

THE RELATION BETWEEN THE ABSORPTION SPECTRA AND THE
CHEMICAL CONSTITUTION OF DYES. SOME EFFECTS OF POLAR
GROUPS, INSULATING LINKS, AND STERIC NON-COPLANARITY
ON THE ABSORPTION SPECTRA OF UNSYMMETRICAL TRISAZO
BENZIDINE DYES

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Earlier papers in this series have dealt with the effects of conjugation and insulation of chromophore groups in monoazo and diazo dyes. These studies have generally shown a marked dissimilarity between the absorption spectra for a dye molecule with two or more chromophoric groups in conjugation and that for the composite prepared from the summation of the absorption spectra of the separated chromophores in the single dye molecule (1-3).

For symmetrical and unsymmetrical benzidine dyes it has been shown that interrupting the conjugation in the diphenyl nucleus, either by an insulating group or by induced non-coplanarity, caused the absorption spectra of these dyes to be more nearly identical with the composite spectra formed from the appropriate half-structures. Brode and Piper (2, 3) have attained such an insulation in the benzidine structures by the insertion of an insulating methylene or better ethylene link connecting the 1,1' positions of the diphenyl nucleus. Brode and Morris (4, 5) found that nearly complete insulation could be achieved in these dye structures by inducing insulation through enforced non-coplanarity in the benzidine nucleus by the substitution of methyl groups in the 2,2', 6,6' positions. The observed effect was attributed to the inability of the tetramethyl nucleus to attain a coplanarity necessary for complete conjugation.

In a study of unsymmetrical structures several purified commercial offerings of trisazo benzidine dyes (4) gave an absorption spectra resembling that formed from the composite of the half-structures. As no insulating link or steric loadings were present in the diphenyl nucleus for these dyes, the observed insulation was at least partly ascribed to the induction effect of the polar loadings in the dye molecules investigated. However, as the exact structures of these trisazo dyes were not known, no absorption curves were prepared for these structures.

In the present paper, the absorption spectra of two unsymmetrical trisazo dyes, the dibenzyl and 2,2', 6,6'-tetramethyl diphenyl counterparts and their exact half-structures were investigated. The easily resolvable absorption spectra for these structures and their appropriate half-structures permitted a more detailed study of the restriction to molecular resonance appearing at the 1,1' bond in the benzidine nucleus.

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EXPERIMENTAL

All the intermediates used in the synthesis of the dyes were commercial products of established purity. In the case of H-acid the equivalent weight of the available product was also found (6). This value was taken in calculating the molar quantities to be used. In all cases the dyes were carefully purified and analyzed before absorption measurements were taken.

The procedures used in the preparation of the dyes were essentially those described in Fierz-David (6). The dyes containing acid groupings were purified by forming the di-*ortho*-tolylguanidine salts after the method of Rose (7). Extensive comparisons of the spectra of these salts with their corresponding sodium derivatives indicated no dissimilarity for wavelength values exceeding 240 $m\mu$.

The methods of determining the purity of these dyes were developed by Knecht (8), who used $TiCl_3$ as the reducing agent for the azo linkages. Because of the low molecular weights of the monoazo dyes, their purities were better determined by the modification of Siggia (9).

As these methods determine the relative amount of azo linkages present, the absorption spectra was easily corrected to 100% purity for plotting purposes, by using a factor calculated from the actual purity obtained. In most cases the actual purity of the prepared trisazo dyes and their intermediates was relatively high (Table I).

The absorption measurements were made by the use of a Beckman model DU quartz spectrophotometer. The dyes were made up for absorption studies in a 0.000015 *M.* solution in 95% ethanol and in some cases in solutions of concentrated hydrochloric acid or 3% sodium hydroxide. They were then introduced into a 1.00-centimeter silica cell and were measured against the proper comparison solvent. Molecular extinctions were calculated and corrected to 100% purity. In preparing the absorption curves illustrated in Figures 1 through 8, molecular extinction as the ordinate was plotted against frequency expressed in fresnels. In all figures the corresponding wavelengths in $m\mu$ are also indicated. To facilitate interpretation of the graphs, the differences in the molecular extinction values between the disazo and the composite absorption spectra from 400 to about 600 fresnels have been slightly exaggerated permitting the two curves to retain their individual identity. However, for all practical purposes these spectral curves would merge into a single curve at frequencies below 600 fresnels.

