Dichroism of Dyes in the Stretched PVA Sheet. IV.[1] *Absorption Spectra of Carbocyanines and Note on the Chemical Structures**

By Yoshié TANIZAKI and Hisataké ONO

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In the previous paper[1], the dichroic behavior of Pinacyanol in the stretched polyvinylalcohol (PVA) sheet was discussed in detail. It was pointed out that the directions of absorptions, which were judged by an inspection of the dichroic curves observed at a high stretch ratio, are in agreement with those obtained from a quantitative analysis of the relation between the density ratio R_d and the stretch ratio R_s[1].

The purpose of this paper is to analyze the dichroism of carbocyanines by this method of inspection, to confirm the fact that the result thus obtained can be explained consistently by the conclusion derived from Pinacyanol[1], and to add some new information about the visible absorption phenomena after the inclusive discussion on the further experimental facts obtained here.

Experimental

Here were used the following four dyes, which were prepared by the known methods:

1, 1′-Diethyl-2, 2′-cyanine iodide, — m. p. 274°C (277°C in literature[2]). Found: C, 59.92; H, 5.04; N, 6.32. Calcd. for $C_{23}H_{23}N_2I$: C, 60.79; H, 5.07; N, 6.18%.

1, 1′-Diethyl-2, 2′-dicarbocyanine iodide, — m. p. 268~9°C (270°C in literature[4]).

1, 1′-Diethyl-2, 2′-tricarbocyanine iodide, — m. p. 222~3°C (225°C in literature[4]). Found: C, 61.30; H, 5.75; N, 4.80. Calcd. for $C_{29}H_{29}N_2I\cdot 2H_2O$: C, 61.30; H, 5.81; N, 4.93%.

1, 1′-Diethyl-4, 4′-cyanine iodide, — m. p. 282°C (271~3°C in literature[5]). Found: C, 60.96; H, 5.35; N, 6.37. Calcd. for $C_{23}H_{23}N_2I$: C, 60.79; H, 5.07; N, 6.18%.

Let us use the notations, $j=0(2,2')$, $j=2(2,2')$, $j=3(2,2')$ and $j=0(4,4')$, for the respective dyes described above. At the same time, the Pinacyanol used in the previous paper[1] will be denoted by $j=1(2,2')$.

The preparation of the sample sheet, the measurement, etc. followed the manner reported before[1,6]. Here, the dyeing bath of the dye which failed to dissolve in water at the necessary concentration was prepared by adding a calculated amount of water to the hot ethanol solution of the dye concentrated as much as possible.

Results

Let us number the absorption bands of each dye in the order of wavelength, for the convenience of the following description (see figures and tables).

Figs. 1 and 2 show, the interpretation of the dichroism of $j=0(4,4')$ in the near ultraviolet and in the visible regions, respectively. In Fig. 1, it is seen as a distinctive feature that the $D_{\parallel}$ and $D_{\perp}$ curves cross in the neighborhood of Band VII, that $D_{\perp}$ of Band VIII is apparently higher than $D_{\parallel}$, and that D_{θ} of Band V does not change much with increasing θ.

Figs. 3 and 4 indicate the dichroism of $j=0$ (2, 2′) in the ultraviolet and visible regions respectively. Their special feature is that $\lambda_{\max}$'s in the region longer than 300 mμ are

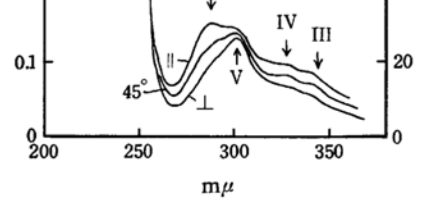

Fig. 1. The dichroism of 1, 1′-diethyl-4, 4′-cyanine iodide, $j=0(4,4')$, in the stretched PVA sheet. $R_s=5.7$. The broken line indicates the polarization degree curve of the polaroid used, taken from Y. Tanizaki, This Bulletin, **30**, 935 (1957).

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* Presented at the Electronic Structure, Symposium, Tokyo, Sep. 1959.

[1] Part III of this series, Y. Tanizaki, This Bulletin, **33**, 979 (1960).

[2] F. M. Hamer, *J. Chem. Soc.*, **1928**, 208.

