

Absorption Spectra of Dyes. VI.¹⁾ Steric Effects in Conjugated Systems of Benzidine Disazo Dyes and their Copper Derivatives

By Teruaki KOBAYASHI, Yoshié TANIZAKI and Noboru ANDO

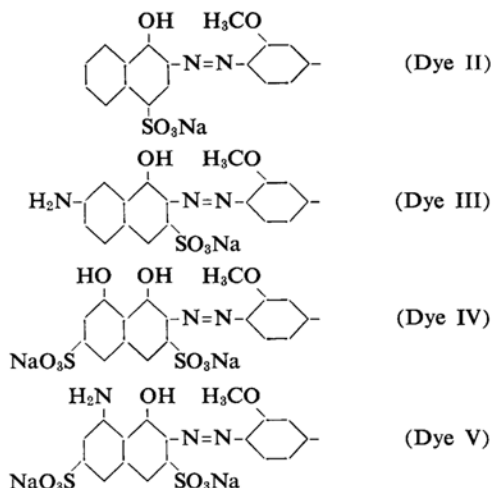
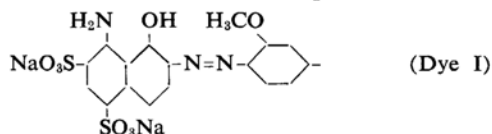
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The first absorption bands of dyes are considered to be due to the longest conjugated systems connected with auxochromes, and as is well known, their intensities are the highest when these systems are coplanar. For examples, ϵ_{\max} of the first absorption band of Benzopurpurine 4B in methanol is 55,000, compared with 42,000 for that of meta-Benzopurpurine²⁾. The case is the same with Congo Red. The corresponding value of it in ethanol is 54,000, while there can always be seen remarkable reductions in those of its dimethyl, dichloro and dibromo derivatives, which are prepared with the substituents introduced into the 2- and the 2'-positions of the diphenyl nucleus³⁾. Such a decrease in intensity should apparently be caused by steric effects of the substituents. The same phenomena are also found for other dyes: Chlorazol Sky Blue FF has ϵ_{\max} of 100,000, compared with 74,000 for Direct Sky Blue 5B which is different from the former only in positions of sulfonic groups. Further, their copper derivatives have weaker intensities. Such difference in intensity also seems to be caused by steric effects.

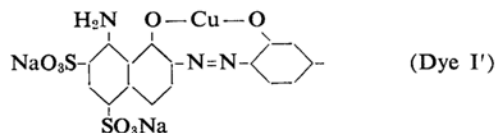
In previous works of this series, absorption spectra of dyes under various conditions have been studied mainly with respect to their first absorption bands, in order to see how they vary with aggregation or formation of complexes. In this paper, absorption spectra in aqueous solutions of both benzidine disazo dyes such as Chlorazol Sky Blue FF and their copper derivatives have been studied in connection with their stereochemical forms and steric hindrances.

Experimental

Preparation of Samples.—The following dyes were used in the present work. They will be called the abbreviations shown in the parentheses.



Where the halves of their structures are shown. Their copper derivatives will be called Dye I', Dye II', etc., corresponding to each of them. These copper derivatives are known to have the following structures⁴⁾; e. g., Dye I' is



Dye I—Dye V were purified by Robinson and Mills' method⁵⁾. The copper derivatives were prepared from these dyes by a method reported elsewhere.⁴⁾* The purification of them followed the above method. Found values of copper contents of Dye III' and Dye V' were 90% and 86%, respectively²⁾. The concentrations of dye solutions were $(1\sim130)\times10^{-6}$ mol./l., which were determined by weight.

Absorption Spectra.—All the absorption spectra were measured in 0.2 to 10 cm. cells by a Shimadzu QR-50 spectrophotometer at room temperature (ca. 20°C).

Results

The absorption spectra of Dye I and Dye I' and of Dye V and Dye V' are illustrated as

4) U. S. Pat., 2,036,159 (1935).

5) C. Robinson and H. A. T. Mills, *Proc. Roy. Soc. (London)*, A131, 576 (1931).

* Some of the dyes were presented by Mr. Yoshiji Ishii of the Faculty of Technology, the Gumma University.

²⁾ For the other dyes see the reference, Y. Ishii, *J. Soc. Tex. Cell. Ind. Japan*, 14, 718 (1958).

