The Spectroscopic properties of Conjugated Systems

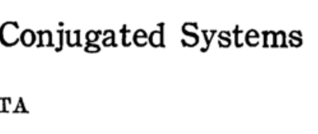
By Kazuo SHIBATA

(Received April 11, 1952)

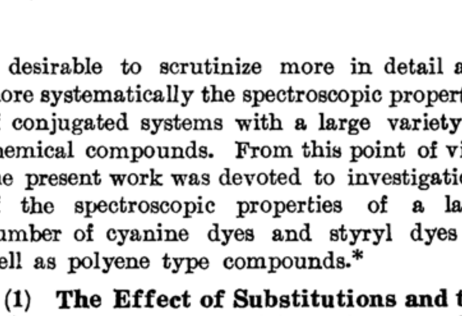
The spectroscopic properties of conjugated systems in organic molecules have already been the subject of repeated investigations, and many efforts have been devoted to finding out the relationship existing between the positions of absorption maxima and the structures of the molecules. Based on the observations made on a large number of cyanine dyes, especially by Hamer(1) and Brooker(2), it has been stated that there exists an approximately linear relationship between the wave length of the absorption maximum and the length of conjugated system, whereas Kuhn and Hausser(3) showed that in the case of other types of conjugated systems such as diphenyl polyenes, the square of the wavelength of absorption maximum is related linearly to the length of conjugated systems.

These relationships, especially the one found for cyanine dyes were interpreted by Lewis and Calvin(4) semi-classically and later by Sklar and Herzfeld(5) and Bayliss(6) quantum mechanically. It should, however, be noticed that the linear relationships in question are not only the approximate ones, but also that there have been found a number of cases that are apparently at variance with them. In order to obtain a coherent understanding of the electronic states of conjugated systems, it is desirable to scrutinize more in detail and more systematically the spectroscopic properties of conjugated systems with a large variety of chemical compounds. From this point of view the present work was devoted to investigations of the spectroscopic properties of a large number of cyanine dyes and styryl dyes as well as polyene type compounds.*

(1) The Effect of Substitutions and the Solvents upon the Position of Absorption Maximum.—Preliminary observations were



(I)



(II)

---

(1) Hamer, *J. Chem. Soc.* 125, 1348 (1924); **1930**, 995 **1936**, 1225; **1932**, 251; **1928**, 206.

(2) Brooker, *J. Am. Chem. Soc.* **57**, 2480, 2488, 2492 (1935); **58**, 659, 662 (1936); **59**, 67, 74 (1937).

(3) Hausser and Kuhn, *Z. Physik. Chem.*, B, **29**, 371, 378, 384, 391, 417 (1935).

(4) Lewis and Calvin, *Chem. Rev.*, **25**, 273 (1939); Branch and Calvin, "The Theory of Organic Chemistry", 1941, p. 155.

(5) Herzfeld and Sklar, *J. Chem. Phys.* **10**, 508, 521 (1942).

(6) Bayliss, *J. Chem. Phys.* **16**, 287 (1948).

* The observations were made by photoelectric measurements, the accuracy of which was about ± 10 A.

The styryl and cyanine dyes used in this work were synthesized in the laboratories of Prof. E. Ochiai and of Dr. T. Ogata, to whom the writer wishes to express his hearty thanks for their kindness in placing the materials at the author's disposal.

made with various derivatives of cryptocyanine (I) and neocyanine (II), using water as the solvent.

As a rule, these cyanine compounds display two absorption bands in the visible region, the one at longer wave length being always stronger than the other. In some cases the existence of the weaker band is more or less obscured by the other. In the following, these two bands are referred to as the "first" (stronger) and the "second" absorption band. To begin with, we shall restrict our consideration only to the first absorption band. The results of our observations are summarized in Table 1 and 2, where λ_1 (in A.) means the wave length of the maximum of the first absorption band. From these data it may be seen that in so far as it concerns alkyl groups, the substitution of R and R′ does not cause any profound difference in λ_1, the maximum difference observed being only a few mμ. Nor does the substitution of the halogen X cause any significant shift of λ_1. Quite the same was true when, instead of water, ethanol was used as the solvent, for which the comprehensive data will be given in the latter part of this paper.