[3] F. Kimura, F. Homma and F. Kobayashi, *Japan*, **228**, 529 (1957).

[4] T. Ogata and T. Shiozaki, *Bull. Iust. Phys. Chem. Res.* (*Tokyo*), **13**, 511 (1934).

[5] T. Ogata and S. Sakurai, *Bull. Inst. Phys. Chem. Res.* (*Tokyo*), **3**, 77 (1924).

[6] Y. Tanizaki, This Bulletin, **32**, 75 (1959); Y. Tanizaki and N. Ando, *J. Chem. Soc. Japan, Pure Chem. Sec.* (*Nippon Kagaku Zasshi*), **78**, 542 (1957).

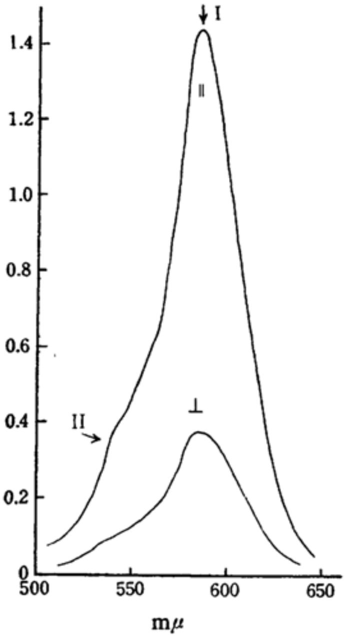


Fig. 2. The dichroism of 1, 1'-diethyl-4, 4'-cyanine iodide, $j=0(4,4')$, in the stretched PVA sheet. $R_s=10$.

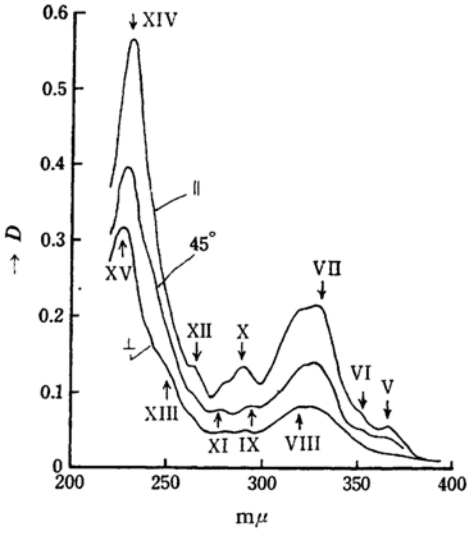


Fig. 3. The dichroism of 1, 1'-diethyl-2, 2'-cyanine iodide, $j=0(2,2')$, $R_s=9.0$.

almost independent of θ**, while those in the region thereunder show an apparent change. It is also an interesting fact that the shapes of absorption bands in the visible and 300~400 mμ regions resemble each other considerably (see Figs. 3 and 4), though not so closely as in the case of Pinacyanol, $j=1(2,2')$[1].

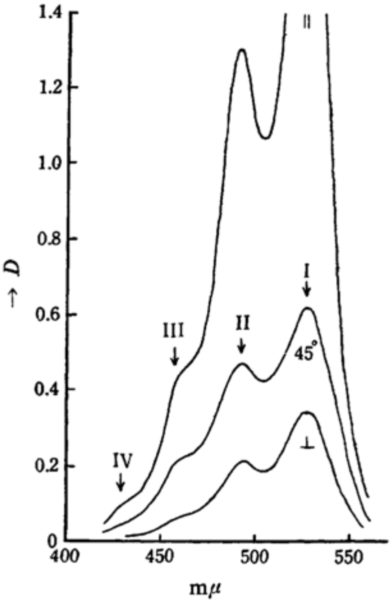


Fig. 4. The dichroism of 1, 1'-diethyl-2, 2'-cyanine iodide, $j=0(2,2')$, $R_s=9.0$.

Figs. 5 and 6 show the dichroism of $j=2$ $(2,2')$ at 220~500 mμ and 500~850 mμ, respectively. In this case, too, λ_{max}'s as above 400 mμ show little change with θ**, while those below 400 mμ show a clear change.

