[Contribution from the Department of Chemistry of the Ohio State University]

THE RELATION BETWEEN THE ABSORPTION SPECTRA AND THE CHEMICAL CONSTITUTION OF DYES. XXI. SOME EFFECTS OF NON-COPLANARITY ON THE ABSORPTION SPECTRA OF UNSYMMETRICAL DISAZO BENZIDINE DYES.

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In an earlier paper in this series Brode and Piper (1) have studied the effect of the separation of chromophores for a number of unsymmetrical disazo dyes, and have noted that the introduction of a methylene or ethylene link in such unsymmetrical dyes produced the same effect as was evident for the symmetrical dye structures; namely, that each chromophore in a single dye structure acts independently. In a preceding paper in this series (2) a study of the effects on induced non-coplanarity on the absorption spectra of a number of symmetrical disazo benzidine dyes was reported. This study revealed that the establishment of non-coplanar conditions for the benzidine nucleus caused an insulation of the two chromophores involved in the disazo molecule, permitting each half-structure to show an independent absorption. In the present paper an investigation of the absorption characteristics for a series of unsymmetrical benzidine dyes has been completed. Because of the easily resolvable absorption bands resulting from the significantly different half-structures obtained for molecules of this kind, a further investigation of the restriction to molecular resonance appearing at the 1,1′-bond in the benzidine nucleus was possible.

EXPERIMENTAL

The dyes for this study, when used for the proof of the addition of absorption curves, were synthesized from intermediates of known purity. However, in order to include a greater variety of similar structures in this investigation, absorption studies on a number of commercial dye samples were prepared. In all cases the dyes were carefully purified and analyzed before absorption measurements were taken.

The general methods available for the preparation of disazo dyes by tetrazotization and coupling were employed. The commercial dyes were examined for shading agents and salt content before further purification (3). All the dyes were then converted to their corresponding di-*o*-tolylguanidine salts for continued purification, analysis, and absorption studies. This conversion not only served in further elimination of undesirable organic and inorganic impurities but also increased their spirit solubility by destroying the water-solubilizing properties of the strongly acid groups present.

Since the absorption studies were made using the dyes in their di-*o*-tolylguanidine salt modifications, extensive comparisons of the absorption spectra for these salts with their corresponding sodium salts were made. These comparisons indicated that the only variation not attributable to the necessity of using different solvent systems occurred between 220 and 240 mμ. This was probably due to the absorption of the di-*o*-tolylguanidine constituent. However, since the absorption characteristics for this region were relatively unimportant to the data presented, the agreement was considered sufficient to allow conclusions to be drawn on the absorption spectra for these dye salts.

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All the dyes after suitable purification were analyzed for purity by use of a standardized titanium trichloride solution. Corrections to 100% purity on the basis of these determinations were applied to all absorption spectra taken.

The absorption measurements were made by the use of a Beckman quartz spectrophotometer. The properly diluted samples were introduced into a 1.00-centimeter silica cell and absorption curves measured against a comparison solvent. A dilution to 0.000015 *M* served for obtaining the complete absorption spectra on all the dyes. In neutral solution this concentration was attained by the proper dilution of a 0.00006 *M* alcoholic stock solution of the dye with more 95% ethanol. For measurements in basic media, dilution to a final concentration of 0.000015 *M* was attained by the dilution of the 0.00006 *M* stock with aqueous sodium hydroxide. Determinations in concentrated acid media were made by dilution of the stock solution to 0.000015 *M* with 12 *N* HCl. Absorption spectra, after correction to one hundred per cent purity, were recorded with molecular extinction as ordinates and frequency (fresnels) as abscissa.

DISCUSSION OF RESULTS

In the classification of complex structures exhibited by dye molecules, it has been shown that a consistent multiple frequency effect was evident in their absorption spectra. Investigations of this nature (4) have clearly indicated that a definite correlation between the calculated and observed positions of absorption band maxima exists and that the calculated positions may be located by assuming them to be small whole number multiples of a fundamental frequency for a given dye structure. In this investigation this correlation was found to be very useful for permitting a satisfactory classification of the observed absorption spectra when applied to a series of unsymmetrical benzidine dyes. The absorption curves of the azo dyes reported in Table I can be satisfactorily interpreted on a frequency basis by assigning a fundamental frequency for the observed band system of each dye investigated. The observed absorption peaks agree closely in number and position to those that may be calulated. Furthermore, each of the unsymmetrical polyazo dyes listed in the Table require the assumption of two fundamental frequencies for a proper interpretation of the observed maxima, indicating that their absorption was characteristic of a summation of the band systems for each of the two partially insulated chromophores, assuming a non-coplanar configuration for the benzidine nuclei involved. Examples of the absorption spectra evident for structures of this kind may be observed in Figure 1.