Table 1

Absorption Maxima of Cryptocyanines

R	R′	X	λ_1 in A.
$-CH_3$	$-R$	$-I$	6940
$-C_2H_5$	$-R$	:	6960
:	$-isoC_5H_{11}$	:	6960
:	$-CH_2-CH_2$ $-OAc$	:	6950
$-CH_2-CH_2-\phi$	$-R$	:	7320
$-CH_2-CO-NH_2$	$-R$	:	7220
$-CH_2-COOC_2H_5$	$-R$	$-Cl$	6960

Table 2

Absorption Maxima of Neocyanines

R	X	λ_1 in A.
$-CH_3$	$-I$	7560
$-C_2H_5$	:	7590
$-nC_3H_7$	:	7570
$-isoC_3H_7$	:	7540
$-nC_4H_9$	:	7590
$-isoC_4H_9$	:	7560
$-nC_5H_{11}$	:	7590
$-isoC_5H_{11}$	:	7550
$-CH_2-CH_2-OAc$	:	7580
$-CH_2-CH_2-\phi$	:	7620
$-CH_2-CH_2-O-CH_2-\phi$	:	7610
$-C_2H_5$	:	7590
:	$-Cl$	7520
:	$-SCN$	7520
:	$-NO_2$	7520
:	$-NO_3$	7530
:	$-SO_3-OC_2H_5$	7520
:	$-SO_3-\phi CH_3$	7510

Table 3

The Absorption Maxima of (I) and (II) observed in Various Solvents

Solvents	(I)	(II)
Water	6960	7610
Acetnitrile	7020	—
Acetic anhydride	7040	7720
Acetaldehyde	7045	—
Methanol	7050	7720
Ethyl acetate	7055	7750
Nitromethane	7055	7750
Acetone	7060	7730
Ethylene glycol	7085	—
Ethanol	7090	7760
Formamide	7090	7800
Chloroform	—	7830
Acetyl acetone	7100	—
Isobutanol	7110	—
Amyl acetate	7115	—
Pyridine	7155	8100
Benzyl alcohol	7185	—
Tetra-chloroethylene	7190	7730
Aniline	7205	—
Nitrobenzene	7235	7990

Using the compounds having ethyl group as R and R′ and iodine as X, the effect of solvents upon the value of λ_1 was investigated. The results obtained are summarized in Table 3. From this table it is apparent that λ_1 has the smallest value when water is used as solvent. It should be noticed that the absorption spectra observed in that case were markedly different from those observed in other organic solvents. Moreover, for reasons not yet clear, the light absorption in that case did not obey Beer's law which was found to hold satisfactorily true when ethanol or acetone were used as the solvent. Significant is the fact that ethanol gave the values of λ_1 which coincided within the limit of only ±40 A. with those observed with the following solvents;

Acetic anhydride, Acetaldehyde, Methanol, Ethyl acetate, Nitromethane, Acetone, Ethylene glycol, Formamide and Chloroform.

Based on these findings, the measurements of λ in our further experiments were carried out, using exclusively ethanol as the solvent. In the discussions to be made later, reference will also be made to a number of data reported by other workers, especially those by Brooker⁽²⁾

and Hamer.⑴ All data to be referred to are those obtained by using either ethanol or methanol as the solvent.

(2) The Relationship between λ^2 and the Number of Bonds in the Conjugated Systems of Various Symmetric Cyanine Dyes. — For various kinds of symmetric cyanine dyes, we made the plot of the square of λ_1 against the number of bonds in the conjugated systems, after the precedent of Lewis and Calvin⑷ for the polyene type compounds. In this plot, only those substances having alkyl groups as R or R′ were taken into consideration, and taking into account the fact established in our preliminary experiments, the differences in those alkyl groups as well as in the halogen X were disregarded.

For a series of substances having the same terminal nuclei, a curve bending concavely towards the λ_1^2-axis was obtained, and for another series of symmetric cyanine dyes with different kinds of terminal nuclei, another curve bending also in the same way was obtained. These curves do not generally coincide, but run almost exactly parallel to each other. This is schematically illustrated in Fig. 1, where n′ means the number of bonds between the two terminal nuclei and the curves CGD and EHF are those obtained for

$$\mathrm{A-(CH=CH)_{\mathit{l}}-CH=A} \qquad (\mathrm{III})$$

and

$$\mathrm{B-(CH=CH)_{\mathit{l}}-CH=B} \qquad (\mathrm{IV})$$

respectively. For this rule we shall adduce a large number of concrete examples in later paragraphs. Interesting is the fact that the similar relation also holds for the second absorption band, as will be discussed later.

