet region, however, with decrease in wavelength, not only D_{\parallel} and D_{\perp} but their differences increases gradually, and these are all dependent on R_s . Accordingly, in the dichroic measurement the error arising from the incongruity in the stretch directions of the sample sheet and the correction sheet with each other (in the same R_s -value) becomes considerably large in general in the ultraviolet region. For this reason, the correction in the ultraviolet region, especially for the comparatively small density absorption, is of importance. So it was taken into consideration that the specific directions—the stretch directions—of the stained and the unstained sheet must be kept parallel with each other. An example of the observed relation between angle θ and optical density D_{θ} is illustrated in Fig. 1, in which θ

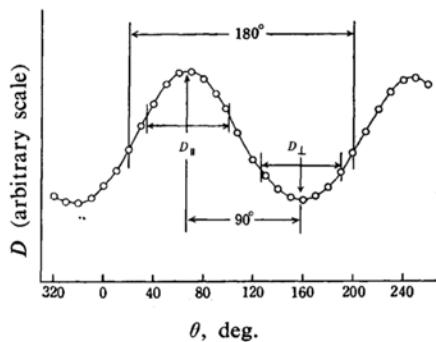


Fig. 1. Relation of optical density of pinacyanol in the stretched PVA sheet to the angle θ graduated on the disk of the sheet rotation apparatus. $R_s=5.4$, $\lambda=284 \text{ m}\mu$.

means the angle graduated on the disk of the sheet-rotation apparatus (see Figure 1 of Ref. 1). In Fig. 1, D_{θ} for a given angle θ coincides with $D_{(\theta+180^\circ)}$ for $(\theta+180^\circ)$. When the angle of the middle point of equivalent densities on both sides of the maximum is denoted as \parallel and that for the minimum as \perp , the angle scale difference between \parallel and \perp is equal to just 90° . The optical densities for \parallel and \perp are indicated by D_{\parallel} and D_{\perp} , respectively. A revolution of the disk gives two D_{\parallel} 's and two D_{\perp} 's. Two D_{\parallel} 's ought to be equivalent to each other, and the same must be said with two D_{\perp} 's, but sometimes they were not. These differences, however, were small, so that the mean value of each was used for the purpose of analysis.

Results

Absorption spectra of pinacyanol in the non-stretched PVA sheet are shown by solid lines in Figs. 2 and 3. In these figures, spectra in ethanol are also shown by broken lines for the comparison. Pinacyanol reveals absolutely corresponding absorption bands in both media, where every band in the sheet only shifts more or less to the longer side ($200\sim300 \text{ cm}^{-1}$) compared with that in ethanol.

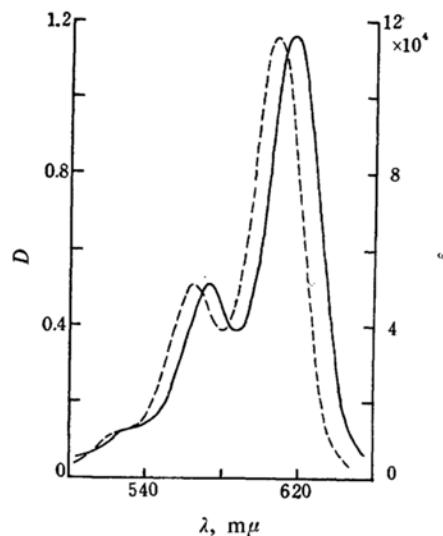


Fig. 2. Absorption spectra both in visible region of pinacyanol in the non-stretched ($R_s=1.0$) PVA sheet (solid line) and in an ethanolic solution of $2.79 \times 10^{-5} \text{ mol./kg.}$ (broken line).

