[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, THE OHIO STATE UNIVERSITY]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. VII. The Separation of Chromophores in Symmetrical Disazo Dyes

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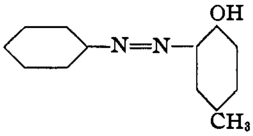
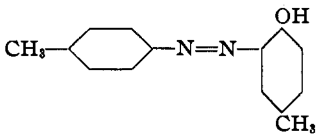
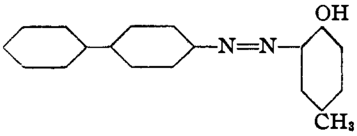
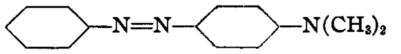
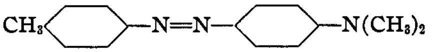
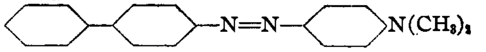
In the preceding paper of this series[1] it was shown that the meta coupling of azo groups in a disazo dye did not appreciably transmit chromophoric influences, whereas para coupling was equivalent in its effect to conjugated linkage with the apparent formation of a single chromophore. In this paper a study has been made of the influence of separation of para-coupled azo groups in symmetrical disazo dyes, in which both end groups are alike.

The absorption spectra measurements were made with a Hilger sectorphotometer and a Bausch and Lomb spectrograph in the ultraviolet and a Bausch and Lomb spectrophotometer in the visible, in accordance with methods previously described.[2] In view of the fact that basic dyes have been introduced into the series in this paper, an additional solvent, dilute hydrochloric acid, was added to the three previous solvents, alcohol, dilute sodium hydroxide and concentrated hydrochloric acid. For purposes of comparison and to economize on space the curves are shown in groups and on a scale which prevents the indication of observational points. Each curve, however, is based on from fifty to one hundred points, determined with the same methods and accuracy as have been previously described.[2]

The dyes were prepared by diazotization or tetrazotization of the corresponding amine or diamine and coupling to either *p*-cresol or dimethylaniline. In order to compare accurately the absorption spectral influences in the disazo dyes, a number of "component" monoazo dyes were prepared (Table I, Figs. 1 and 2). These "component" dyes contained the same auxochrome nuclei as the disazo dyes (*i. e.*, *p*-cresol or dimethylaniline). The aromatic groups were phenyl, *p*-tolyl and *p*-diphenyl. By doubling the absorption values produced by a unit molecular concentration of any one of these dyes (which is equivalent to the absorption values of a solution of twice the unit molecular concentration), or by the addition of the absorption values of two properly chosen dyes (which is equivalent to the absorption values of a mixture of a unit molecular concentration of each of the two dyes) one should obtain a nearly theoretical curve for the corresponding disazo dye, providing there has been no

TABLE I

MONOAZO COMPONENT DYES (ALL MONOAZO DYES WERE CRYSTALLIZED FROM ALCOHOL)

Dye	Formula	M. p., °C. Obsd.	M. p., °C. Lit.
1		108–109	108–109
2		112.3–112.8	
3		97.1– 97.6	
4		116.5–117	115
5		171–171.5	
6		220.0–220.5	

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(1) Funkhouser and Brode, THIS JOURNAL, **56**, 2172 (1934).

(2) Brode, *Bureau of Standards J. of Research*, **2**, 501 (1929).

mutual influencing effect of the two chromophores in the disazo dye. Variations from these component addition curves will indicate the degree and character of the mutual influence of the two chromophores in the disazo dyes.

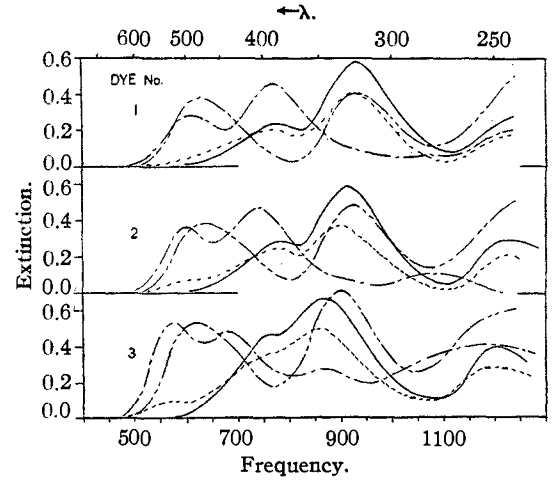


Fig. 1.—The absorption spectra of monoazo acidic "component" dyes: ——, alcohol solution ($c = 3.0 \times 10^{-5}$ mole per liter); - - - - - - -, dilute hydrochloric acid (2.5×10^{-5} mole per liter); — · — -, concd. hydrochloric acid (2.5×10^{-5} mole per liter); — - - — - - —, 3% aqueous sodium hydroxide (4.0×10^{-5} mole per liter); cell thickness, 1 cm. (see Table I for explanation of dye numbers).

