β-phenylethyl and γ-phenylpropyl chloride have been obtained in the vapor phase and in cyclohexane solution.

2. A theoretical discussion of the results is given.

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

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XX. Induced Non-Coplanarity in Symmetrical Benzidine Dyes[1]

BY ROBERT J. MORRIS[2] AND WALLACE R. BRODE[2]

In an earlier paper in this series[3] an investigation was made on the separation of chromophores in disazo dyes by the introduction of insulating methylene, ethenylene and ethylene groups. This study was made on both symmetrical and unsymmetrical disazo dyes and from the data obtained it was shown that when two chromophores were separated by one or two methylene groups, the chromophores function almost as though they were in separate molecules. However, the frequency of each chromophore was slightly diminished by the presence of the other. This was considered due either to the mutual influence of the two chromophores or to added molecular weight. The closer the separated chromophores approached each other when directly connected, the greater their mutual effect. When the azo chromophores were connected by a well-defined conjugate system, each chromophore strongly influenced the electronic excitation of the other.

The observed shift of the principal absorption band to lower frequency caused by an increase in molecular weight of the compound was, however, of a low order of magnitude compared with the shift caused by the conjugation of chromophoric systems.

In azo dye structures, the conditions effecting the coplanarity of the dye molecule would also be expected to have considerable effect on their absorption spectra. As early as 1923, Ley and Rincke[4] made comparisons of the absorption spectra of planar *trans*-stilbene with *trans*-α-methylstilbene. Interpretation of their results indicated that the methyl group in the latter crowds an ortho hydrogen of the more remote benzene ring. Planarity was therefore inhibited, as was, in consequence, the resonance interaction between the two benzene rings. The unsubstituted benzidine nucleus has been shown to exhibit some steric inhibition to complete coplanarity because of the bond angles and distances involved in its structure.[5] Moyer and Adams[6] have shown that the compound 3,3′-diaminodimesityl, because of the steric effects of the methyl groups in the 2,2′,6,6′-positions, was definitely non-coplanar. It was further predicted that the characteristic effect of the conjugation of the biphenyl molecule on the absorption spectra would vanish for compounds possessing this inhibited structure. This hypothesis was supported by observations conducted by Pickett.[7] In this investigation it was shown that the absorption spectra of bimesityl was almost identical with that of mesitylene but differed significantly from biphenyl. Other examples of the effect of 2,2′-substitution on the absorption spectra of the biphenyl molecule have been recorded by Rodebush.[8] Jones[9] has also presented data and a general review on steric hindrance of resonance.

Experimental

The dyes prepared for this study were synthesized from intermediates of known purity by standard procedures for diazotization and coupling. The cresols used were available in grades of acceptable purity. Benzidine, 3,3′-dimethylbenzidine and 3,3′-dimethoxybenzidine obtained from Eastman Kodak Company were analyzed and shown to be of acceptable purity. The 2,2′-dimethyl[10] and 2,2′,6,6′[11]-tetramethyl benzidine derivatives were synthesized and purified before use.

All the dyes prepared were purified by repeated recrystallization from dilute acetic acid until a constant purity resulted. The analysis for the purity of all dye samples was accomplished by the use of a standardized titanium trichloride solution.

Absorption measurements were made by the use of a Beckman quartz spectrophotometer. The properly diluted samples were introduced into 1.00-cm. fused silica cells and their absorption spectra determined using the corresponding solvent as a reference solution. Readings were generally taken at 10 $m\mu$ intervals, although in some places determinations were made at closer intervals to increase the accuracy of the measurements. A dilution to 0.000015 *M* served for obtaining the complete absorption spectra of all the dyes measured. In neutral solu-

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[2] Present address. (R. J. M.) Department of Chemistry, University of Nevada, Reno, Nevada; (W. R. B.) National Bureau of Standards, Washington 25, D. C.

[3] W. R. Brode and J. D. Piper, THIS JOURNAL, **57**, 135 (1935); **63**, 1502 (1941).

[4] H. Ley and F. Rincke, *Ber.*, **56**, 771 (1923).