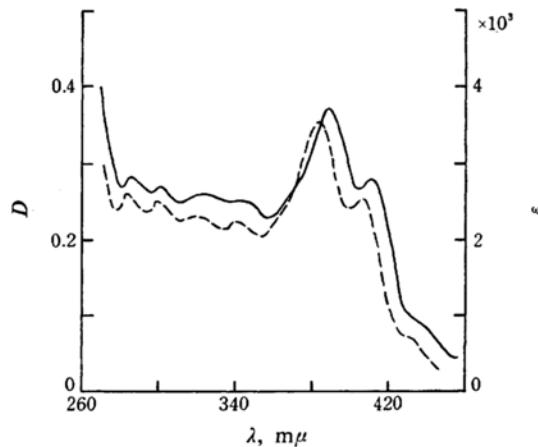


Fig. 3. Absorption spectra both in the near ultraviolet region of pinacyanol in the non-stretched ($R_s=1.0$) PVA sheet (solid line) and in ethanolic solution of $2.79 \times 10^{-5} \text{ mol./kg.}$ (broken line).

Curves indicated in Figs. 4 and 5 corresponding to respective ones of Figs. 2 and 3 are obtained by stretching the sheet and then observing it with polarized light. None of the bands in Fig. 4 nor those around $400 \text{ m}\mu$ in Fig. 5 have any change either in shape or in maximum position, with the change of angle θ , and they have the same order of the optical density ratio R_d , with a considerably large value compared with the rest of the bands.

The rest, on the other hand, change in shape and maximum position, together with θ . The behavior with θ of the absorption curves near

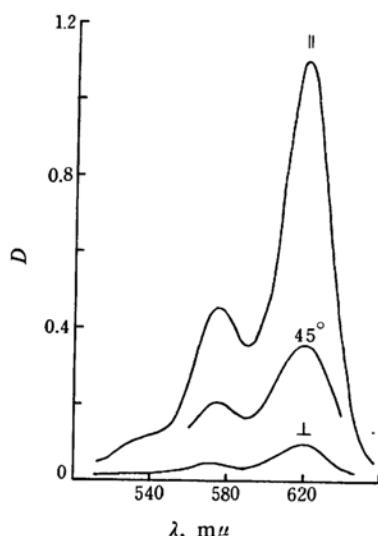


Fig. 4. Dichroism of pinacyanol in the stretched sheet at $R_s=8.2$, corresponding to Fig. 2. The sheet reflection is already corrected. \parallel , 45° and \perp mean the absorptions for the polarized light of which the direction of the electric vector is parallel, 45° and right angles to the stretch direction of the sheet, respectively.

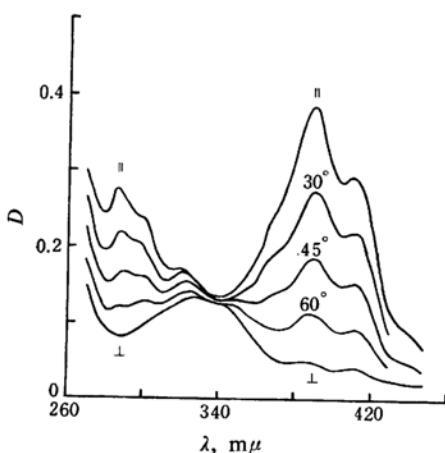


Fig. 5. Dichroism of pinacyanol in the stretched sheet at $R_s=8.0$, corresponding to Fig. 3. Corrected as for the absorption and reflection of the sheet. \parallel , 30° , 45° , etc. have the same meaning as these in Fig. 4.

340 m μ is especially noticeable in the point that the absorption intensity has no great change with θ .

Expansion of observation from the first bands to the long wavelength found out a weak but single band at 700 m μ . This is as shown in Fig. 6 and has similar behavior as other visible bands. Moreover, there were noticed weak absorptions at about 470 m μ and at 440 m μ ,

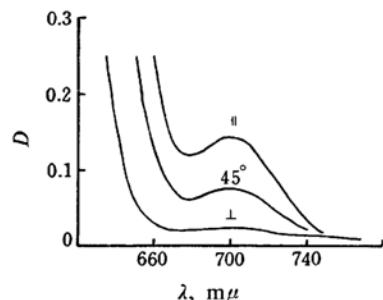


Fig. 6. Dichroism of the pinacyanol weak band at 700 m μ . $R_s=11$.