1) Part V of this series, *This Bulletin*, 33, 661 (1960).

2) H. A. Standing and M. Stein, *J. Text. Inst.*, 44, T224 (1953).

3) F. H. Holmes, *Trans. Faraday Soc.*, 54, 1166 (1958).

TABLE I. COMPARISON OF THE FIRST ABSORPTION BANDS OF THE DYES

Dyes	Concn. mol./l $\times 10^6$	Temp. °C	λ_{\max} m μ	$\epsilon_{\max} \times 10^{-4}$			Oscillator strength		
				ϵ	ϵ_c	$\frac{\epsilon - \epsilon_c}{\epsilon} \times 100$	f	f_c	$\frac{f - f_c}{f} \times 100$
I	0.946	18~19	620	10.1			1.44		
I'	1.000	"	596		5.1	50		1.01	30
II	1.008	"	568	6.7			1.14		
II'	1.006	"	555		4.1	39		0.75	34
III	15.62	15~16	562	6.2			1.22		
III'	19.65	"	548		4.6	26		0.96	21
IV	1.003	18~19	612	7.6			1.20		
IV'	0.997	"	588		6.0	21		1.04	13
V	1.509	"	612	7.4			1.21		
V'	1.275	"	611		6.5	12		1.09	10

* See foot note 3.

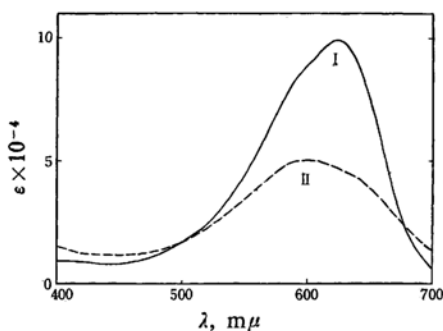


Fig. 1. Absorption spectra of Chlorazol Sky Blue FF (Dye I) and its copper derivative (Dye I') in aqueous solution at room temperature.

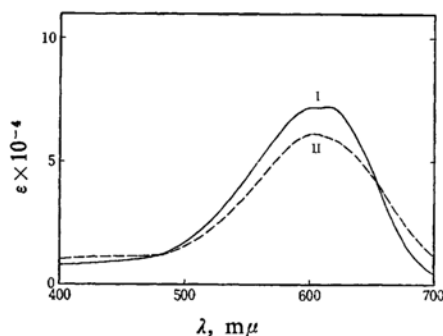
I: Dye I, 1.03×10^{-5} mol./l.; II: Dye I', 1.01×10^{-5} mol./l.

Fig. 2. Absorption spectra of Direct Sky Blue 5B (Dye V) and its copper derivative (Dye V') in aqueous solution at room temperature.

I: Dye V, 1.13×10^{-5} mol./l.; II: Dye V', 0.946×10^{-5} mol./l.

examples in Figs. 1 and 2 respectively, in which the full lines mean the results of Dye I and Dye V and the dotted lines those of

Dye I' and Dye V'. Inspection of them shows that the absorption intensity of Dye I is high compared with that of Dye V, and the copper derivatives have remarkably decreased intensities. The same phenomena are observed for the other dyes. In order to investigate these changes in spectra in more detail, λ_{\max} , ϵ_{\max} and oscillator strengths of the first absorption bands of the dyes are shown in Table I. Variation of the concentrations of these dyes over a wide range revealed that λ_{\max} , ϵ_{\max} and the shapes of their first bands all vary with concentrations: e. g., results of Dye IV' are shown in Fig. 3. Therefore, the values in Table I correspond only with the respective concentrations shown in the same table and

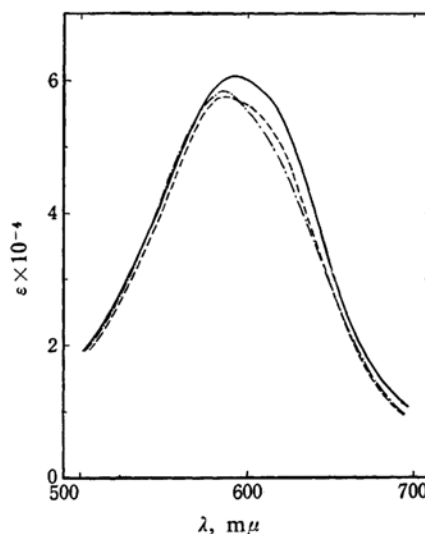


Fig. 3. Absorption spectra of Dye IV' in aqueous solution at room temperature.