[5] J. M. Robertson and I. Woodward, *Proc. Roy. Soc.* (*London*), **A142**, 333 (1933).

[6] W. W. Moyer and R. Adams, THIS JOURNAL, **51**, 630 (1929).

[7] L. W. Pickett, G. F. Walter and H. France, *ibid.*, **58**, 2296 (1936).

[8] B. Williamson and W. H. Rodebush, *ibid.*, **63**, 3018 (1941).

[9] L. A. Jones, *Chem. Reviews*, **32**, 1 (1943); *ibid.*, **63**, 1658 (1941); **67**, 2127 (1945).

[10] P. Jacobsen, *Ber.*, **28**, 2541 (1895).

[11] R. B. Carlin, THIS JOURNAL, **67**, 928 (1945).

tion this concentration was attained by the proper dilution of a 0.00006 *M* alcoholic solution (referred to as the stock solution) of the dye by use of additional 95% ethanol. For measurements in basic media, the final concentration of 0.000015 *M* was attained by 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* hydrochloric acid (concd. HCl). Absorption data on the dyes, after correction for salt and inert non-absorbing material as indicated by the analytical data, were recorded with molecular extinction as ordinates and frequency (fresnel) as abscissa. (fresnel = vibrations per sec. × 10^{-12} = wave number per cm. × speed of light in cm. per second, *i. e.*, $1/\lambda = \nu' = \nu/c$ where λ = wave length, ν' = wave number, ν = frequency and c = speed of light.) Molecular extinction (ϵ) is defined as k × molecular weight where k is the specific extinction. $k = E/cd$; where E = extinction, c = concn. in g. per l. and d = cell length in cm.

Discussion of Results

The curves obtained for these azo dyes show definite changes in the absorption spectra as a noncoplanar condition becomes established for the benzidine nucleus. This is evident by the shift of the absorption to higher frequencies with the establishment of these conditions. Such a shift is contrary to the expected change with the increasing molecular weight. Although a partial restriction to complete molecular conjugation has been previously reported for the diphenyl molecule because of the interference of the hydrogen atoms in the 2,2′,6,6′-positions, it is believed that the unsubstituted benzidine dyes possessing this structure show considerable conjugation through the 1,1′-bond. This was demonstrated by the distinct change in the absorption bands of these dyes when the relatively large, unreactive methyl groups are introduced in the 2,2′- and 2,2′,6,6′-positions on the benzidine nucleus. Figures 1, 2 and 3 show the definite shift in the absorption band with these molecular changes. The marked change in the absorption observed is undoubtedly

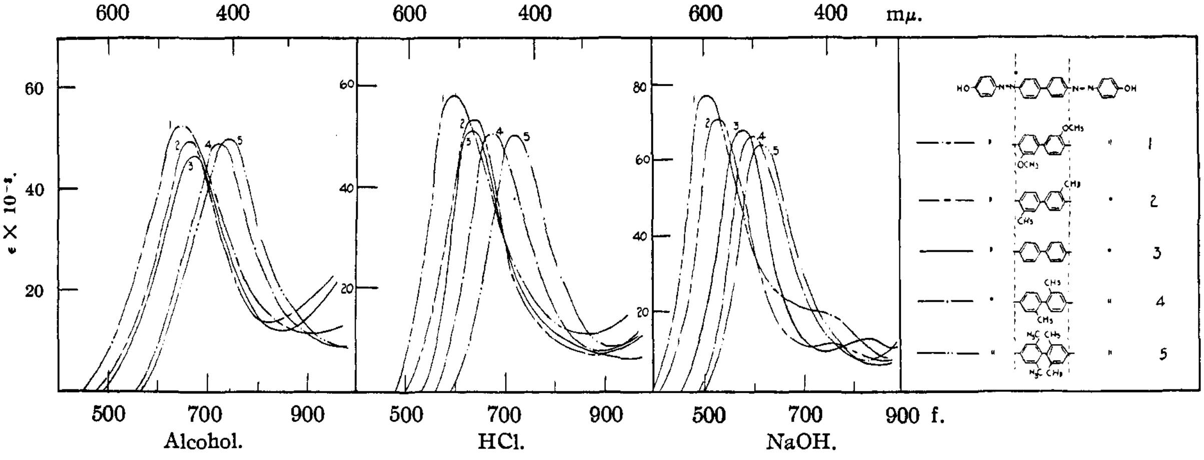


Fig. 1.—The absorption spectra recorded for the dyes prepared by tetrazotization and coupling benzidine and the indicated substituted benzidines with phenol. The absorption spectra from left to right were taken in 95% ethanol, 3% sodium hydroxide and concentrated hydrochloric acid.