Although a partial restriction to complete molecular conjugation appears at the 1,1′-(diphenyl) bond in the benzidine nucleus, there is still evidence of conjugation through this bond as observed in the absorption spectra. This is shown in Figure 2 by the comparison of the absorption spectra of the disazo dye (A) with the separate (C and D) and composite spectra (B) observed for its component half-structures. It may be noted from this figure that the absorption values of the band maxima of the disazo molecule are increased in intensity and shifted to lower frequency values, a characteristic property for conjugate structures.

The interpretation based on a non-coplanar configuration is further strengthened by the comparison (Figure 4) of the absorption spectra of the dye prepared

TABLE I

DATA ON THE BAND SYSTEMS OF THE DISAZO AND TRISAZO DYES (SOLVENT C_2H_5OH)
TWO BAND SYSTEMS

DYE (COLOR INDEX NO. INDICATED AS C. I. NO.)	PURITY ANALYTICAL DATA	FUNDAMENTAL FREQUENCY, (F)	LOCATION OF THE OBSERVED AND CALCULATED BAND FREQUENCIES, THE RATIO OF THE OBSERVED TO FUNDAMENTAL FREQUENCIES, AND THE EXTINCTION VALUE OF THE PEAK FOR THE PRINCIPAL BAND IN EACH BAND SYSTEM			
PART I. DISAZO DYES						
No. 1 in Figure 1	89%	*A*. 290f	Observed	580f	920f	
			Calculated	580(2)	870(3)	
			Molecular Extinction	40.0×10^3		
		B. 395	Observed	790	1170	
			Calculated	790(2)	1185(3)	
			Molecular Extinction	42.0×10^3		
No. 2 in Figure 1 (C.I. No. 431)	95%	*A*. 300	Observed	600	960	1200
			Calculated	600(2)	900(3)	1200(4)
			Molecular Extinction	36.0×10^3		
		B. 395	Observed	790	1200	
			Calculated	790(2)	1185(3)	
			Molecular Extinction	36.0×10^3		
No. 3 in Figure 1 (C.I. No. 419)	96%	*A*. 295	Observed	590	960	1210
			Calculated	590(2)	885(3)	1180(4)
			Molecular Extinction	37.0×10^3		
		B. 395	Observed	790	1210	
			Calculated	790(2)	1185(3)	
			Molecular Extinction	43.0×10^3		
No. 8 in Figure 4	88%	*A*. 300	Observed	600	910	
			Calculated	600(2)	900(3)	
			Molecular Extinction	31.0×10^3		
		B. 420	Observed	840	1210	
			Calculated	840(2)	1260(3)	
			Molecular Extinction	44.0×10^3		
PART II. TRISAZO DYES						
C. I. No. 581	72%	*A*. 250	Observed	500	750	
			Calculated	500(2)	750(3)	
			Molecular Extinction	48.0×10^3		
		B. 310	Observed	620	940	
			Calculated	620(2)	930(3)	
			Molecular Extinction	33.0×10^3		

TABLE I—*Continued*

DYE (COLOR INDEX NO. INDICATED AS C. I. NO.)	PURITY ANALYTICAL DATA	FUNDAMENTAL FREQUENCY, (F)	LOCATION OF THE OBSERVED AND CALCULATED BAND FREQUENCIES, THE RATIO OF THE OBSERVED TO FUNDAMENTAL FREQUENCIES, AND THE EXTINCTION VALUE OF THE PEAK FOR THE PRINCIPAL BAND IN EACH BAND SYSTEM			
			PART II. TRISAZO DYES—*Continued*			
C. I. No. 582	73%	*A*. 250	Observed	500	750	
			Calculated	500(2)	750(3)	
			Molecular Extinction	50.0×10^3		
		B. 315	Observed	630	940	
			Calculated	630(2)	945(3)	
			Molecular Extinction	34.0×10^3		
C. I. No. 593	74%	*A*. 230	Observed	460	680	900
			Calculated	460(2)	690(3)	920(4)
			Molecular Extinction	61.0×10^3		
		B. 390	Observed	780	1180	
			Calculated	780(2)	1170(3)	
			Molecular Extinction	42.0×10^3		
C. I. No. 594	75%	*A*. 230	Observed	460	680	930
			Calculated	460(2)	690(3)	920(4)
			Molecular Extinction	58.0×10^3		
		B. 400	Observed	800	1180	
			Calculated	800(2)	1200(3)	
			Molecular Extinction	58.0×10^3		