DISCUSSION OF RESULTS

Table I shows the development of the principal band systems for these dye structures through multiple frequency effects (10). A very satisfactory resolution of the absorption spectra for the benzidine trisazo dyes in alcohol solvent appeared to be a two-band system, separated at the 1, 1' position in the diphenyl nucleus. This required the assumption of two different fundamental frequencies for the proper placement of the absorption maxima observed. Good agreement between the experimental and calculated maxima was obtained. This interpretation indicated that in every case there was sufficient restriction to conjugation at the 1, 1' positions of the diphenyl nucleus, when measured in alcohol, to divide the entire chromogen into two partially insulated chromophores. Examples of the absorption spectra obtained for these restricted structures may be observed in Figures 1 and 5. It may be further noted from Figures 2 and 6 that the absorption spectra obtained in the alcohol solvent for the trisazo dyes with no apparent insulating or steric barriers to conjugation at the 1, 1' position of the diphenyl nucleus, satisfactorily follow the composite spectra prepared from the exact half-structures. This indicated that a polar induced insulation was effective

TABLE I
DATA ON THE PRINCIPAL BAND SYSTEMS OF THE TRISAZO DYES AND THEIR EXACT
HALF-STRUCTURES

Dye (Color Index No. Indicated as C. I. No.)	Purity Analytical Data, %	Fundamental Frequency, (F)	Location of 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 (1.) Diphenyl Nucleus and Half Structures (Figure 2)						
Synthetic counterpart C. I. 581	97	A. 250	Observed	508	760	950
			Calculated	500(2)	750(3)	1000(4)
			Molecular extinction	63×10^3		
		B. 315	Observed	635	950	
			Calculated	630(2)	945(3)	
			Molecular extinction	53×10^3		
Half-structure (A. Fig. 2)	74	260	Observed	525	780	960
			Calculated	520(2)	780(3)	1040(4)
			Molecular extinction	46.5×10^3		
Half-structure (B. Fig. 2)	100	360	Observed	730	1070	
			Calculated	720(2)	1080(3)	
			Molecular extinction	21×10^3		
(2.) Tetramethyl Substituted Nucleus and Half-Structures (Figure 3)						
Tetramethyl nucleus C. I. 581	84	A. 260	Observed	530	750	940
			Calculated	520(2)	780(3)	1040(4)
			Molecular extinction	43×10^3		
		B. 360	Observed	715	1050	
			Calculated	720(2)	1065(3)	
			Molecular extinction	40×10^3		
Half-structure (A. Fig. 3)	70	260	Observed	535	800	950
			Calculated	520(2)	780(3)	1040(4)
			Molecular extinction	37×10^3		
Half-structure (B. Fig. 3)	100	360	Observed	730	1070	
			Calculated	720(2)	1080(3)	
			Molecular extinction	21×10^3		
(3.) Dibenzyl Nucleus and Half-Structures (Figure 4)						
Dibenzyl nucleus C. I. 581	94	A. 260	Observed	526	730	930
			Calculated	520(2)	780(3)	1040(4)
			Molecular extinction	45×10^3		