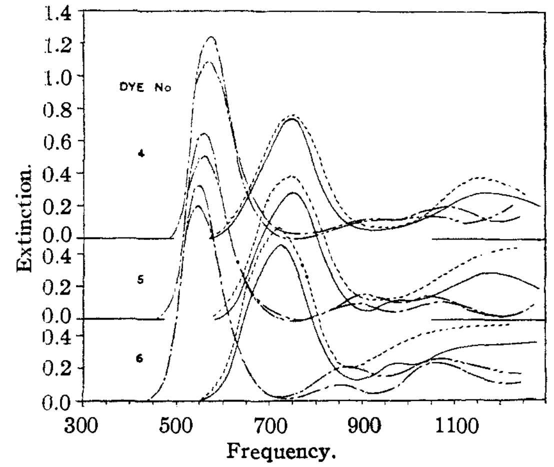


Fig. 2.—The absorption spectra of monoazo basic "component" dyes: ——, alcohol solution; — - —, concd. HCl; — - - — - - —, dilute HCl; - - - - - - - -, 3% NaOH; concentrations and cell thickness the same as in Fig. 1 (see Table I for explanation of dye numbers).

In Figs. 3 to 7 are given the observed absorption spectra curves of the disazo dyes listed in Table II. There is also shown in each of these figures a component addition curve (heavy line). This latter curve was obtained, in the case of the acid dyes, from twice the absorption curve of a unit molecular concentration of *p*-tolylazo-*p*-cresol (dye No. 2), and in the case of the basic dyes, from twice the absorption curve of a unit molecular concentration of *p*-tolylazodimethylaniline (dye No. 5). Except for the component curves, the data as shown graphically are all on an equimolecular concentration basis for each of the solvents used.

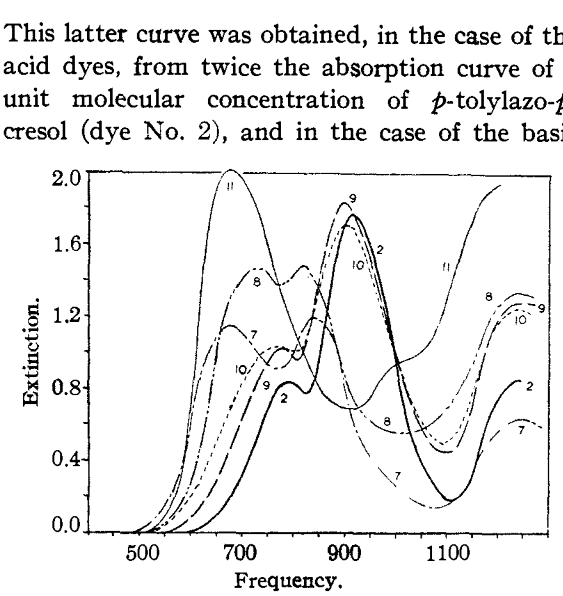


Fig. 3.—The absorption spectra of acidic disazo dyes in alcohol: (concn. 4.5×10^{-5} mole per liter; cell thickness, 1 cm.) (see Table II for explanation of dye numbers); "component" dye No. 2 (see Table I) (concn. 9.0×10^{-5} mole per liter).