— 1.01×10^{-6} mol./l.
 --- 1.01×10^{-5} "
 0.87×10^{-4} "

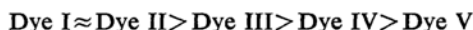
will somewhat vary with concentrations^{*3}. Oscillator strengths f were calculated by⁶⁾

$$f = 4.31 \times 10^{-9} \int \epsilon_\nu d\nu$$

As the calculation was carried out for the absorptions longer than 460 m μ because their train in short wavelengths were obscure, the values are not true ones. However, they will at least satisfy the purpose of mere mutual comparisons. The molecular extinction coefficients and the oscillator strengths of the copper derivatives were distinguished by the suffix c as ϵ_c and f_c from those of the non-copper dyes. The table shows that

1. The absorption intensity of Dye I is the highest of all.

2. All the intensities of the dyes are decreased by the introduction of copper into them. The relative order of the percentage decrease in intensity is



The copper derivatives have nearly equal intensities to one another, except Dye II'

3. λ_{max} of each dye shifts somewhat to shorter wavelengths by the introduction of copper^{*4}.

Discussion

As shown in the previous section, the intensities of the first absorption bands of Dye I—Dye V all decrease by the introduction of copper. Comparison of the intensities of Dye I, Dye IV and Dye V which have similar structures to one another shows that while Dye IV and Dye V have nearly equal values, Dye I has a very large one relative to them. If the first absorption bands of these dyes are due to the conjugated double bond chains connecting their auxochromes, they should be the same with one another, because they have the same conjugated chains and auxochromes. The difference in the structures of the dyes is found in positions of sulfonic groups. It should reasonably be considered that the difference in intensity was caused not by the difference in auxochromic effects of the sulfonic groups due to their positions on the naphthalene rings, but rather by their steric effects.

On the other hand, the strain in a conjugated system generally causes a decrease in absorption intensity^{*5}. Some of the present results seem to be the case: the intensity of Dye IV or Dye V, which has sulfonic groups in the positions adjacent to the azo groups is remarkably weak compared with that of Dye I which has sulfonic groups in the positions far from the azo groups. Consequently, it would be proper to discuss the experimental results with respect to the positions of sulfonic groups from the stand point of steric effects.

If the dyes are of coplanar structures, scale drawings give conformations as in Fig. 4, in which the halves of the structures of Dye I, Dye II and Dye V are shown. The figure clearly shows that a repulsion between the sulfonic group and the unshared electrons of N may be anticipated in Dye V, but not in

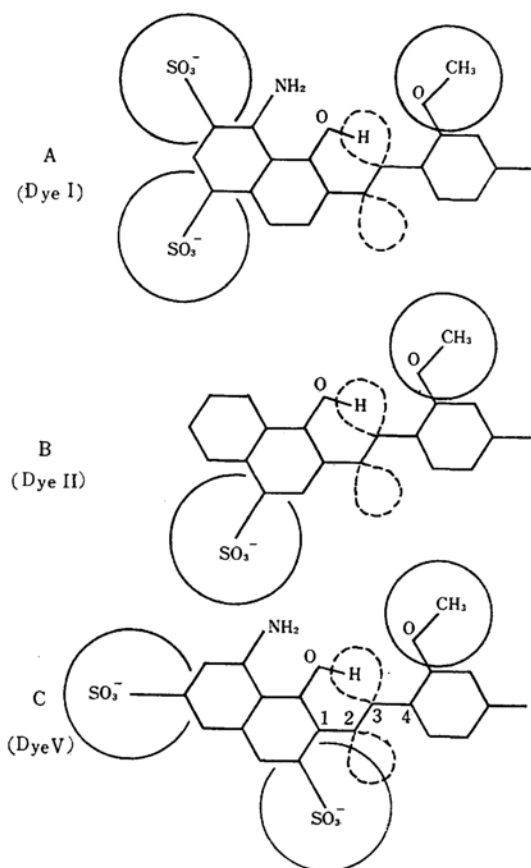


Fig. 4. Models of Dye I, Dye II and Dye V.

^{*3} The first absorption band of Dye III' varied remarkably with changes in outside conditions and time from preparation of its solutions till measurements. Hence, its values in Table I are less valid.