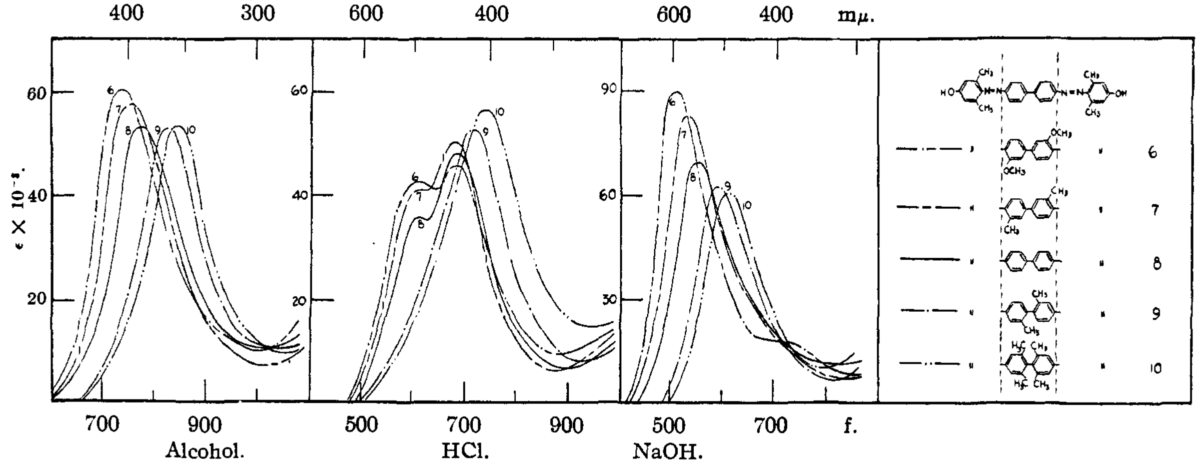


Fig. 2.—The absorption spectra recorded for the dyes prepared by tetrazotization and coupling benzidine and the indicated substituted benzidines with *p*-xylenol. The absorption spectra from left to right were taken in 95% ethanol, 3% sodium hydroxide and concentrated hydrochloric acid.

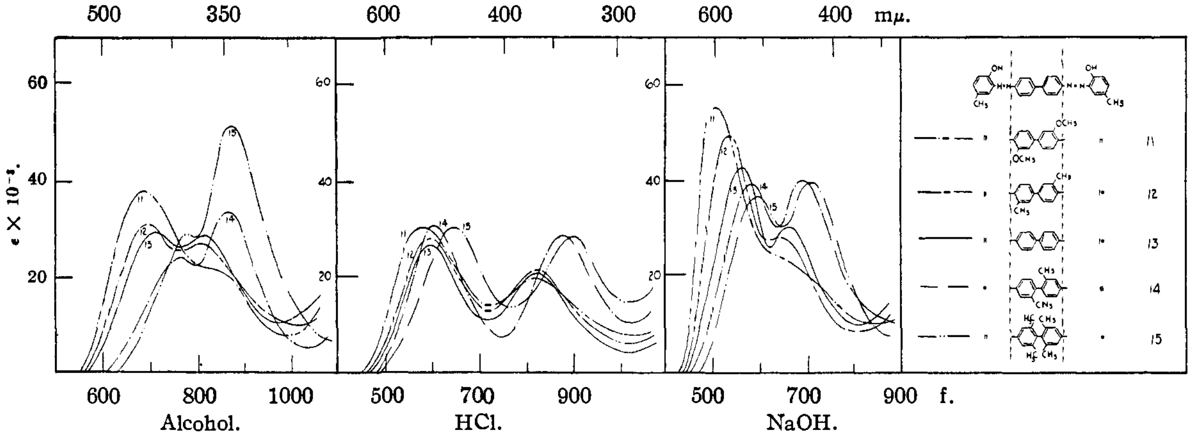
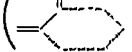
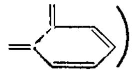