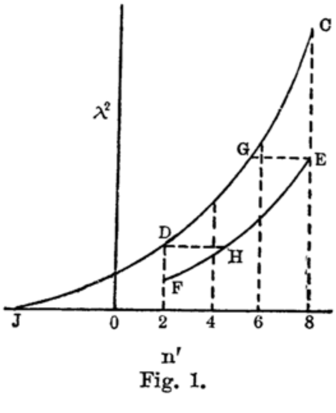


Fig. 1.

(3) The Concept of the "Color Factor" and its Characteristics.—The fact that the curves mentioned above run parallel to each other indicates that the lateral position of each curve is determined by the nature of the terminal nuclei. Let us assume a corresponding curve starting from the origin of the coordinate. Referring to this standard curve, the length JO may be regarded as due to the effect of the two nuclei of A.

In the following this value will be called the "color factor" of the nuclei of A. Color factors found experimentally for various kinds of nuclei are listed in Table 4. About half of the data given in the table are those obtained for polyene type compounds, which will be considered in later discussions.

Of great interest is the fact that in some cases there exists an additivity relation in the values of color factors. The difference between the color factor for a nucleus and that of the corresponding benzo-nucleus was found to be always 0.3. Therefore, the color factor of benzothiazole, for example, can be calculated by adding 0.3 to the color factor of thiazole (1.80).

Extending the concept of the color factor to the whole molecule of a compound, its value can be computed by adding the color factors of nuclei in the molecule and the number of bonds in the conjugated system. For example, the color factor of cryptocyanine is 11.10, because the color factor of quinoline linked at the position 4 is 3.55, and the number of bonds connecting the two quinoline nuclei is 4. We shall designate the color factor of a molecule by n in later discussions.

(4) Empirical Formula for the Standard λ^2-n-curve. — The significance of the color factor of each compound lies in the fact that it enables us to calculate the value of λ_1 with appreciable accuracy. It was found that the following equations fit in well with the standard curves for λ_1 (in $10^3\times$A. unit).

$$\lambda_1^2 = n/(0.36-0.0123\,n) \qquad (1)$$

The curve C_1 in Fig. 2 is drawn according to Eq. (1) by plotting the square of the observed values of λ_1 against n, which in turn was calculated from the values given in Table 4.

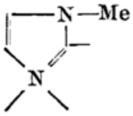
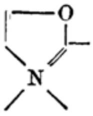
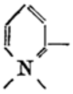
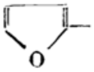
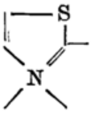
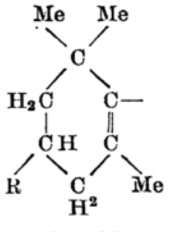
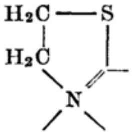
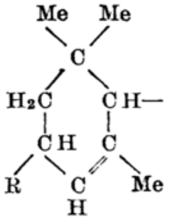
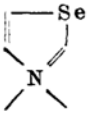
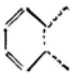
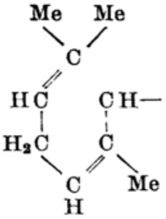
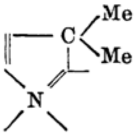
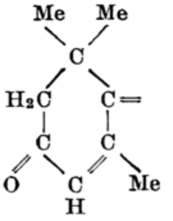
By plotting the square of the observed values of λ_2 against the same values of n, as was done for the first absorption bands, we obtain the standard curve for λ_2. In this case, Eq. (2) of the same form fits in fairly well.

$$\lambda_2^2 = n/(0.40-0.0124\,n) \qquad (2)$$

The curve C_2 in Fig. 2 is drawn according to this equation.