TABLE I—*Continued*

Dye (Color Index No. Indicated as C. I. No.)	Purity Analytical Data, %	Fundamental Frequency, (F)	Location of 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 (3.) Dibenzyl Nucleus and Half-Structures (Figure 4)— <i>Continued</i>						
Dibenzyl nucleus C. I. 581— <i>Cont.</i>		B. 360	Observed Calculated Molecular extinction	730 720(2) 43×10^3	1060 1080(3)	
Half-structure (A. Fig. 4)	73	260	Observed Calculated Molecular extinction	525 520(2) 44×10^3	760 780(3)	940 1040(4)
Half-structure (B. Fig. 4)	100	360	Observed Calculated Molecular extinction	730 720(2) 21×10^3	1070 1080(3)	
Part II (1.) Diphenyl Nucleus and Half-Structures (Figure 6)						
Synthetic counterpart C. I. 593	97	A. 235	Observed Calculated Molecular extinction	470 470(2) 72×10^3	730 705(3)	890 940(4)
		B. 395	Observed Calculated Molecular extinction	790 790(2) 52×10^3	1200 1185(3)	
Half-structure (A. Fig. 6)	92	240	Observed Calculated Molecular extinction	485 480(2) 50×10^3	730 720(3)	920 960(4)
Half-structure (B. Fig. 6)	98	420	Observed Calculated Molecular extinction	855 840(2) 29×10^3	1250 1260(3)	
(2.) Tetramethyl Substituted Nucleus and Half-Structures (Figure 7)						
Tetramethyl nucleus C. I. 593	95	A. 235	Observed Calculated Molecular extinction	473 470(2) 69×10^3	730 705(3)	900 940(4)
		B. 415	Observed Calculated Molecular extinction	830 830(2) 52×10^3	1200 1245(3)	

TABLE I—Concluded

Dye (Color Index No. Indicated as C. I. No.)	Purity Analytical Data, %	Fundamental Frequency (F)	Location of 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			
(3.) Dibenzyl Nucleus and Half-Structure (Figure 8)						
Half-structure (A. Fig. 7)	85	240	Observed Calculated Molecular extinction	480 480(2) 62×10^3	730 720(3)	920 960(4)
Half-structure (B. Fig. 7)	95	420	Observed Calculated Molecular extinction	855 840(2) 29×10^3	1250 1260(3)	
Dibenzyl nucleus C. I. 593	90	A. 240	Observed Calculated Molecular extinction	480 470(2) 64×10^3	730 720(3)	920 960(3)
		B. 420	Observed Calculated Molecular extinction	850 840(2) 47×10^3	1245 1260(3)	
Half-structure (A. Fig. 8)	86	240	Observed Calculated Molecular extinction	480 480(2) 59×10^3	730 720(3)	920 960(4)
Half-structure (B. Fig. 8)	100	420	Observed Calculated Molecular extinction	855 840(2) 29×10^3	1250 1260(3)	

tive at the 1, 1' link in preventing the complete conjugation of the entire molecule. For this solvent then, the restriction was ascribed to a decrease in the freedom of the electrons ordinarily available for double bond formation at the 1, 1' link, probably caused by the inductive influence of the polar loadings on either side of this bond. This effect was more apparent for the synthetic replica of C. I. 593, Figure 6 than for C. I. 581, Figure 2 (11). This difference was believed to be due to the enhanced polar conditions occasioned by the *p*-nitro, *p*-phenolic loadings present in that structure.

As earlier predicted from studies on the commercial products (4) the absorption spectra prepared in ethanol for the synthetic trisazo dye molecules definitely supported the existence of a barrier to complete conjugation at the 1, 1' bond in the diphenyl nucleus. Although no absorption curves have been included, studies of the absorption data for the trisazo structures indicated that the establishment of polar conditions favoring quinoid development greatly reduced or eliminated

TABLE II

DATA SHOWING THE EFFECT OF INCREASING INSULATION IN THE TRISAZO NUCLEUS ON THE POSITIONAL FREQUENCY AND MOLECULAR EXTINCTION OF THE PEAK FOR THE PRINCIPAL BAND (Solvent C_2H_5OH)

C.I. No. (Synthetic)	Trisazo Dye Nucleus	Peak Frequency For The Principal Band (F)			Difference (F)	Molecular Extinction For The Principal Band ($E \times 10^3$)			Difference ($E \times 10^3$)
		Trisazo	Disazo	Monoazo		Trisazo	Disazo	Mono- azo	
581	Diphenyl	A. 508	525		17	63	46.5		16.5
		B. 635		730	95	39*		21	
	Tetramethyl	A. 530	535		5	43	37		6
		B. 715		730	15	26*		21	
	Dibenzyl	A. 526	525		1	45	44		1
		B. 730		730	0	24*		21	
593	Diphenyl	A. 470	485		15	72	50		22
		B. 790		855	65	36*		29	
	Tetramethyl	A. 473	480		7	69	62		7
		B. 830		855	25	31*		29	
	Dibenzyl	A. 480	480		0	64	59		5
		B. 850		855	5	30*		29	