Figs. 7 and 8 show the dichroism of $j=3$ $(2,2')$. Here is found the important fact that λ_{max}'s of D_θ in Fig. 8, which shows the absorptions supposedly along the long axis of the molecule[1], apparently shift with θ. Similar behavior was also recognized in the case of $j=0$ (Fig. 4) and $j=2$ (Fig. 6), though very slightly. Band II (493 mμ) in Fig. 4, for example, shows a slight shift in λ_{max} towards shorter wavelengths with a change from $D_\perp$ to $D_\parallel$ curve. Such a tendency may be due principally to the following fact: small directional differences originally existing between the absorptions along the molecular axis come to be appreciable owing to a sharpening in the

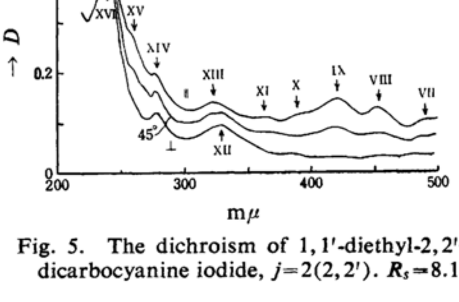


Fig. 5. The dichroism of 1, 1'-diethyl-2, 2'-dicarbocyanine iodide, $j=2(2,2')$. $R_s=8.1$.

** A detailed inspection revealed a slight shift of λ_{max} with θ in the visible region. This we will discuss later.

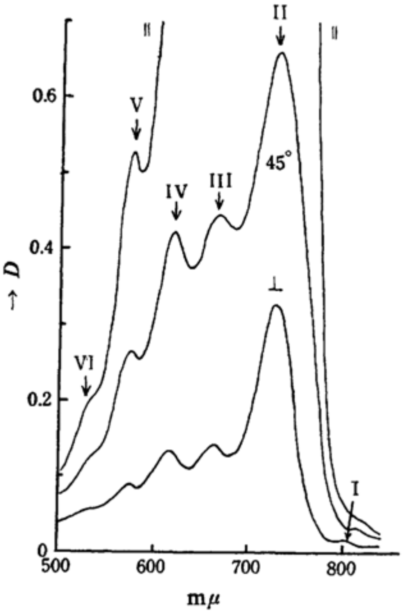


Fig. 6. The dichroism of 1, 1′-diethyl-2, 2′-dicarbocyanine iodide, $j=2(2,2')$. $R_s=8.1$.

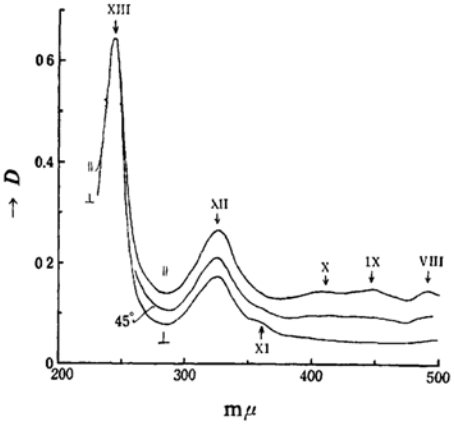


Fig. 7. The dichroism of 1, 1′-diethyl-2, 2′-tricarbocyanine iodide, $j=3(2,2')$. $R_s=6.1$.

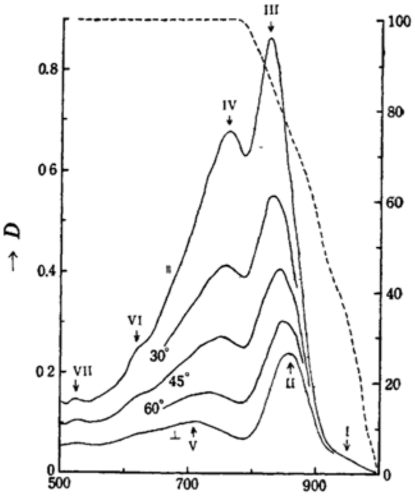


Fig. 8. The dichroism of 1, 1′-diethyl-2, 2′-tricarbocyanine iodide, $j=3(2,2')$. $R_s=6.9$. The broken line indicates the polarization degree curve of polaroid used, taken from Y. Tanizaki, This Bulletin, **30**, 935 (1957).

