sure of 2600 lb. per sq. in. 1.5 g. of duril gave 0.67 g. of duroin.

Table I gives the melting points and analytical data for the new compounds prepared in this study.

Experimental

2,3,5,6-Tetramethylbenzoic Acid.—From 50 g. of bromodurene, 32.7 g. of ethyl bromide and 16.2 g. of magnesium was obtained 25.5 g. (61%) of the acid; m. p. 179–180° (cor.).[4] The acid chloride was prepared by the action of thionyl chloride; b. p. 105–106° (6 mm.); m. p. 59–60°.

2,3,4,6-Tetramethylbenzoic Acid.—In this synthesis 100 g. of bromoisodurene gave 47.3 g. of the acid; m. p. 164–166°.[4] The acid chloride boiled at 102–103° (3 mm.); n^{20}_{D} 1.5380; d^{20}_{20} 1.1087.

Summary

Duril and isoduril have been prepared and converted to the corresponding enediols. Each of the latter has been isolated in *cis* and *trans* modifications.

The corresponding benzoins and 1,2-diarylethanes have also been made.

URBANA, ILLINOIS RECEIVED MARCH 12, 1941

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

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

BY WALLACE R. BRODE AND JOHN D. PIPER

It was pointed out in a preceding paper[1] that a study of unsymmetrical disazo dyes should yield valuable information concerning the relative influence of the chromophores. In the present paper a spectrophotometric study has been made of a series of such dyes. The intermediates for the two ends, *p*-cresol and dimethylaniline, were chosen because of the markedly different type of absorption bands produced by these intermediates in monoazo and symmetrical disazo dyes. The *p*-cresol dyes, due to their *o*-hydroxy-azo coupling, give a set of double banded maxima quite similar to the β-naphthol type (which is also an *o*-hydroxyazo coupling). The dimethylaniline dyes produce a single intense band which is characteristic of para coupled auxochromes.[2]

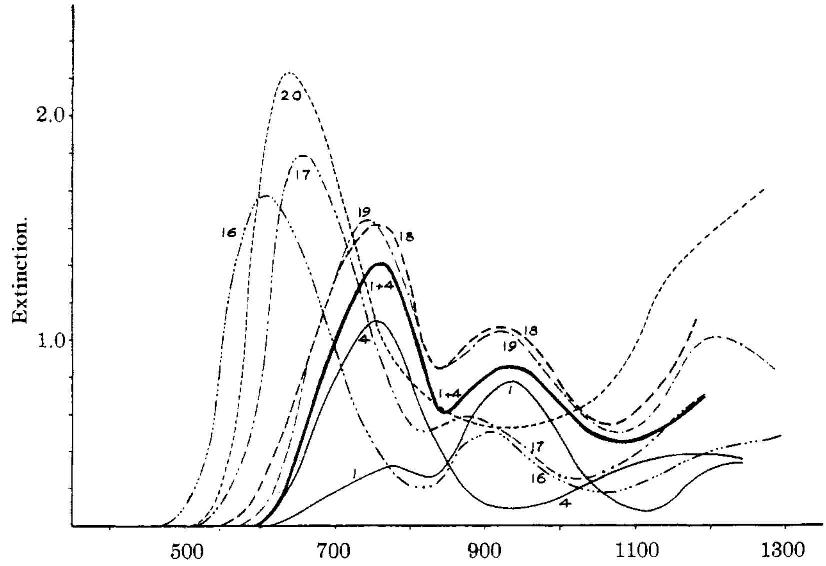

Fig. 1.—Absorption spectra of disazo dyes in 95% ethyl alcohol: dye 1, *o*-phenylazo-*p*-cresol; dye 4, *p*-phenylazodimethylaniline; dyes 16 to 20 as indicated in Table I.

Preparation.—In the preparation of the previously described[1] symmetrical disazo dyes the process of direct

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(1) Piper and Brode, THIS JOURNAL, **57**, 135 (1935).

(2) Brode, *ibid.*, **51**, 1204 (1929).