Fig. 3.—The absorption spectra recorded for the dyes prepared by tetrazotization and coupling benzidine and the indicated substituted benzidines with *p*-cresol. The absorption spectra from left to right were taken in 95% ethanol, 3% sodium hydroxide and concentrated hydrochloric acid.

caused by the establishment of more exaggerated non-planar conditions for the half-structures involved. The Fig. 1 shows a typical series of curves using phenol as the coupling constituent; similar types of curves were also obtained when ortho cresol and meta cresol were coupled, except for a very slight displacement to lower frequency due to the additional weight. In Fig. 2, a change in the general absorption curves of the dyes derived from *p*-xylenol was evident in the basic media. This is probably due to the increased difficulty that such dyes would encounter in establishing a quinoid structure due to the interference of the large groups ortho to the azo chromophores. In Fig. 3, the double band formation evident throughout the absorption for these compounds may be ascribed to the two possible chromophoric paths in the quinoid form of phenylazo-*p*-cresol ( and ). This would result in a resolvable difference in the absorption for each conjugate system. Figures 3 and 5 illustrate this tendency. These ortho-coupled compounds do not appear at first to bear the simple relationship between the various substituted members as that shown by the para-coupled members. However, when the average of the frequencies of the component parts of the ortho-coupled bands are taken and compared with the frequency changes observed for the para-coupled bands, it will be noted that a similar relationship exists.[12]

Complete insulation of the two chromophores present in these disazo molecules was not accomplished by 2,2′-dimethyl substitution. So pronounced was this insulation for the 2,2′,6,6′-tetramethylbenzidine structure, however, that the absorption spectra exhibited by these dyes not only closely resembled the spectra for a suitable concentration of a corresponding half structure, but also was almost identical with the absorption of a molecule of like structural type in which the insulation at the 1,1′-bond was accomplished by the insertion of a methylene or ethylene link. In Fig. 4 an example of these similarities may be noted. This similarity serves to further indicate the pronounced restriction to complete molecular conjugation through the 1,1′-bond, when a definite non-coplanarity for the two half structures is present.

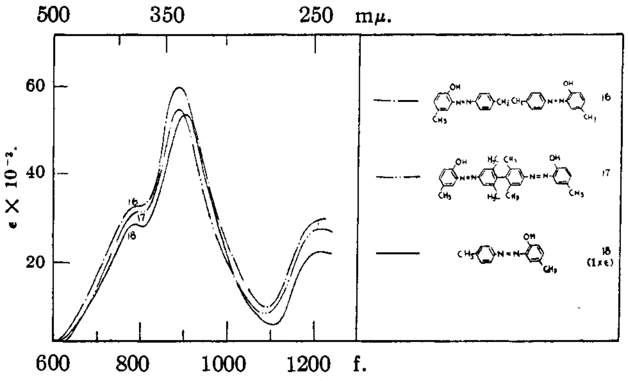


Fig. 4.—Comparison data are presented for the absorption spectra in alcohol solution of two disazo dyes showing restriction to molecular conjugation and a monoazo dye of suitable construction to most nearly represent a half-structure for these molecules.

Absorption spectra taken in acidic and basic media again illustrate the decisive effects of non-coplanarity. With the establishment of more polar conditions for the molecule, either by the use of a solvent that favors the quinoid form for these structures or by introducing the more polar methoxy groups into the 3,3′-position on the benzidine nucleus, even the partial restriction evident for the unsubstituted benzidine nucleus was greatly reduced. This is shown by the marked shift of the

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[12] W. R. Brode, "Major Instruments of Science and their Applications to Chemistry" (Vol. 4 of "Frontiers in Chemistry"), Interscience Pub., New York, N. Y., 1945, p. 115.