TABLE I. THE ABSORPTION BANDS OF 1, 1′-DIETHYL-4, 4′-CYANINE IODIDE, $j=0(4,4')$, IN THE STRETCHED PVA SHEET

Band No.	λ mμ	ν cm^{-1}	$\Delta\nu$ cm^{-1}	Direction	Group	$\widetilde{\Delta\nu}$ cm^{-1}
I	585	17100	1480	l	1st	1480
II	538	18580	10640	l		
III	342	29220	1440	?	2nd	1440
IV	326	30660	2540	?		
V	301	33200	1500	$\perp (L_{\parallel})$	3rd	
VI	288	34700	4980	$\parallel (L_{\perp})$		
VII	252	39680	1620	$\parallel ?(L_{\perp}?)$	4th	
VIII	242	41300		$\perp (L_{\parallel})$		

Note: $\Delta\nu$ and $\widetilde{\Delta\nu}$ indicate the distance between the adjacent bands and the mean of the band distance among the group, respectively. The notation "l" means the longitudinal direction of the molecule, and "∥" or "⊥" means the direction more parallel or more normal to the l-direction, respectively, among transitions in the quinoline parts. In this table, ∥ corresponds to $L_{\perp}$, the short axis of the quinoline nucleus, and ⊥ to $L_{\parallel}$. In the following tables, ∥ corresponds to $L_{\parallel}$ and ⊥ to $L_{\perp}$.

distribution for the direction of the statistic orientation axis attendant on the molecule with the increase of its length. On the other hand, the directional properties of the short wavelength absorptions show a tendency to become indistinct with the increase of j. They are most indistinct in the case of $j=3$. It should be noticed that even the absorptions below 350 mμ have no change in $\lambda_{\max}$ with θ. Moreover, $D_{\parallel}$ and $D_{\perp}$ of Band XIII coincide with each other (Fig. 7), with the incident light of 50% polarization in this region (cf. Fig. 1).

Tables I—V involve the transition directions, the classification of band-groups, etc., as in the previous paper¹⁾, judged from the data mentioned above. Here, table III shows again the data of Pinacyanol obtained previously¹⁾. Band-groups in tables have the following meaning: the absorptions in the first and the second group are both due to the transitions along the long axis of the molecule, and the absorption intensities of the second group are considerably

TABLE II. THE ABSORPTION BANDS OF 1,1'-DIETHYL-2,2'-CYANINE IODIDE IN THE STRETCHED PVA SHEET

Band No.	λ mμ	ν cm^{-1}	$\Delta\nu$ cm^{-1}	Direction	Group	$\widetilde{\Delta\nu}$ cm^{-1}
I	527	18960	1320	*l*	1st	1450 ±150
II	493	20280	1600	*l*		
III	457	21880	1380	*l*		
IV	430	23260	4040	*l*		
V	366	27300	1180	*l*	2nd	1050 ±100
VI	351	28480	950	*l*		
VII	330	30300	950	?		
VIII	320	31250	2650	?		
IX	295	33900	500	?	3rd	
X	290	34480	1470	∥		
XI	278	35950	1630	⊥?		
XII	266	37580	2240	∥		
XIII	251	39820	3280	⊥	4th	
XIV	232	43100	950	∥		
XV	227	44050		⊥		

Note: See the note of Table I.

TABLE III. THE ABSORPTION BANDS OF 1,1'-IODIDE DIETHYL- 2,2'-CARBOCYANINE IN THE STRETCHED PVA SHEET

Band No.	λ mμ	ν cm^{-1}	$\Delta\nu$ cm^{-1}	Direction	Group	$\widetilde{\Delta\nu}$ cm^{-1}
I	700	14280	1840	*l*	1st	1500 ±300
II	620	16120	1260	*l*		
III	575	17380	1480	*l*		
IV	530	18860	2410	*l*		
V	470	21270	1440	*l*?	2nd	1500 ±200
VI	440	22710	1670	*l*		
VII	410	24380	1380	*l*		
VIII	388	25760	1640	*l*		
IX	365	27400	1600	*l*?		
X	345	29000	1500	⊥	3rd	
XI	328	30500	2800	⊥		
XII	300	33300	1700	∥		
XIII	286	35000	3900	∥		
XIV	257	38900	2750	⊥	4th	
XV	240	41650	1850	∥		
XVI	230	43500		⊥		

Note: See the note of Table I. Cited from Ref. 1.

weak compared with those of the first one. There is a clear boundary between these two groups, as seen in their band distances, e. g. the separation of Bands IV and V in Table II is 4040 cm^{-1}. Consequently the first and the second groups can be distinguished from each other. The third and the fourth groups consist of the ∥ ⊥ character-absorptions. The third group bands are weak and the fourth strong.