Table 4

The Values of "Color Factors" for Various Nuclei

CH—CH=CH	2.00		0.98	C=O	2.00
	0.98		2.30		4.0
	1.80		3.25		2.0
	0.85		2.35		1.5
	1.85		+0.30		3.5
	1.63		3.00		5.0

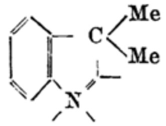
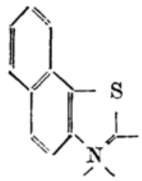
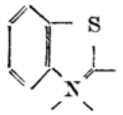
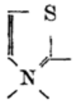
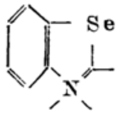
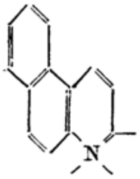
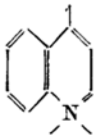
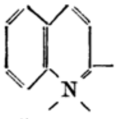
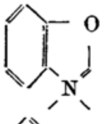
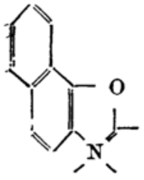
For some important symmetric and asymmetric cyanine dyes, the calculated and observed values of λ_1 are compared in Tables 5 and 6. As may be seen from these tables, the agreement between the two values is satisfactory for symmetric dyes, while the values calculated for asymmetric dyes are always somewhat lower than the observed ones. The reason of this disagreement will be discussed later.

(5) Analogous Relation Existing for Polyene and some other Compounds.—It may be highly interesting to note that what we have established for cyanine type compounds was also found to hold, mutatis mutandis, for other types of compounds with conjugated systems. The polyene type compounds are known to have, in general, three absorption bands, among which the second one is the strongest and the other two have almost the same intensity. For these compounds a close examination of the λ^2-n'-relation shows that it is non-linear; contrary to the case of cyanine dyes, the curves bend concavely toward the n′-axis. Using the spectroscopic data for diphenyl polyenes ϕ—(CH=CH)$_l$—ϕ reported by Kuhn and Hausser⁽³⁾, and assuming the color factor of

Table 5

The Symmetric Cyanine Dyes

$A-(CH=CH)_l-CH=A$

A	l	$\lambda_{cal.}$	$\lambda_{obs.}$
	1	5460	5450
	2	6420	6360
	3	7430	7450
	0	4980	4550
	1	5930	5950
	2	6910	6890
	3	7970	7990
	0	4650	4220
	1	5590	5570
	2	6570	6500
	3	7590	7620
	0	4380	4380
	1	5670	5700
	2	6640	6600
	3	7670	7700
	0	5430	5530
	1	6400	6350
	2	7400	7380
	1	6290	6300
	0	6050	5910
	1	7040	7090
	2	8100	8100
	3	9290	9320
	0	5150	5220
	1	6100	6050
	2	7090	7080
	3	8160	8080
	0	3870	3720
	1	4840	4850
	2	5790	5800
	0	4170	3990
	1	5130	5140
	2	6070	6070

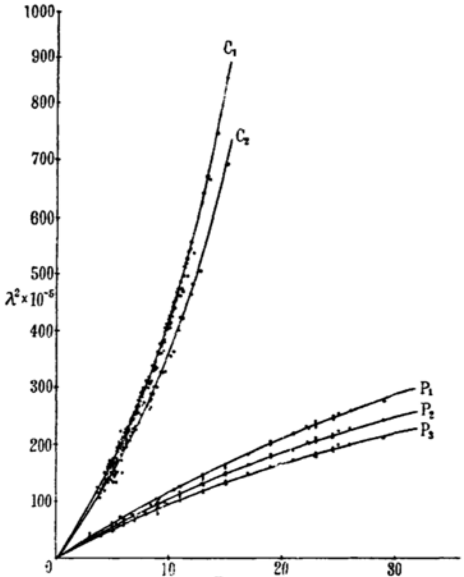
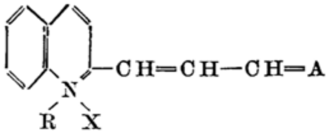
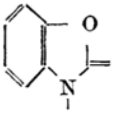
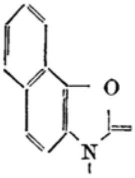
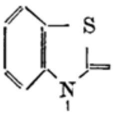
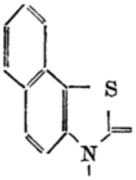
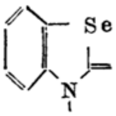


Fig. 2.