⁶⁾ W. West, "Technique of Organic Chemistry", Interscience Publisher, New York (1956), Vol. IX, p. 66.

^{*4} The first absorption bands of these dyes are considered to be composed of two bands [Y. Tanizaki, T. Kobayashi and N. Ando, This Bulletin, 32, 119 (1959)]. In fact, their behaviors are complicated, apart from variations owing to changes in concentrations. This leads us to difficulty in our exact investigation of their behaviors.

^{*5} It is not always easy to predict whether absorption bands are shifted to red or blue by steric hindrances. Recently Dewar has discussed the relationship between noncoplanarity of cyanine dyes and shifts of wavelengths of their absorption (M. J. S. Dewar, "Steric Effects in Conjugated Systems", Proceedings of a Symposium held at the University, Hull, 1958, by the Chemical Society (Butterworths, London, 1958), p. 46).

Dye I and Dye II*⁶. Hence, Dye V (also Dye III and Dye IV) seems to be less planar relative to Dye I (or Dye II) because of the repulsion owing to the sulfonic group. Propriety of this expectation is proved by the fact that ϵ_{\max} of Dye I is 100,000, compared with 74,000 for that of Dye V which has the same structure as Dye I except the positions of the sulfonic groups.

Now, let us suppose simply that in such a dye as Dye V the repulsion by the sulfonic group only results in twist of the 1-2 bond (see Fig. 4C). Then, owing to the bond twist, the repulsion between the sulfonic group and the unshared electrons of N in position 2 (N(2)) will decrease, whereas the one by the unshared electrons of N(3) will increase. The exchange integral of the 1-2 bond also changes. Hydrogen of the auxochrome OH is generally considered to form a hydrogen bond with N(3), hence the energy of the bond will also change with the twist. On the basis of such consideration, an approximate calculation of the change in energy of the molecule with the twist will be performed.

The change of the exchange integral of a bond with twist has already been studied⁷. According to this procedure, the exchange integral of the 1-2 bond is expressed by

$$V_1(\theta) = \beta S(R) \cos \theta / S(1.39) \quad (1)$$

$$\frac{S(R) - S(1.47)}{S(1.40) - S(1.47)} = \cos \theta \quad (2)$$

where $S(1.39)$, $S(1.47)$, $S(1.40)$ and $S(R)$ are the π - π overlap integrals of the C-C bond of benzene, the normal C-N single bond, the conjugated C-N bond of azobenzene and the 1-2 bond when its length is R corresponding to the angle of twist θ , respectively. These values can be obtained from Mulliken's Table⁸.

The repulsion between the charges on the sulfonic group and of the unshared electrons may roughly be estimated, if the center of the charge on the sulfonic group is approximately taken at the point where the extension of the C-S bond crosses the plane decided by the three oxygen atoms, and the distance between this point and the center of the unshared electrons (1.2 Å from the nitrogen nucleus) is taken as that between the two charges, though the effective charges spread widely. Let us put $a_S e$ and $a_N e$ (where a_S and a_N are numerical constants) as the effective charges,

with $a_S a_N = a$, and the repulsive energy is expressed by

$$V_2(\theta) = ae^2 \{1/r_2(\theta) + 1/r_3(\theta)\} \quad (3)$$

where $r_2(\theta)$ and $r_3(\theta)$ are the distances between the sulfonic group and the unshared electrons of N(2) and N(3) respectively.

As mentioned above, the auxochrome OH is considered to form a hydrogen bond with N(3). If the energy of the hydrogen bond O-H...N is approximately estimated to be -5 kcal. and is assumed to be electrostatic, it becomes

$$V_3(\theta) = -2.45/r(\theta) \quad (4)$$

where $r(\theta)$ means the distance between hydrogen and the unshared electrons.

On putting $V(\theta) = V_1(\theta) + V_2(\theta) + V_3(\theta)$ (5) the change in energy of the molecule becomes

$$\Delta V(\theta) = V(\theta) - V(0)$$

Fig. 5 illustrates $\Delta V(\theta)$ - θ curves, which were drawn by use of various values of a appeared in Eq. 3. As a relates mainly to the effective charges of the sulfonic group and the unshared electrons, it would not exceed two. Although the above calculation is quite simple, the appearance of minima in the curves in a certain range of a suggests that the molecule becomes stable when the 1-2 bond was twisted by 50° to 60° on account of the repulsion. This coincides with the result that the absorption intensity of the dyes in which a sulfonic group is adjacent to the C-N bond is remarkably weak compared with that of the dye which has no such sulfonic group.