from the unsubstituted benzidine nucleus (No. 1) with the 2,2′-dimethyl derivative (No. 8). In this case, the substitution reduced the intensity of the low frequency absorption band and shifted it to a higher frequency, causing it to conform more nearly with the absorption contour of the composite half-structures. The disazo dye prepared from the 2,2′,6,6′-tetramethylbenzidine nucleus showed absorption maxima of the principal bands which closely agree with those shown for a composite of the component half-structures. However, as this dye, due to some difficulties in preparation, was considered somewhat impure, its absorption spectra was not reproduced.

Studies made in acid and basic media support the contention that non-coplanarity is present in these dye molecules. With the establishment of more polar conditions for the molecule either by the use of a solvent that would favor the establishment of the quinoid form (Figures 3, 5, and 6) or by introducing the more polar methoxyl groups into the benzidine nucleus in the 3,3′-position (Figure 4, Dye No. 7), the partial restriction previously observed for dyes containing the unsubstituted benzidine nucleus either vanishes or is greatly reduced. This becomes evident when the absorption spectra for the dye molecules altered in the above manner are examined. Close scrutiny reveals that the absorption maxima for these compounds no longer conform to two principal band systems, but may be analyzed by a single system. Therefore, dyes altered in this respect show no evident restriction to molecular resonance at the 1,1′-bond, resulting in a more complete molecular conjugation, with the molecular extinction values for the principal band greatly increased and the resulting band shifted to a lower frequency.

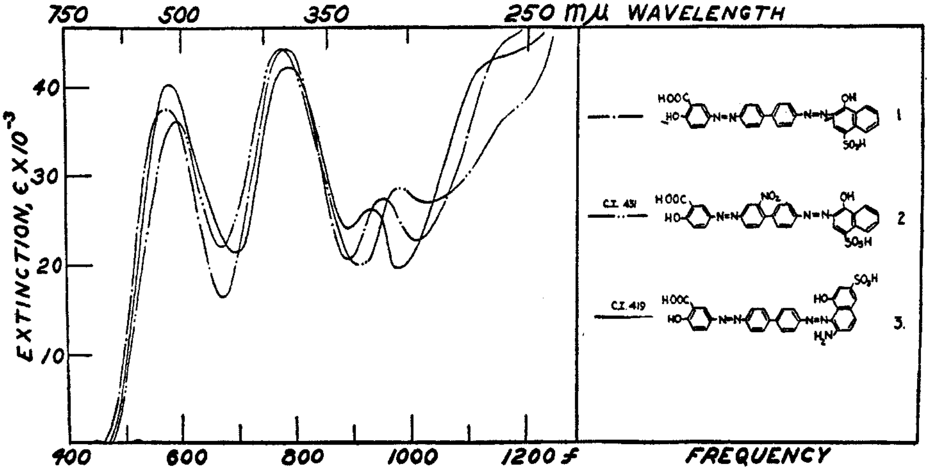

FIG. 1. THE ABSORPTION SPECTRA OF THREE UNSYMMETRICAL DISAZO DYES (IN 95% ETHANOL). (SEE TABLE I)

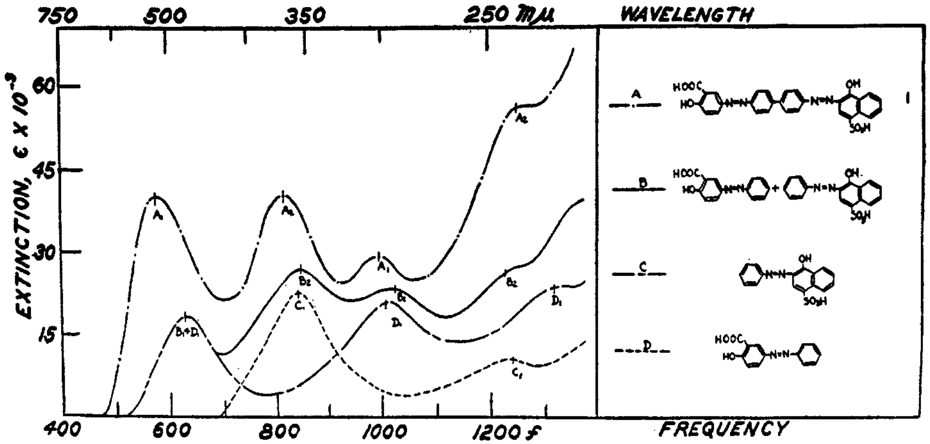

FIG. 2. THE ABSORPTION SPECTRA OF AN UNSYMMETRICAL DISAZO DYE COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (IN 95% ETHANOL).