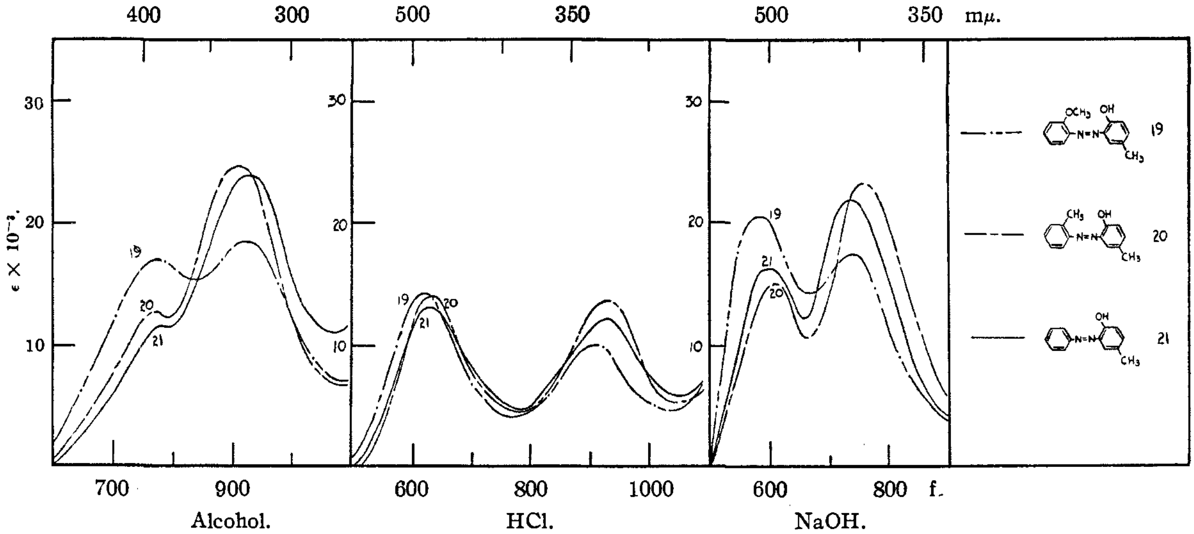

Fig. 5.—The absorption spectra recorded for the monoazo dye phenylazo-*p*-cresol and its derivatives. The absorption spectra from left to right were taken in 95% ethanol, 3% sodium hydroxide and concentrated hydrochloric acid.

absorption to lower frequency attendant with a distinctive increase in the molecular extinction for the molecules altered in the aforementioned ways. The establishment of these more coplanar conditions was most evident in the changes in the absorption spectra recorded for the benzidine dyes as illustrated in Figs. 1, 2 and 3. However, even the more simple monoazo dyes revealed these tendencies as indicated in the Fig. 5. The study of the steric effects in symmetrical dyestuffs as reported in this paper has been extended to unsymmetrical disazo dyes and to trisazo dyes and will be reported in a separate discussion.[13]

Summary

A spectrophotometric study has been made on twenty-five symmetrical benzidine dyes and the absorption spectra for fifteen of these structures have been reproduced as recorded in neutral, acidic and basic media. An absorption study of phenyl-azo-*p*-cresol dye and its methyl and methoxy derivatives was made. The absorption spectra exhibited by the insulated disazo structures caused by non-coplanarity was compared with a corresponding half structure as well as a similar molecule in which the insulation was derived from the insertion of an ethylene link. These data indicate that compounds with restricted rotation differ markedly in their absorption spectra from those capable of free rotation. The partial conjugation present in these dyes is aided by the establishment of a more coplanar configuration for the benzidine nucleus. This molecular conjugation is progressively inhibited by the introduction of the relatively large, unreactive methyl groups in the 2,2′- and 6,6′-positions on the benzidine nucleus. For the dyes prepared from the tetramethyl substituted nucleus, the insulation to molecular conjugation at the 1,1′-bond appears almost complete.

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[13] W. R. Brode and R. J. Morris, *J. Org. Chem.*, **13**, 200 (1948).