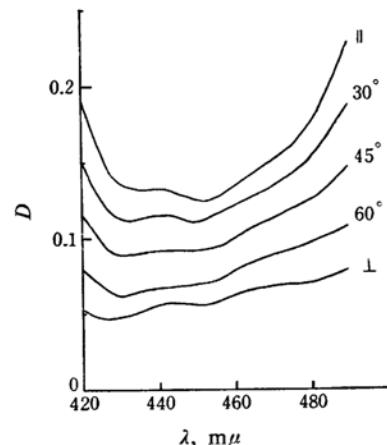


Fig. 7. Dichroism of the Pinacyanol weak band at about 470 m μ and at 440 m μ . $R_s=6.0$.

but their properties could not be judged owing to the nearby strong absorptions (Fig. 7).

The polarization degree of the polaroid used decreases in short region of 300 m μ and follows a curve as shown in Fig. 8. That is to say, the incident light in this region is a partially polarized light. Absorption spectra by this light are indicated by solid lines in Fig. 8. Curves in this figure show an obvious absorption band at 240 m μ and a shoulder at 260 m μ . The absorption at 240 m μ becomes more indistinct as it moves from D_{\parallel} to D_{\perp} curve, and that of 260 m μ stands just on the reverse.

All the absorption bands that could be recognized by the measurement are summarized in Table I, being numbered in order from high to low wavelength. These bands in Table I were distinguished by their shape in this way as follows. The number, wavelength and wavenumber of a band have no mark when it indicated a distinct maximum at least in one of D_{\parallel} and D_{\perp} (in general D_{θ}) curve, are put in parentheses when it indicated distinct shoulder, and are put in brackets when it showed indistinct shoulder or curvature.

Experimental relations between each R_d and

TABLE I. *r*-VALUES, DIRECTIONS AND CLASSIFICATION OF THE ABSORPTION BANDS OF PINACYANOL RECOGNIZED IN THE PVA SHEET BY DICHROIC MEASUREMENTS

Band No.	λ m μ	ν cm $^{-1}$	<i>r</i> -Value	Angle	Direction	Classification
I	700	14280			longi.	
II	620	16120	2.60~2.00	21.0~26.5	longi.	
III	575	17380	2.60~2.00	21.0~26.5	longi.	First group
(IV)	(530)	(18860)			longi.	(strong)
[V]	[470]	[21270]			longi. ?	
(VI)	(440)	(22710)			longi.	Second group
VII	410	24380	2.60~2.00	21.0~26.5	longi.	(weak)
VIII	388	25760	2.60~2.00	21.0~26.5	longi.	
[IX]	[365]	[27400]			longi. ?	
(X)	(345)	(29000)	0.75	53.1	\perp	
XI	328	30500	0.85	49.6	\perp	
(XII)	(300)	(33300)	1.15	41.0	\parallel	Third group
XIII	286	35000	1.30	37.6	\parallel	(weak)
(XIV)	(275)	(38900)			\perp	
XV	240	41650			\parallel	
[XVI]	[230]	[43500]			\perp	

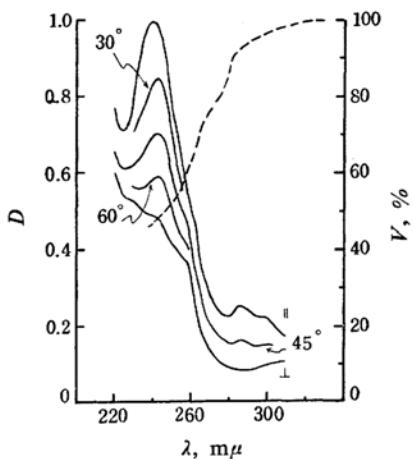


Fig. 8. Dichroism in the ultraviolet region of pinacyanol at $R_s=5.4$. The broken line represents the polarization degree of the polaroid used. Taken from Y. Tanizaki, This Bulletin, 30, 935 (1957).