Table 6

The Asymmetric Cyanine Dyes



A	$\lambda_{cal.}$	$\lambda_{obs.}$
	5470	5450
	5610	5640
	5850	5600
	6020	5990
	5880	5820

the phenyl group to be 3, we obtain the following empirical formulas for the standard curves of the three bands, which are again of the same form as before;

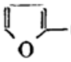
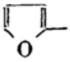
$$\lambda_1^2 = n/(0.80+0.008\,n) \qquad (3)$$

$$\lambda_2^2 = n/(0.84+0.012\,n) \qquad (4)$$

$$\lambda_3^2 = n/(0.92+0.015\,n) \qquad (5)$$

Striking is the fact that these empirical formulas not only fit in well with diphenyl polyenes but also with the other compounds listed in Table 7 and with carotinoids (α- and β-carotene, lycopine, cryptoxanthine, crocetin etc.) if we assume the suitable values of the color factors given in the last column of Table 4. These assumed values of color factors are resonable from the consideration of the number of double bonds in the nucleus.

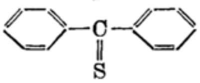
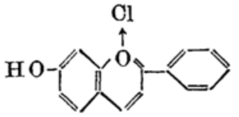
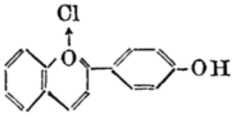
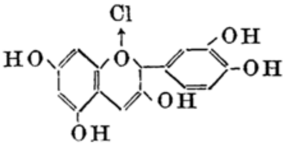
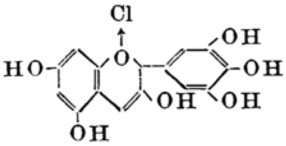
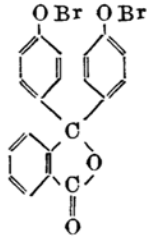
Table 7

Compounds	l
ϕ—$(CH{=}CH)_l$—ϕ	1—7
CH_3—$(CH{=}CH)_l$—CH_3	4—6
CH_3—$(CH{=}CH)_l$—CH_2—OH	1—4
ϕ—$(CH{=}CH)_l$—H	1—2
CH_3—$(CH{=}CH)_l$—$COOH$	1—3
CH_3—$(CH{=}CH)_l$—CHO	1—3
 —$(CH{=}CH)_l$—$COOH$	0—3
 —$(CH{=}CH)_l$—CHO	0—3

The curves P_1, P_2 and P_3 in Fig. 2 were drawn according to these equations and the points on these curves are those obtained by plotting the observed values of λ^2 against n, which were calculated from the values of color factors given in Table 4.

Besides cyanine and polyene compounds, there is another group of coloring substances which apparently, and in a peculiar manner, obey the above mentioned rule. The compounds listed in Table 8 have the property in common that they have two distinct absorption bands separated rather widely. If we plot the square of λ_2 (the absorption band at shorter wave length) on the standard line P_2 in Fig. 2, the point for the square of λ_1 was found to fall exactly upon curve C_1 against one and the same value of the color factor. For example, the points for λ_1 and λ_2 of thiobenzophenone fall on curves C_1 and P_2, respectively, with the color factor of 9.5. The same was true with all other compounds listed in Table 8, in which the color factors estimated in the above mentioned manner are also given for comparison.

Table 8

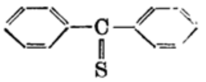
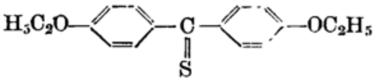
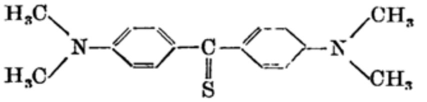
Compounds	λ^2 (λ in $10^3\times$A. unit)		n
	9.9	38.4	9.5
	5.9	19.8	5.7
	6.3	21.2	6.0
	7.3	26.0	7.0
	7.6	27.6	7.2
	9.3	32.1	8.3

From the facts described above, it may be inferred that the compounds listed in Table 8 have both cyanine and polyene types of absorption bands. It should, however, be added that while unsubstituted thiobenzophenone follows our rule satisfactorily, the applicability of the rule is rather unsatisfactory in the case of some substituted thiobenzophenones. In Table 9 are shown the data reported by Burawoy⁽⁷⁾. For substituted thiobenzophenones we cannot find any definite value of color factor, on the basis of which the points for the two bands may be brought exactly upon the curves C_1 and P_2, respectively, in Fig. 2. If we assume for these substances the value of color factor which had been used for unsubstituted thiobenzophenone, the point for λ_1 falls lower than curve C_1 and the point for λ_2 falls above curve P_2.

---

(7) Burawoy; *J. Chem. Soc.*, **1939**, 1177.