According to the polarization degree curve indicated in Fig. 8, the polarization degree of incident light begins to fall precipitously at about 800 mμ, becomes about 50% at 900 mμ,

TABLE IV. THE ABSORPTION BANDS OF 1,1'-DIETHYL-2,2'-DICARBOCYANINE IODIDE IN THE STRETCHED PVA SHEET

Band No.	λ mμ	ν cm^{-1}	$\Delta\nu$ cm^{-1}	Direction	Group	$\widetilde{\Delta\nu}$ cm^{-1}
I	804	12440	1400	*l*	1st	1300 ±200
II	725	13790	1240	*l*		
III	665	15030	1090	*l*		
IV	620	16120	1270	*l*		
V	575	17390	1470	*l*		
VI	530	18860	1340	*l*?		
VII	495	20200	1880	*l*?		
VIII	453	22080	1720	*l*	2nd	1800 ±100
IX	420	23800	1980	*l*		
X	388	25780	1820	?		
XI	362	27600	2880	?		
XII	328	30480	570	⊥	3rd	
XIII	322	31050	3900	∥		
XIV	278	35950	2480	⊥?	4th	
XV	260	38430	3390	∥		
XVI	239	41820	900	⊥		
XVII	234	42720		∥		

Note: See the note of Table I.

TABLE V. THE ABSORPTION BANDS OF 1,1'-DIETHYL-2,2'-TRICARBOCYANINE IODIDE IN THE STRETCHED PVA SHEET

Band No.	λ mμ	ν cm^{-1}	$\Delta\nu$ cm^{-1}	Direction	Group	$\widetilde{\Delta\nu}$ cm^{-1}
I	950	10520	1110	*l*	1st	ca. 1000
II	860	11630	530	*l*		
III	825	12120	980	*l*		
IV	763	13100	980	*l*		
V	710	14080	2050	*l*		
VI	620	16130	2830	*l*	2nd	ca. 2400
VII	527	18960	2150	*l*		
VIII	492	20320	2150	*l*		
IX	445	22470	1330	*l*?		
X	420	23800	3810	∥	3rd	
XI	362	27610	3150	⊥		
XII	325	30760	10370	∥		
XIII	243	41130		⊥	4th	

Note: See the note of Table I.

TABLE VI. AVERAGE WAVENUMBER OF THE ABSORPTION BANDS IN THE FIRST AND THE SECOND GROUP, DIFFERENCE AND RATIO

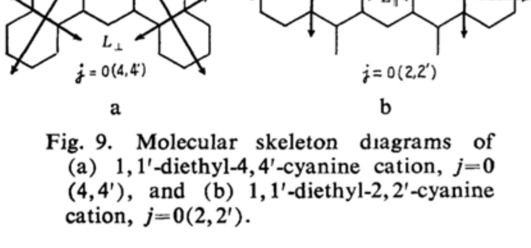
Dyes	$\tilde{\nu}$ cm^{-1} 1st group	$\tilde{\nu}$ cm^{-1} 2nd group	$\Delta\tilde{\nu}$ cm^{-1}	Ratio (2nd/1st)
$j=0$ (4,4′)	17840	29940	12100	1.68
$j=0$ (2,2′)	21100	29330	8230	1.39
$j=1$ (〃)	16660	24300	7640	1.46
$j=2$ (〃)	16260	24820	8560	1.53
$j=3$ (〃)	12290	19470	7180	1.58

and then vanishes at 1000 mμ. For this reason, it will be expected that when the absorption of 860 mμ (Band II) in Fig. 8, $j=3(2,2')$, is measured with the perfect polarized light, the band maximum will be shifted towards the longer wavelength side. Consequently, the distance between Bands I and II in Table V becomes smaller, while the distance between Bands II and III becomes greater. As a result, it will be expected that the two band distances approach the mean value of the first group in Table V.