R_s of Bands II, III, VII, VIII and X—XIII are shown in Fig. 9. Curves in the figure are theoretical ones corresponding to respective *r*-values^{1),*2). Observed values of each Band II, III, VII and VIII approximately fall between these curves which have peculiar *r*-values. Angles between transition directions and an orientation axis of the molecule are evaluated from the *r*-values and indicated in Table I.}

Assignment of Transition Direction.—As shown in Figs. 2—8, all the absorption bands in visible region and around 400 m μ had so large R_d values that they were distinguished

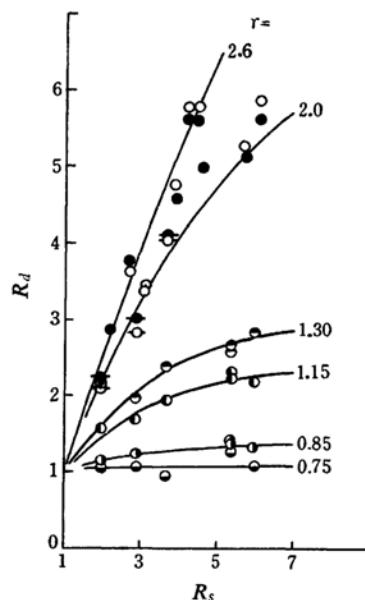


Fig. 9. Relations of R_d to R_s of absorption bands. Circles represent the observed values; \circ : 620 m μ (Band II), \bullet : 570 m μ (III), $-o-$: 410 m μ (VII), $-\bullet-$: 388 m μ (VIII), \odot : 286 m μ (XIII), \bullet : 344 m μ (X), \bullet : 300 m μ (XII), \bullet : 328 m μ (XI). Curves are the calculated ones for respective *r*-value from the R_d expression of Ref. 1.

from others. It is considered that the double bond system which runs through over the molecular axis responsible for the first band of cyanines of this kind (here Band II)⁴⁾. If

*2 Cot⁻¹*r* gives the angle between the direction of orientation and that of transition of the absorption.

4) For example, H. Kuhn, *J. Chem. Phys.*, 17, 1198 (1949); G. S. Levinson, W. T. Simpson and W. Curtis, *J. Am. Chem. Soc.*, 79, 4314 (1957).

this is the case, it must be expected that such an absorption band gives the maximum R_d when the longitudinal axis of the molecule meets the stretching direction of the sheet. In effects, the fact that the R_d -value of the first band is always larger than that of any band in the region below 360 m μ , means that this molecular axis approaches most completely its orientation axis. Accordingly, it is concluded that a group of bands, of which r -values fall between 2.0~2.6, as indicated in Fig. 9, is all due to transitions parallel to the long axis of molecule.

When two transition directions are at right angles to each other in a molecule, a product of these r -values must be unity. Namely,

$$r_{\parallel} \times r_{\perp} = 1 \quad (1)$$

According to Table I, the following two pairs are approximately unity*³.

$$r_x \times r_{XIII} = 0.975 \quad (2)$$

$$r_{XI} \times r_{XII} = 0.978 \quad (3)$$

Moreover, Table I indicates $r_x < r_{XI}$ and $r_{XIII} > r_{XII}$. If they lie in a common absorption plane¹⁰ (made of an orientation axis and a transition direction) and if Relation 1 is held, relations $r_{\perp} = r_x = r_{XI}$ and $r_{\parallel} = r_{XIII} = r_{XII}$ must be kept. These disagreements would be due to the following reason. Because there are two bands XI and XII of opposite character existing close to each other, as is clarified in Fig. 5, R_d of Band XI might be elevated by might be elevated by XII, while that of XII might be lowered by XI. For this reason, concerning r -values in this case, r_x and r_{XIII} are believed to be a most reliable r_{\perp} and r_{\parallel} respectively. From the above discussion, it may be concluded that the product of each pair of r -values in Relations 2 and 3 is in fact unity and therefore satisfies Relation 1 in itself, and that the relations $r_{\perp} = r_x = r_{XI}$ and $r_{\parallel} = r_{XII} = r_{XIII}$ should come into existence.

If Bands XV (240 m μ) and XIV (260 m μ) in Fig. 8 were measured by perfect polarized light*⁴, R_d for XV would perhaps be found to be larger and for XIV smaller. Consequently, it can be expected that r -values for these bands approach r_{XIII} and r_x , respectively. In this case, therefore, r_{XV} presumably corresponds to

*³ In fact, however, these products are slightly smaller than unity. This may be interpreted by the following reason. From the polarization degree curve in Fig. 8, it is noticed that Bands XIII and XII were observed by the light of 93% and 97% polarization respectively. In this case, therefore, R_d becomes smaller than when observed by 100% polarization light, and r -value might be estimated to be exceedingly small.