* These values representing the contribution of the monoazo half-structures to the peak extinction for the B band of the trisazo absorption spectra were arrived at by subtracting the molecular extinction contributed by the disazo half-structure at the peak frequency from the molecular extinction values for the trisazo B-band maxima recorded in Table I.

this apparent restriction in dye molecules showing no structural barrier to complete conjugation. This permitted the interpretation of the band maxima by the use of a single fundamental frequency. It is probable that the inductive effect of polar loadings in restricting double-bond formations in such molecules was largely overcome by the stronger resonance effect accompanying the enhanced polar conditions.

Table II shows the recorded frequency shifts and the molecular extinction values for the principal band in the trisazo nuclei in comparison with similar recorded values for the exact half-structures. The effects of differing degrees of insulation are clearly evident from the relative shifts of the absorption bands and molecular extinction values for the structures studied. From Table II and Figures 1 through 8, it is to be noted that the best insulation at the 1,1' bond was afforded by the insulating ethylene link, followed closely by the 2,2', 6,6'-tetramethyl substitution, and finally that believed due to induced polar effects.

Figures 3 and 7 indicate that there is a pronounced similarity in both frequency position and band height between the tetramethyl restricted nuclei and the composite spectra prepared from their half-structures. This similarity is even more evident with the slightly better insulation afforded by the ethylene link depicted in Figures 4 and 8. A study of these figures reveals that both structural modifications greatly enhance the partial restriction ascribed to the polar induction illustrated in Figures 2 and 6.

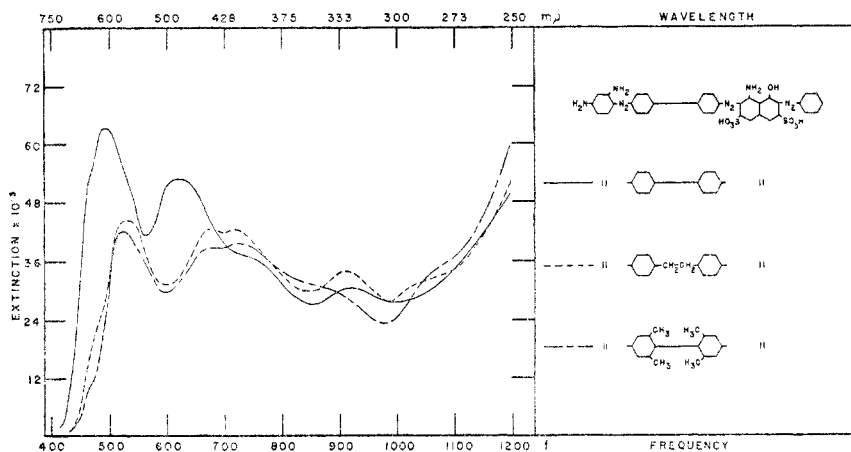


FIG. 1. THE ABSORPTION SPECTRA FOR THE COUNTERPART OF C. I. 581 COMPARED WITH THE ABSORPTION OF ITS STRUCTURALLY INSULATED DERIVATIVES (In 95% Ethanol) (See Tables I and II).