Table VI includes the mean wave numbers of the absorption bands in the first and the second group, the difference and the ratio between these wavenumbers having been derived from Tables I—V. The ratio is approximately constant at about 1.5, except for the case of $j=0$ (4,4′) dye.

Discussion

Absorptions in the Short Wavelength Region.— It has already been clarified from a detailed analysis of Pinacyanol that the absorption bands in the third and the fourth group are originated from the electronic transitions, in two directions at right angles, localized in the quinoline nucleus parts¹⁾. If this is the case with these absorptions, and if both (4,4′) and (2,2′) dye of $j=0$ have the planar structures indicated in Figs. 9(a) and (b) as respective possible ones, the dichroism similar to Pinacyanol should be expected for the latter rather than for the former. Nevertheless, according to Figs. 1 and 3, the distinct differences in direction among l, $L_{\parallel}$ and $L_{\perp}$ indicated in Fig. 9 are obviously recognized in (4,4′) but not in (2,2′) dye. This may be due to the steric hindrance; these molecules ($j=0$), as is well known, can not keep the planar structure. Both quinoline planes are inclined to each other, and this may be contributed mostly by the twisting of the central methine bonds. In Fig. 9(a), therefore, two $L_{\parallel}$ directions through the twisting of the methine bonds approach to being parallel with each other and normal to the l-direction. But the relative directions of $L_{\perp}$ are not altered by the twisting just mentioned. On the other hand, in Fig. 9(b), the twisting of methine bonds makes two $L_{\parallel}$'s and two $L_{\perp}$'s oblique to each other, respectively, and it may possibly occur that their oblique angles against l-direction become the same in their degree. Owing to this situation, (4,4′) dye might reveal such dichroic behavior as that shown in for Fig. 1: instance the 288 mμ band (VI) has the similar tendency as the absorptions parallel with l-direction (Fig. 2), and the 301 mμ (V) and the 242 mμ band (VIII) have a tendency to be considered almost normal to l-direction. As for (2,2′) dye (Fig. 9(b)), on the other hand, on account of certain resultant inclinations of $L_{\perp}$ and $L_{\parallel}$ against l-direction produced by steric hindrance, it has the dichroism indistinctive in ∥ ⊥ character as shown in Fig. 3. In contrast with this, in case of $j=1(2,2')$ (Pinacyanol) in which a steric hindrance is considered to be not so great as in $j=0$, the dichroism similar to that in Fig. 1 in appearance was observed with distinct difference in direction among $L_{\parallel}$, $L_{\perp}$ and l. This dichroism was already illustrated in the previous paper¹⁾. Thus, at least concerning $j=0$ dyes, the dichroism is reasonably understood by regarding the third and the fourth group absorptions as being caused by the transition at right angles to one another.



a b

Fig. 9. Molecular skeleton diagrams of (a) 1,1′-diethyl-4,4′-cyanine cation, $j=0$ (4,4′), and (b) 1,1′-diethyl-2,2′-cyanine cation, $j=0(2,2')$.

According to the conventional consideration, the dye molecule becomes more planar with an increase in the number of methine bond, namely j. From this point of view, the ∥ and ⊥ character of absorptions of the third and fourth groups ought to be much more manifest with the increase of j. As for the (2,2′) dyes, however, there is found a tendency to the contrary: the increase of j obscures the ∥ ⊥ character in dichroism. This character is observed typically in the case of Pinacyanol¹⁾ with small j. This fact suggests that the whole strain angle of the molecule in the case of $j>1$ results from the successive summing up of the twisting angle peculiar to one methine bond. That this consideration is correct will also be supported by the discussion in the following section.

Absorptions in the Long Wavelength Region.— It was considered previously that the second group absorptions correspond to an overtone of those of the first group[1]. One of the reasons for such consideration is also found in the dyes used here. That is to say, the second group resembles generally the first group in shape and the former is much weaker in intensity than the latter. Moreover, the ratios of their transition energies lie between 1.4 and 1.7 This fact can be interpreted in quite the same way by *second order absorption* theory on the absorptions with the same direction, proposed by Lewis et al.[7]. For this reason, there seems now no room for doubt that the absorptions of the first group and those of the second group are associated with each other as the first and the second order absorption, respectively.