*⁴ From Fig. 8, it is estimated, $R_d(XV)=2.0$ and $R_d(XIV)=1.5$ at $R_s=5.4$. As for r -values, $r_{XV}=1.1$ and $r_{XIV}=0.9$, and the former is smaller than 1.3 of r_{XIII} and latter is larger than 0.75 of r_x . But the product is again approximately unity.

r_{\parallel} and r_{XIV} to r_{\perp} . Moreover, the weak band XVI (230 m μ) is not thought of conclusively.

According to the above discussion, the absorptions of Pinacyanol will be distinguished into the following three groups. One of these groups is such that the transition direction runs along the molecular axis. And to this groups Bands I~IX belong, although it is not certain regarding Bands V and IX. The other two groups contain the bands of which any two transition directions taken from each group separately are orthogonal. Let us decide to make " \parallel " represent those near to the molecular axis and make " \perp " represent the others; then Bands XII, XIII and XV become " \parallel " and X, XI, XIV and XVI become " \perp ".

The transition direction assigned above was based on an analysis of the observed R_d ~ R_s relation. However, when we compare again the dichroic behavior of the band in the curves of Figs. 4~8 with their transition directions indicated in Table I, we see that the direction can well be decided only by an inspection of the dichroic behavior without the help of the R_d ~ R_s relation: for instance, absorption bands which have the maximum R_d for the same R_s in the whole region with no change in shape and in λ_{\max} can be decided as " longi. " (bands shown in Fig. 2 and around 400 m μ in Fig. 3). Others in general change in their shape of absorption and in λ_{\max} for D_d : this fact suggests the superposition of absorptions with different directions. R_d -values of these bands are so small as to be easily distinguished from " longi. ". This absorption group is considered to be formed of $\parallel \perp$ absorptions. Accordingly, of these absorptions the ones with the larger R_d may be decided as \parallel and the others with the smaller R_d as \perp .

Discussion

It is evident from Figs. 2 and 3 that pinacyanol shows the identical absorption both in PVA sheet and in ethanol. Therefore, the following discussion on the light absorption in PVA sheet may be thought to apply to that in ethanol.

In the last section, the absorption bands have been classified only from the standpoint of their transition directions. Now, turning attention to the absorption position and intensity, we can roughly divide them again into four groups (Table I and Figs. 2~8): the first group includes Bands I~IV, the second group Bands V*⁵~IX, the third group Bands X~XIII,

*⁵ According to the apparent shape of the curve in Fig. 7, it seems plausible that Band V belongs to the 1st group. But, from the standpoint of band distance, as will be seen later, it will reasonably be put into the 2nd group.

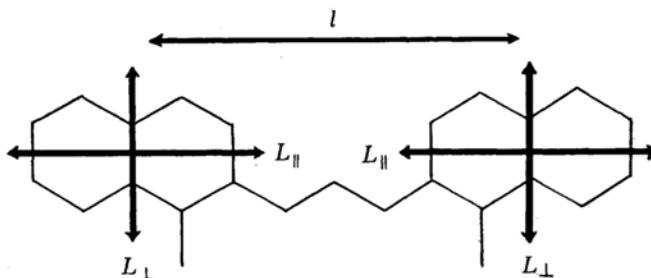


Fig. 10. The molecular skeleton of pinacyanol.

and the fourth groups Band XIV—XVI.

As already mentioned, the absorptions of the first and the second group lie on the long axis of the molecule. Accordingly, if the molecular skeleton of Pinacyanol cation is just as shown in Fig. 10, the direction of these absorptions may correspond to *l*-direction of the figure. And again as mentioned, the \parallel and the \perp transition are normal to each other in the same plane. This is visually understood from the fact that the sum of angles between the transition direction and orientation axis in Table I, for example, Band X(\perp) and XIII(\parallel), is approximately 90 degrees. Thus, it may conclusively be said that the \parallel and the \perp transition coincide with the long and the short axis of the quinoline nucleus, respectively.