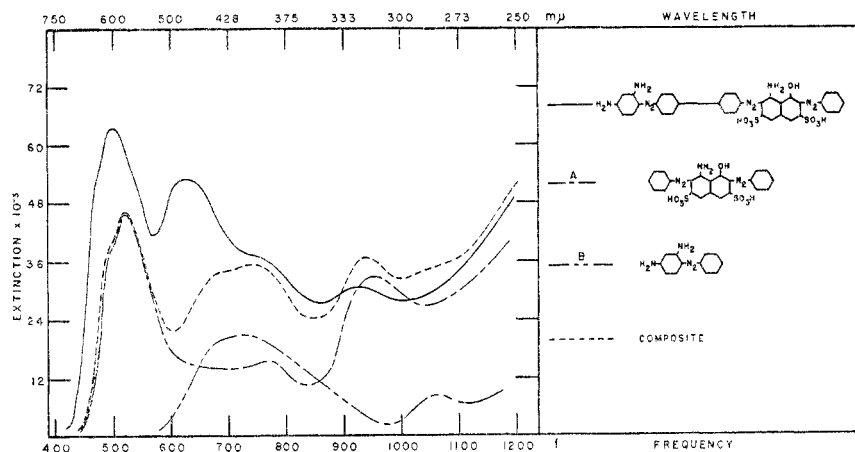


FIG. 2. THE ABSORPTION SPECTRA FOR THE COUNTERPART OF C. I. 581 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

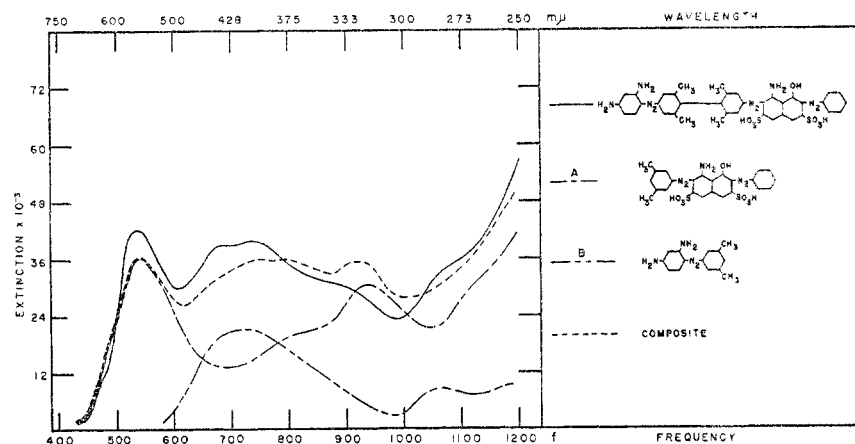


FIG. 3. THE ABSORPTION SPECTRA FOR THE TETRAMETHYL DERIVATIVE OF C. I. 581 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

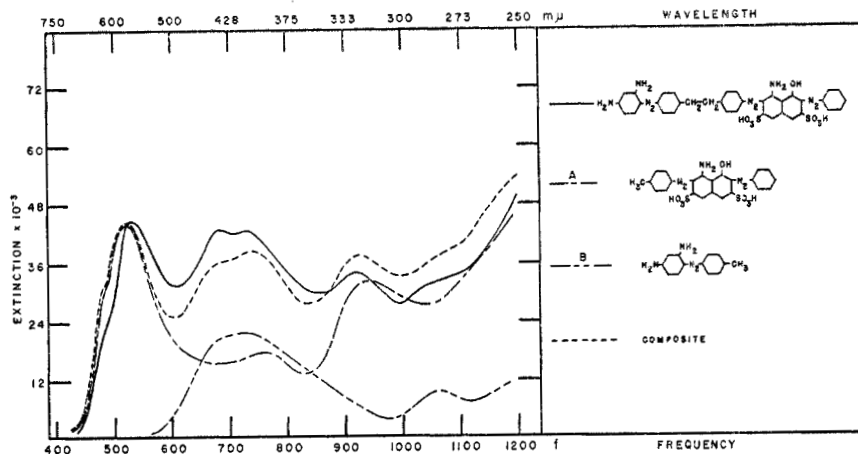


FIG. 4. THE ABSORPTION SPECTRA FOR THE DIBENZYL DERIVATIVE OF C. I. 581 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