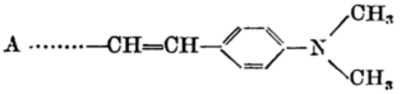
Table 9

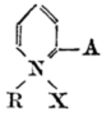
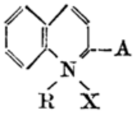
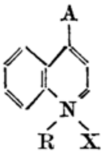
Compounds	λ^2	(λ in $10^3 \times$ A. unit)	Solvents
	9.9 —	38.4 36.9	hexane ether
	11.8 12.5	35.5 33.5	hexane ethanol
	—	32.8	hexane

The similar discrepancy from our rule was observed with styryl dyes. In Table 10, are given the values of λ which we have found for some styryl dyes. The value of color factors of these compounds can be calculated from the values given in Table 4. When we plot the square of λ against the color factor, the point for λ falls between curves C_1 and P_2. This was the case with all styryl dyes investigated.

Table 10

The Absorption Maxima of Styryl Dyes



Compounds	λ_{max} in A. unit
	4670
	5270
	5460

As we have seen, our rule has proved to be quite satisfactory for certain groups of compounds, while it gives more or less deviating values for some other groups of compounds. In the following, an attempt will be made to elucidate the causes underlying the diversity of spectroscopic properties of different types of compounds.

(6) Interpretations of the Different λ^2-n-Relationships shown by Different Groups of Compounds.—In 1939 Burawoy⁽⁷⁾, investigating the spectroscopic properties of various kinds of compounds, made the interesting observation that the two absorption bands shown by thiobenzophenones behave differently under certain conditions. On changing the solvent from a non-polar one to a polar one, it was found that the band at longer wave length was shifted towards shorter wave length, while the other band was displaced towards longer wave length (See Table 9). A similar phenomenon was observed when the dipole moment of the substance was enhanced by introducing some radical in it. These phenomena indicate that the structures in the molecules, which are responsible for the two bands are essentially different in nature. According to Burawoy, the band situated at longer wave length is caused by a chromophore of ionic nature ("chromophore R"), while the band at shorter wave length is brought about by a non-ionic chromophore ("chromophore K").

We have already seen that the first band of thiobenzophenone follows the rule of the bands of cyanine compounds, while its second band behaves exactly like the bands of polyene compounds. The data given in Table 3 show that the bands of cyanine compounds, like the band of thiobenzophenone at longer wave length, are shifted to violet by a change of the solvent which increases the dipole moment of the substances. Just the reverse phonomena are observed with polyene compounds; their bands, like the second absorption band of thiobenzophenone, are shifted to red with the increase of dipole moment by the effect of solvent. The same effect is brought about also by the substitution entailing an increase of dipole moment of polyene compounds.

It may safely be asserted that the polyene type compounds are non-ionic in any kind of solvent, while cyanine compounds will very likely assume ionic form in various solvents. At any rate, it may be certain that the Burawoy's chromophore R and K correspond to the conjugated double bond systems of cyanine and polyene compounds, respectively.

From this point of view, the compounds listed in Table 8 may be regarded as having the property of producing two types of molecule, ionic and non-ionic, in the solution.

(7) **Conclusion.**—By careful and detailed studies of a large number of absorption spectra of organic compounds with conjugated systems, we have found a rule governing quantitatively the relationship existing between the length of conjugated system and the absorption maximum. In alignment with these newly found λ^2-n-relationships, improvement of theoretical explanations such as Herzfeld and Sklar's is awaited with great interest.

As was remarked already, the rule we have found for symmetric cyanine dyes and polyene compounds does not apply with sufficient accuracy to some substituted thiobenzophenone and styryl dyes, nor for some asymmetric cyanine dyes. In these cases, our rule gives always higher values of λ for cyanine type absorption and lower values of λ for polyene type absorption. Systematic deviations in these cases indicate that in these compounds, besides the number of conjugated double bonds and the "color factor" of the terminal nuclei, some other factor plays a role in determining the position of the absorption band. The fact that our rule gives deviating values for substituted thiobenzophenone, while it applies satisfactorily to unsubstituted thiobenzophenone, suggests that the factor in question may be related to the dipole or the symmetry of the compounds. A theoretical explanation of this factor will be reported later in another work with more sufficient data on styryl dyes.

The author wishes to express his sincere thanks to Prof. E. Ochiai and Dr. T. Ogata for their kindness in placing the precious samples at the author's disposal.

The Tokugawa Institute for Biological Research, Tokyo