The absorption bands of the 3rd and the 4th groups, therefore, are attributed to the localized π electron system in the quinoline nuclei: those of the 3rd group would be derived, for example, from the weak 320 and 310 m μ absorption of 2-methyl-*N*-ethyl-quinolinium cation, and those of the 4th group from the strong 240 and 220 m μ absorption.

Now, if the molecule is planar in the shape of Fig. 10, the direction of the long axis (L_{\parallel}) of quinoline nucleus and *l*-direction become parallel, hence these two directions must take any identical angle toward the orientation axis of the molecule. Table I actually shows, however, rather great difference between the two angles^{*6}. This means that two quinolines are to a large extent off the common plane^{*7}.

Absorptions of the 1st and the 2nd group

*6 Namely, if two absorption planes of "longi", and "||" (Band XIII) were coincident, the angle between these transitions would be about 64 degrees. The difference is about 14 degrees, indicating that the molecule is almost planar. That this is not correct would be shown by constructing the structural model corresponding to Fig. 10. Besides, the assumption that the absorption planes coincide with each other has no grounds.

*7 Concerning the double bond character, this is not inconsistent with the concept of the usual planar molecule. Because, if the rotation of quinoline planes is equally shared by the polymethine bonds (here 4 bonds) the double bond character of each bond will be roughly lowered only by about 10 percent of that in case of planar, even though the inclined angle of the planes is 80 degrees.

apparently resemble each other in shape (cf. Figs. 2 and 3). Further, the fact that the latter is weaker than the former in intensity and that their directions are the same suggests that the 2nd group corresponds to an overtone of the 1st group. In this connection, the following fact is of interest: the distances of the adjacent bands in the 1st group are $1500 \pm 300 \text{ cm}^{-1}$ and those in the 2nd group are also $1500 \pm 200 \text{ cm}^{-1}$, indicating a constant space of band-distribution. It is from the standpoint of band distance that we have put Band V into the 2nd group, in the above group classification.

As is already well known, the first group absorption is very sensitive to the solvent nature^{5,6)}. A correspondence of complexes of monomer, dimer, etc. with absorptions were attempted⁶⁾, with the help of the fact that the pinacyanol cation is easily aggregated. At the present stage, however, it can not be decided whether respective absorption bands correspond to those intrinsic to respective complexes possibly considered, e. g. such new absorptions as revealed by a Davidov splitting⁷⁾, or transitions originally existing are intensified by coupling with vibration⁸⁾ on some account involving complex formation.

Summary

1. Dichroism of pinacyanol iodide in the PVA sheet was observed in the region higher than 220 m μ , and at least sixteen absorption bands were recognized.

2. The relation of R_d to R_s was analyzed concerning some absorption bands, and it was verified that there are two groups of transitions,

5) I. M. Klotz, *Chem. Revs.*, 41, 382 (1947); S. E. Sheppard and A. L. Geddes, *J. Chem. Phys.*, 13, 63 (1945).

6) R. C. Merrill and R. W. Spencer, *J. Am. Chem. Soc.*, 72, 2894 (1950).

7) For instance, J. W. Weigl, *J. Chem. Phys.*, 24, 364 (1956).

8) S. E. Sheppard and G. R. Brigham, *J. Am. Chem. Soc.*, 66, 380 (1944); S. E. Sheppard and A. L. Geddes, *ibid.*, 66, 2003 (1944).

one existing along the long axis of the molecule, the other being at right angles to one another in geometry.

3. The absorption group at right angles to one another appears in the shorter wavelength region than about $340\text{ m}\mu$, and it was shown that this is due to the two orthogonal electronic transitions localized in the quinoline nuclei of the molecule.

4. The absorptions of the long axis of the pinacyanol molecule consist of two groups, each involving several bands and it was pointed out that the bands are distributed with nearly constant distance of 1500 cm^{-1} between adjacent one.

5. It was deduced that the molecule is not a planar and both quinoline planes are far from planar.

6. Sixteen absorptions mentioned above were reasonably classified in their relation to the transition direction or in their correspondence to the molecular structure.

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