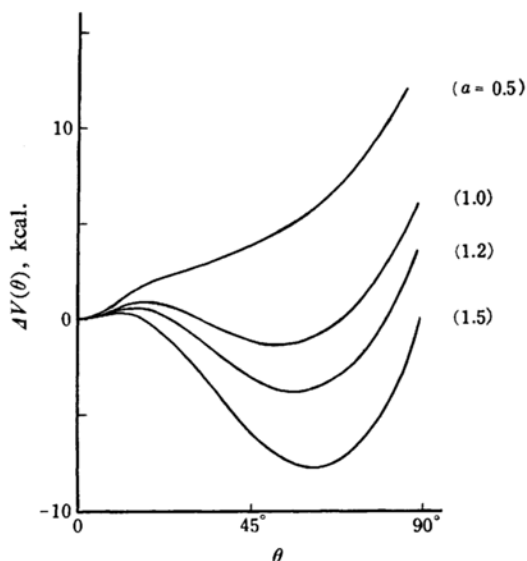


Fig. 5. The change in energy of the sterically hindered dyes with the angle of twist.

*⁶ The steric effect of unshared electrons of N has been discussed concerning phenyl-azo-azulene, and a reasonable result has been obtained [F. Gerson, T. Gäumann and E. Heilbronner, *Helv. Chim. Acta*, **41**, 1481 (1958)].

⁷ H. Suzuki, *This Bulletin*, **25**, 145 (1952); **27**, 597 (1954).

⁸ R. S. Mulliken, C. A. Lieke, D. Orloff and H. Orloff, *J. Chem. Phys.*, **17**, 1248 (1949).

Copper derivatives of *o,o'*-dihydroxy-azo-compounds or of similar compounds have been studied by many workers⁹⁻¹¹, but little is known about their stereochemical forms. In general, coplanar structures seem to be adopted⁹, whereas a structure in which a copper atom is centralized on the $-N=N-$ double bond is also considered¹¹. Consequently, the stereochemical forms of the dyes studied in the present work are not yet clear.

Absorption spectra of copper derivatives of this kind have also been measured. Inspection of them reveals that intensities of their first bands are generally weak or equal as compared with those of the non-copper substances, without showing any tendency to increase. All of the present copper derivatives have decreased intensities, as mentioned in the previous section, and further a certain tendency was observed in the decrease in intensity: the decrease in intensity of the copper derivative of Dye V (or Dye IV or Dye III) which seems to have a strained conformation was slight, compared with the very remarkable one of the copper derivative of Dye I (or Dye II) which is considered to have a relatively planar conformation. Further the absorption intensities of the copper derivatives are nearly

equal to one another. These results prove a great possibility that copper derivatives may have strained conformations.

Summary

1. Absorption spectra of benzidine disazo dyes and their copper derivatives in aqueous solution were measured at room temperature, and they are compared with one another.

2. It was shown by a simple calculation that the dyes, each of which has sulfonic groups adjacent to the azo groups, have strained conformations caused by the repulsion between the sulfonic groups and the unshared electrons of nitrogen. It was also shown that the relationship between the relative positions of sulfonic groups to the azo groups and the relative absorption intensities could well be explained.

3. The absorption intensities of the copper derivatives were nearly equal, having no relation to the positions of the sulfonic groups, and in addition they were near to those of the non-copper dyes which have the sulfonic groups adjacent to the azo groups. Hence, it was pointed out that the introduction of copper caused the same extent of strain in conjugated systems as sulfonic groups did.

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Department of Physical Chemistry
Tokyo Institute of Technology
Meguro-ku, Tokyo

9) H. D. K. Drew and J. K. Landquist, *J. Chem. Soc.*, 1938, 292.

10) M. Elkins and L. Hunter, *ibid.*, 1935, 1598; F. A. Snavely and W. C. Fernelius, *Science*, 117, 15 (1953); H. B. Jonassen, M. M. Cook and J. S. Wilson, *J. Am. Chem. Soc.*, 73, 4683 (1951); H. B. Jonassen and J. S. Wilson, *ibid.*, 75, 4201 (1953).

11) L. G. Van Uitert and W. C. Fernelius, *J. Am. Chem. Soc.*, 76, 379 (1954).