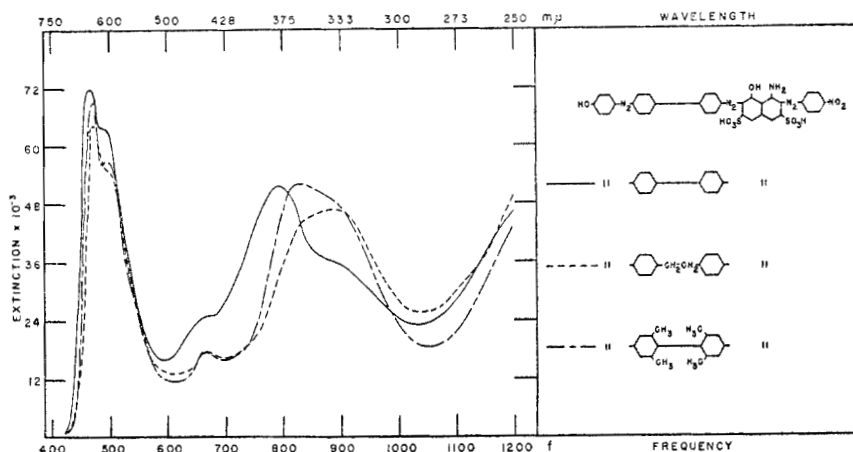


FIG. 5. THE ABSORPTION SPECTRA FOR THE COUNTERPARTS OF C. I. 593 COMPARED WITH THE ABSORPTION OF ITS STRUCTURALLY INSULATED DERIVATIVES (In 95% Ethanol) (See Tables I and II).

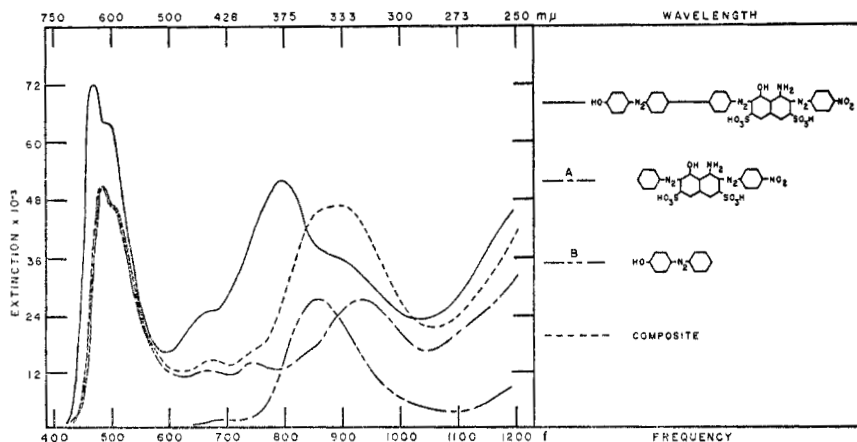


FIG. 6. THE ABSORPTION SPECTRA FOR THE COUNTERPART OF C. I. 593 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

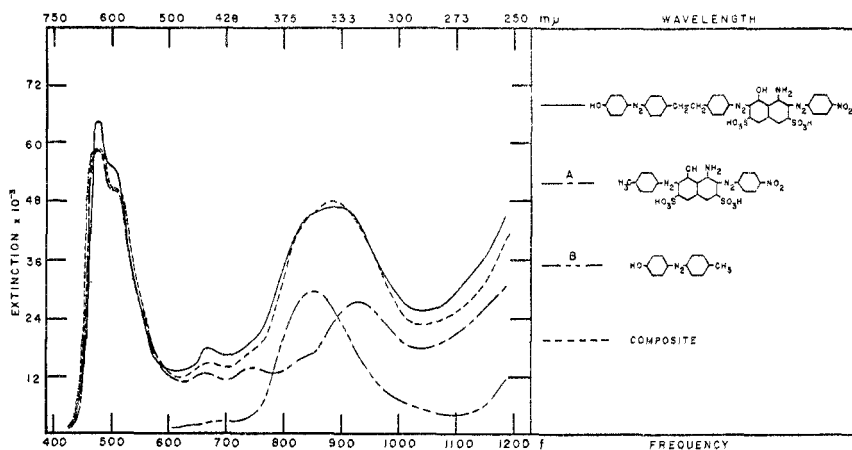


FIG. 7. THE ABSORPTION SPECTRA FOR THE TETRAMETHYL DERIVATIVE OF C. I. 593 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