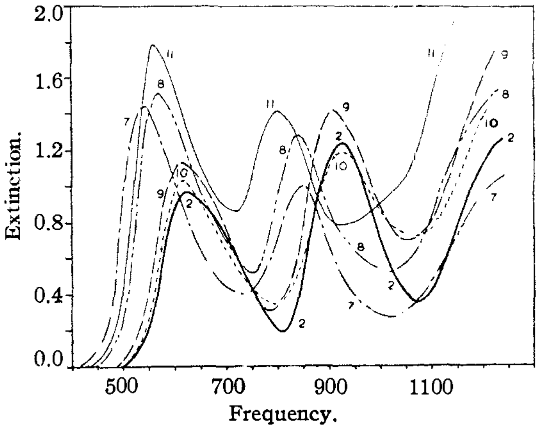


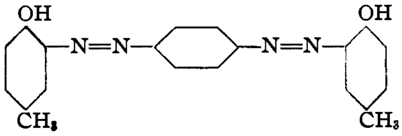
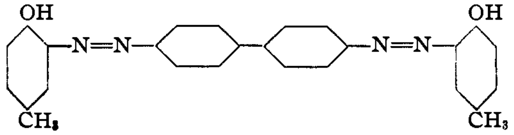
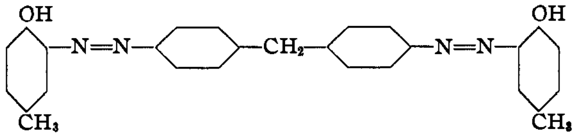
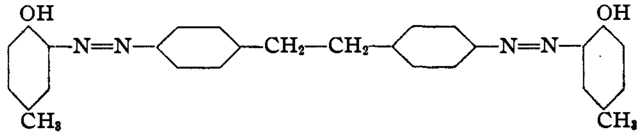
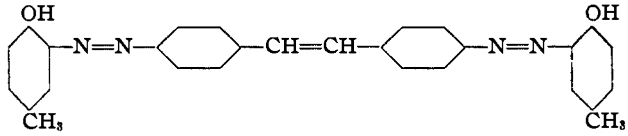
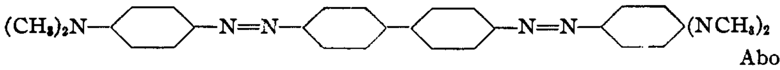
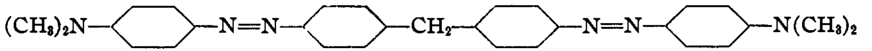
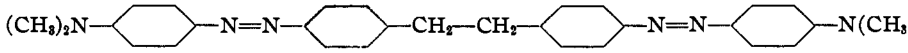
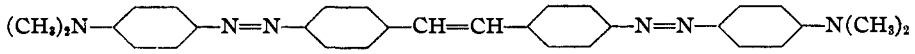
Fig. 4.—The absorption spectra of acidic disazo dyes in 3% aqueous sodium hydroxide: (concn. 5.0×10^{-5} mole per liter; cell thickness, 1 cm.), dye no. 11: (see Table II for explanation of dye numbers): "component" dye No. 2 (see Table I) (concn. 10.0×10^{-5} mole per liter).

Discussion of Data

From the absorption spectra curves of the monoazo dyes (Figs. 1 and 2) the shift of bands

TABLE II

DISAZO DYES

Dye	Formula	M. p., °C.	Cryst. from	N analyses, % Found	Calcd.
7		239–239.5	C_6H_5Br		
8		213–214	Aniline		
9		259–260	C_6H_5Cl	12.70	12.84
10		205–206	C_6H_5Cl		
11		265–266	C_6H_5Br	12.52	12.49
12		Above 325	Aniline		
13		207.5–209.5	*i*-Amyl alc.		
14		Above 320	C_6H_5Br		
15		Above 350	C_6H_5Br	17.47	17.71

to lower frequencies by weighting of the molecule may be noted. In the corresponding disazo dyes (Figs. 3 to 7) a similar shift would be all the change that might be expected, if the two chromophores were independent of each other and produced only additive effects. In the acidic monoazo dyes (Fig. 1) a second effect can be observed, namely, the shift of band intensities, the second band being reduced and the first band intensified as the weighting effects are increased. This shift of band intensities is slight, however, compared with the observed shifts in certain of the disazo dyes, while other disazo dyes show shifts of a magnitude which would be expected from the highly weighted molecule.

It is quite obvious from the absorption spectra data that in all the solvents studied, the para-coupled disazo dyes which are separated by $-CH_2-$ or $-CH_2CH_2-$ between the center aromatic groups (dyes Nos. 9, 10, 13, 14), have chromophores which are quite independent of each other, in that their absorption spectra curves are almost identical with the corresponding component monoazo dye absorption curves (twice the absorption values of dyes Nos. 2 and 5). On the other hand, the attachment of both azo groups to the same benzene ring (para to each other) produces a dye (No. 7) with weaker absorption in alcohol and acid solutions, such as might be expected from a compound in which one of the azo groups was more or less inactive and acted merely as a weighting effect on the other. In the case of this latter dye there is a marked increase in the intensity of the first bands over the second bands, as compared with the intensities of these two bands in the dyes with widely separated chromophores. In the alkali solution of this dye (7) the absorption is quite similar to that produced by the benzidine (8) and *p,p'*-diaminostilbene (11) dyes.