It is clear from many experimental facts that the absorption phenomena of the first group of Pinacyanol is subject to remarkable change on account of its complex formation[8]. When these absorptions correspond to particular ones of respective complexes, the phenomena could be interpreted by the Davidov splitting. If so, in a case when a band in the first group is split by the formation of a complex, a corresponding absorption band in the second group with the same direction should be split in the same way. The fact that the absorptions of the first and the second group are distributed in respective groups, as shown in the tables, may suggest the very occurrence of the Davidov effect***. According to tables I—V, however, the separation of bands in the first and the second group does not change with the same tendency but with different behaviors with an increase of j (see Fig. 10) : when $j=0$, the band distance in the first group is greater than that in the second, while for $j \geqq 1$ the former becomes smaller and the latter greater with the increase of j. These relations are illustrated in Fig. 10. These obvious phenomena do not seem to be explained simply by the consideration of the Davidov effect. One possible interpretation may be given, as below, taking into account the vibrational states whose contribution might be induced by the complex formation.

Interatomic distances, usually, are lengthened by excitation to the upper state unless the ground state is forced to be strained by a particular steric hindrance. In case the molecule is already hindered in the ground state,

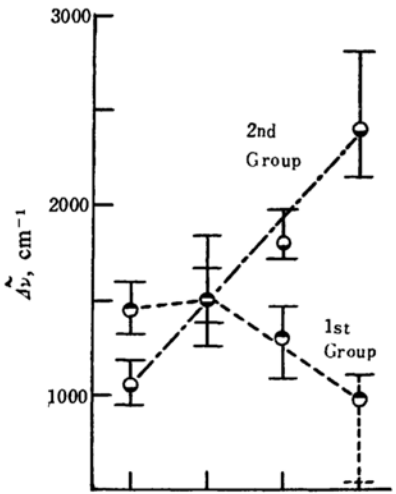


Fig. 10. Relation between $\Delta\tilde{\nu}$ and the number j of the 1st and the 2nd group absorption.

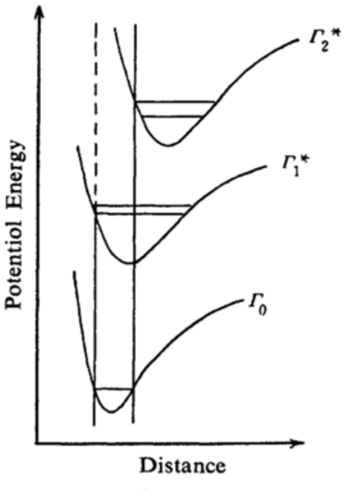


Fig. 11. Schematic potential curves for $j>1$. Γ_0 for the ground state, Γ_1^* and Γ_2^* for the first and the second excited state, respectively. The minimum parts of the respective curves shift to the right hand successively in the order of Γ_0, Γ_1^* and Γ_2^*.

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[7] G. N. Lewis and J. Bigeleisen, *J. Am. Chem. Soc.*, **65**, 2107 (1943).

[8] I. M. Klotz, *Chem. Revs.*, **41**, 373 (1947); H. B. Klevens, *J. Phys. Chem.*, **51**, 1143(1947); R. C. Merrill, R. W. Spencer and R. Getty, *J. Am. Chem. Soc.*, **70**, 2460 (1948); R. C. Merrill and R. W. Spencer, ibid., **70**, 3683 (1948); **72**, 2894 (1950).

*** Davidov splitting of Pinacyanol under a certain condition was found for the electronic transition to the first excited state but not decidedly for the second excited state. In this case the absorption spectrum in acetone was thought to be due to the monomer, though it indicated the α and β bands. See, J. W. Weigl, *J. Chem. Phys.*, **24**, 364 (1956).