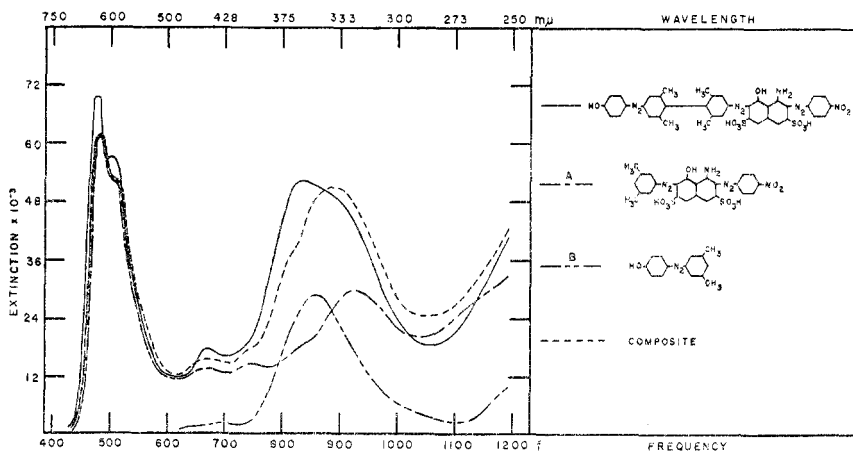


FIG. 8. THE ABSORPTION SPECTRA FOR THE DIBENZYL DERIVATIVE OF C. I. 593 COMPARED WITH THE ABSORPTION OF ITS HALF-STRUCTURES AND ITS COMPOSITE (In 95% Ethanol) (See Tables I and II).

In every case (Table II), the frequency shifts in the positions of the band maxima occasioned by structural alterations in the trisazo diphenyl nuclei were larger for the band system attributable to the monoazo half-structure than those recorded for the disazo half-structure. This variation was expected, due in part, to a considerable difference in the molecular weight of the two half-structures. A further influencing factor to this difference in magnitude was believed to be the relatively greater energy contribution made by the disazo half-structure to the characteristic absorption pattern associated with the entire chromogen.

SUMMARY

Two unsymmetrical benzidine dyes, their closely related, structurally insulated, counterparts, and their corresponding exact half-structures were synthesized and their absorption spectra were prepared. An interpretation of the spectra for these compounds has been submitted. All evidence in this presentation favors the belief that the amount of interaction between chromophoric groups in all the trisazo dye molecules studied, when measured in 95% ethanol, was relatively small even though no structural restrictions were imposed. Hence, it appears that these molecules assume a non-coplanar arrangement in such a solvent. The small amount of interaction permitted these polar restricted structures can either be greatly reduced by the establishment of a steric non-coplanarity at the 2,2', 6,6' positions in the diphenyl nucleus, or practically eliminated by the insertion of the ethylene link connecting the 1,1' positions of this nucleus.

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REFERENCES

- (1) FUNKHAUSER AND BRODE, *J. Am. Chem. Soc.*, **56**, 2172 (1934).
- (2) PIPER AND BRODE, *J. Am. Chem. Soc.*, **57**, 135 (1935).
- (3) BRODE AND PIPER, *J. Am. Chem. Soc.*, **63**, 1502 (1941).
- (4) BRODE AND MORRIS, *J. Org. Chem.*, **13**, 200 (1948).
- (5) MORRIS AND BRODE, *J. Am. Chem. Soc.*, **70**, 2485 (1948).
- (6) FIERZ-DAVID AND BLANGEY, *Fundamentals of Dye Chemistry*, Interscience Publishers, Inc., New York, 1949.
- (7) ROSE, *Ind. Eng. Chem.*, **25**, 1028 (1933).
- (8) KNECHT AND HIBBERT, *New Reduction Methods in Volumetric Analysis*, Longmans, Green, and Co., London, 1925.
- (9) SIGGIA, *Qualitative Organic Analysis via Functional Groups*, John Wiley and Sons, Inc., New York, 1949.
- (10) BRODE, *Bureau Standards J. Research*, **2**, 501 (1929).
- (11) F. M. ROWE, Editor, *Colour Index*, The Society of Dyers and Colourists, D. Van Nostrand and Co., New York, 1924.