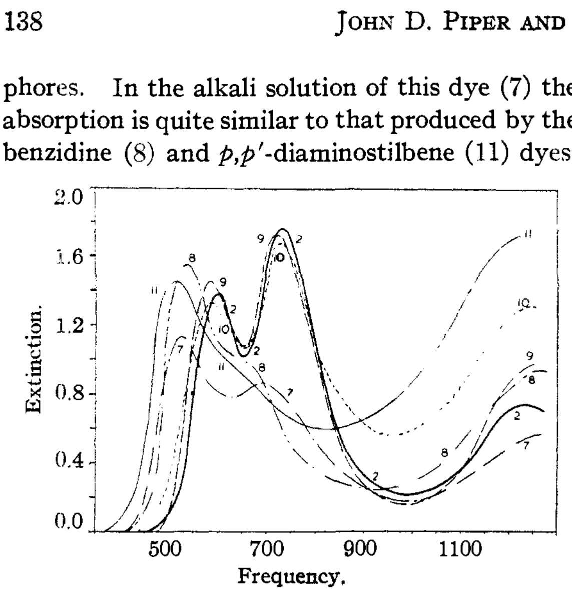


Fig. 5.—The absorption spectra of acidic disazo dyes in concentrated hydrochloric acid: (concn. 4.57 × 10^{-5} mole per liter; cell thickness, 1 cm.); (see Table II for explanation of dye numbers), "component" dye No. 2 (see Table I) (concn. 9.0 × 10^{-5} mole per liter).

The weighting effects are not as prominent in the monoazo basic dyes as in the acid series; they show the same general effects, however, although not always to the same degree. As in the acid dye series, the basic dyes derived from *p,p'*-diaminodiphenylmethane (Dye No. 13) and *p,p'*-diamino-*sym*-diphenylethane (No. 14) show practically the same absorption as twice the absorption of the component monoazo dye (5). The basic dyes derived from benzidine and diaminostilbene show a distinct shift in the position of the absorption bands which is much greater than would be predicted from the simple weighting of the molecule. This latter effect is particularly true in the case of the alcohol curves.

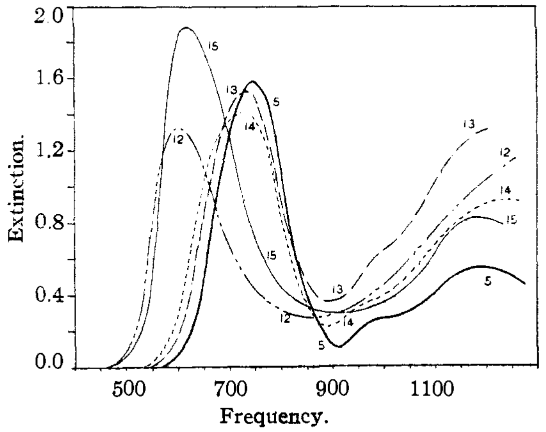


Fig. 6.—The absorption spectra of basic disazo dyes in alcohol: (concn. 4.5 × 10^{-5} mole per liter; cell thickness 1 cm.); (see Table II for explanation of dye numbers); "component" dye No. 5 (see Table I) (concn. 9.0 × 10^{-5} mole per liter).

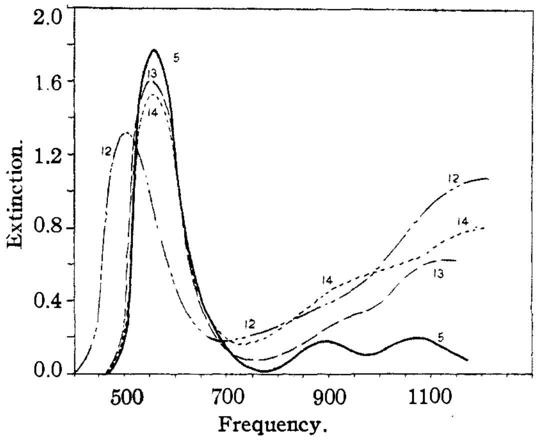


Fig. 7.—The absorption spectra of basic disazo dyes in concentrated hydrochloric acid: (concn. 2.0 × 10^{-5} mole per liter; cell thickness, 1 cm.); (see Table II for explanation of dye number); "component" dye No. 5 (see Table I) (concn. 4.0 × 10^{-5} mole per liter).

Summary

A spectrophotometric study has been made of six monoazo dyes and nine para-coupled symmetrical disazo dyes in various solvents. The data indicate that with sufficient separation the two chromophores in a disazo dye are essentially independent of each other. Conjugated or closely linked para-coupled disazo dyes show marked deviations from a theoretical additive absorption effect. This deviation is influenced to some extent by the solvent conditions and is probably closely associated with both weighting effects and the formation of a single chromophore in the molecule, by means of the conjugated coupling of the azo groups.

As a means of determining the relative influence of weighting and conjugation in the change of absorption bands, a series of unsymmetrical disazo dyes is being studied, in which the two component parts each produce a sufficiently different absorption spectrum to be detected easily in a mixture or combination of the two.

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