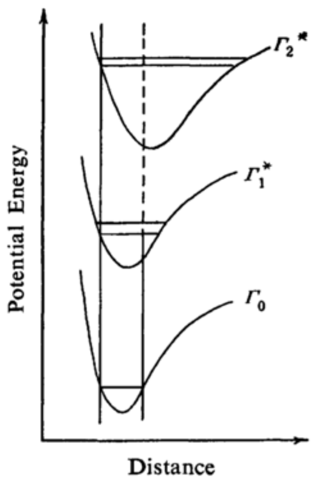

Fig. 12. Schematic potential curves for $j=0$. In this case, the minimum parts of the Γ_0 and Γ_1^* curve do not shift, but only that of the Γ_2^* curve deviates to the right side.

it may happen that the interatomic distances are not changed by excitation. Relative configurations of the potential curves in such cases would be represented schematically by Figs. 11 and 12. Fig. 11 corresponds to $j>1$, and Fig. 12 to $j=0$. In the case of Fig. 11, the minimum positions of the ground state (Γ_0), the first (Γ_1^*) and the second excited state curve (Γ_2^*) may shift towards the right hand, usually in this order. Then, if the configurational relations of Γ_1^* and Γ_2^* to Γ_0 are such as shown in Fig. 11, the band distances of the first group become smaller than those of the second group, for the higher the vibrational states are along the curve the narrower the space between the two adjacent states becomes. On the other hand, in Fig. 12 the band distances of the first group would become greater than those of the second group, if the correlation of Γ_0 and Γ_2^* curves is like that of Γ_0 and Γ_1^* curves in Fig. 11, because there is no shift between the minimum positions of Γ_0 and Γ_1^* curves as presumed above. Thus, we have one plausible interpretation of the experimental facts, according to the above consideration. At the present stage, however, there is no theoretical base for the diagrams in Figs. 11 and 12. Nevertheless, it has an instructive meaning that the phenomena shown in Fig. 10 can be explained qualitatively only by admitting such a possibility as mentioned above for the potential curves of molecules in a complex formed.

It has already been described that the absorption bands of the first group have the tendency to reveal their directional difference in dichroism with an increase of j. This does not seem to agree with conventional consideration that the increase of j makes the molecules approach to planar configurations. The reason is as follows: the better the planarity of the molecule, the better should be the parallelism of any vector in the l-direction, regardless of terminated points on both quinoline planes of a transition vector, on account of the symmetry of the molecule as seen from the structure in Fig. 9(b). That is to say, the larger the number j, the smaller must become the directional difference in dichroism. This is just opposite to the experimental facts. Thus, applying over again the consideration that the peculiar twisting angle per methine bond is added successively with an increase of j as mentioned in the last section, it stands to reason that the angles against l-direction differ in respective absorptions, so far as j is not so large and the terminals of the different transition vectors do not agree with one another; and further taking into account the sharpening of the orientation axis of the molecule, the behavior in dichroism of the first group-bands can be reasonably understood.

Summary

1. Dichroism of the electronic spectra over $220\,\mathrm{m}\mu$ was measured for 1, 1′-diethyl-2, 2′-cyanine, -dicarbocyanine, and -tricarbocyanine iodide, and -4, 4′-cyanine iodide, respectively, in the stretched polyvinylalcohol sheets under the stretch ratio of about $6\sim10$.
2. The correspondence of the transition directions of absorptions and the chemical structures, and the classification of the absorption bands were made into tables.
3. All the dichroic behaviors of the absorption bands could be interpreted by the transitions along the longitudinal axis of the molecule and by those, localized in the quinoline nuclei, of two directions at right angles.
4. It was confirmed that the second group absorptions correspond to the overtone of the first group ones. It was shown by the schematical potential curves that the systematic changes in the band distances in these groups with the variation of the methine bond number may be plausibly explained in connection with the vibrational states.
5. It was pointed out that a reasonable understanding for certain experimental facts in dichroism is given by regarding the molecular structures as follows; 1, 1′-diethyl-2, 2′-cyanine and -4, 4′-cyanine are far from planar because of their particular great steric hindrance, and the other cyanines are strained by the succes-

sive addition of a peculiar twisting angle per methine bond.

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Laboratory of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo (Y. T.)

Research Laboratory
Fuji Film Co., Ltd.
Minami-Ashigaramachi
Kanagawa-Ken (H. O.)