In Table I are given data on examples of some of the dyes studied and the analysis of the observed band frequencies into multiple frequency systems characteristic of the separated resonance forms. Frequency data are given in fresnel units (vibrations per second × 10^{-12}). The first four examples are of unsymmetrical disazo dyes in which restriction at the 1,1′-diphenyl linkage has induced

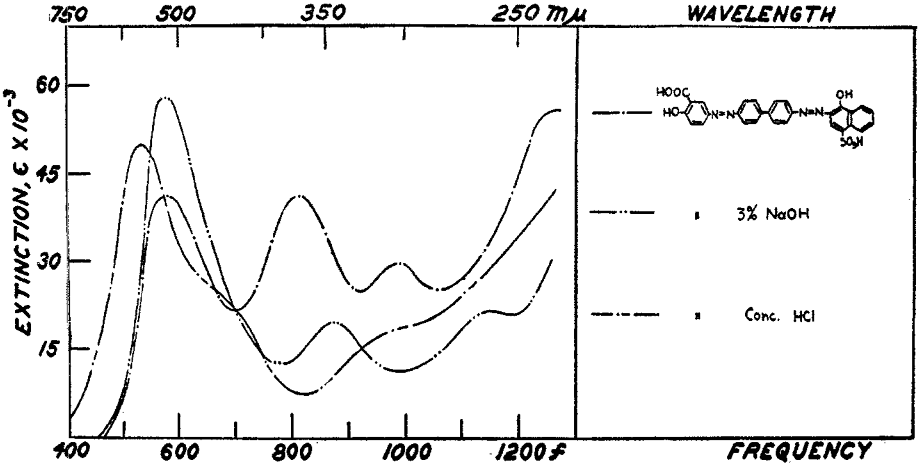

FIG. 3. A COMPARISON OF THE ABSORPTION SPECTRA OF AN UNSYMMETRICAL DISAZO BENZIDINE DYE IN 95% ETHANOL, 3% SODIUM HYDROXIDE AND 12 *N* HYDROCHLORIC ACID.

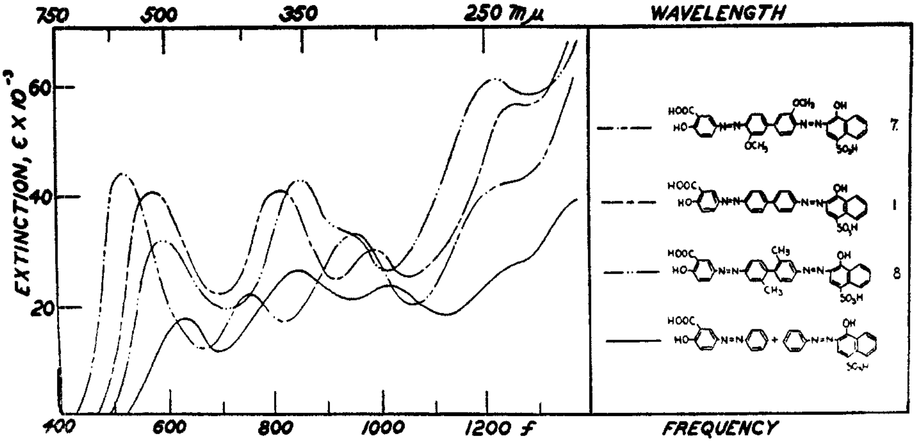

FIG. 4. A COMPARISON OF THE ABSORPTION SPECTRA OF CERTAIN UNSYMMETRICAL DISAZO BENZIDINE DYES WITH AN APPROPRIATE COMPOSITE OF THEIR HALF-STRUCTURES

separate systems corresponding to the addition of the two different component monoazo parts (see also Figures 1, 2, and 3). The separate systems are indicated by *A* and *B* in the Table and correspond to the frequency system of the monoazo component dyes (Figure 2).

The second part of Table I gives examples of some trisazo dyes in which the absorption spectra curves are resolvable into two multiple series of band systems indicating a restriction within the molecule so as to produce separate resonance systems.

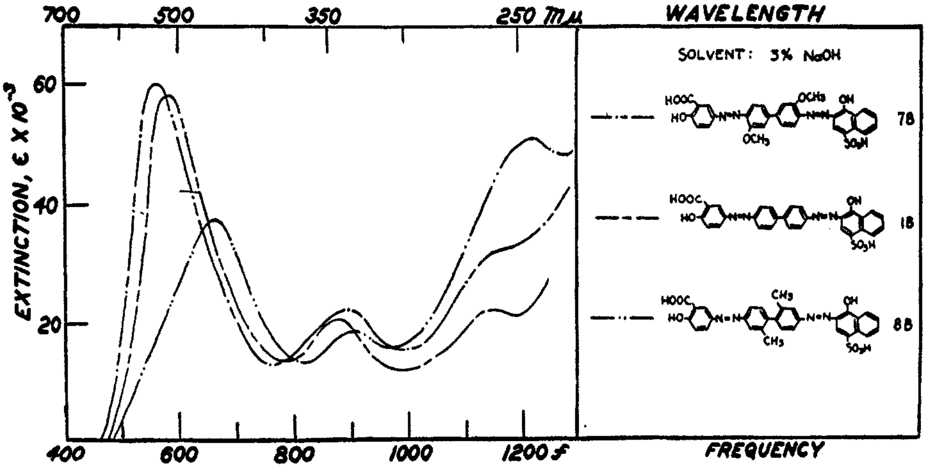

FIG. 5. THE ABSORPTION SPECTRA OF THREE TYPICAL UNSYMMETRICAL DISAZO DYES IN BASIC MEDIA

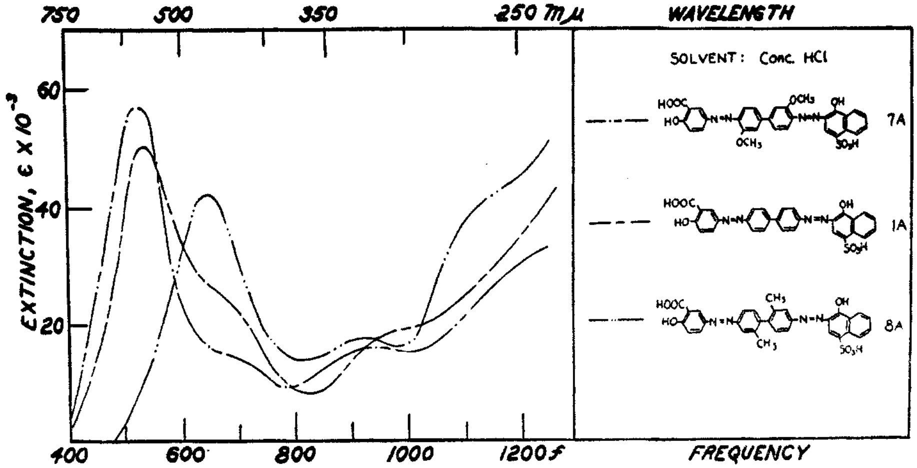

FIG. 6. THE ABSORPTION SPECTRA OF THREE TYPICAL UNSYMMETRICAL DYES IN CONCENTRATED ACIDIC MEDIA

The similarity of the trisazo dye absorption spectra with the composite curves of the addition of the absorption curves of the disazo H acid dye and monoazo residue corresponding to cleavage of the trisazo dye at the 1,1′-diphenyl linkage indicates an induced non-coplanarity and separation of the resonance system at this linkage.

The structure of these trisazo dyes may be indicated as:

C.I. No. 581 *m*-phenylenediamine $\xleftarrow{N_2}$ benzidine $\xrightarrow{N_2}$ H acid $\xleftarrow{N_2}$ aniline

C.I. No. 582 *m*-toluidinediamine $\xleftarrow{N_2}$ benzidine $\xrightarrow{N_2}$ H acid $\xleftarrow{N_2}$ aniline

C.I. No. 593 phenol $\xleftarrow{N_2}$ benzidine $\xrightarrow{N_2}$ H acid $\xleftarrow{N_2}$ *p*-nitroaniline

C.I. No. 594 salicylic acid $\xleftarrow{N_2}$ benzidine $\xrightarrow{N_2}$ H acid $\xleftarrow{N_2}$ *p*-nitroaniline

SUMMARY

An interpretation of the absorption spectra for twelve dis- and tris-azo benzidine dyes has been prepared. The absorption spectra of a series of disazo benzidine dyes and the suitable half-structures has been recorded. These data indicate that the partial restriction evident in the unsubstituted benzidine nucleus is either removed or greatly reduced by increasing the polarity of the dye structures. Increased insulation at the 1,1′-(diphenyl) bond appears when non-coplanarity of the benzidine nucleus is induced by the substitution of methyl groups in the 2,2′- and the 2,2′,6,6′-positions.

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