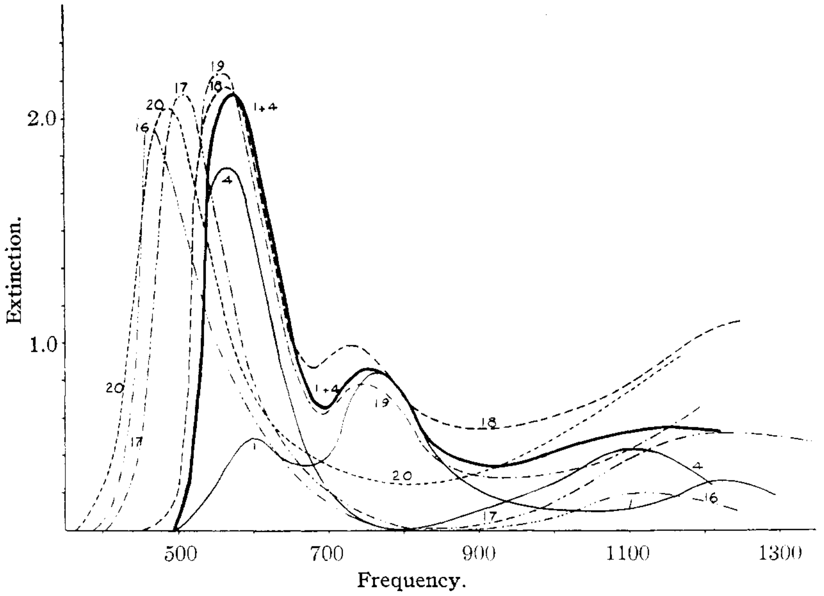

Fig. 2.—Absorption spectra of disazo dyes in concd. hydrochloric acid: dye 1, *o*-phenylazo-*p*-cresol; dye 4, *p*-phenylazodimethylaniline; dyes 16 to 20 as indicated in Table I.

tetrazotization and coupling could be used in most cases; however, in the preparation of the unsymmetrical disazo dyes described in this paper, it was found inadvisable to attempt a partial coupling of the diamine. In order to obtain compounds of definite purity it was necessary to acetylate one of the amino groups to protect it during the diazotization of the other, couple this, hydrolyze off the acetyl group, diazotize and couple to the other intermediate.

methylaniline. The coupling was made in dilute acetic acid and required from two to fourteen days for completion. The resulting monoazo dyes were recrystallized from bromobenzene. The protecting acetyl groups were then removed by hydrolysis in alcoholic solution and the free amines recrystallized from the same solvent. The dyes were purified by crystallization from bromobenzene.

Methods.—The methods and accuracy of observation were the same as in the earlier papers of this series.[1,3]

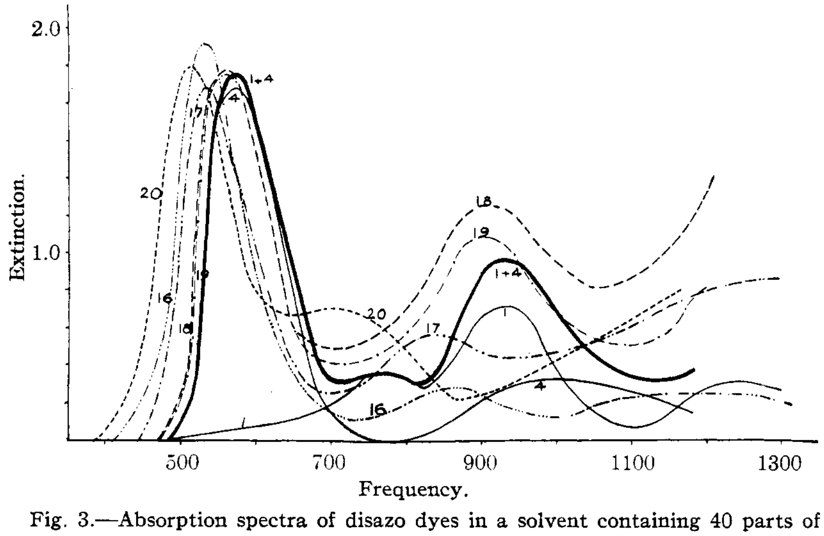

Fig. 3.—Absorption spectra of disazo dyes in a solvent containing 40 parts of 95% ethyl alcohol to 60 parts of concd. hydrochloric acid: dye 1, *o*-phenylazo-*p*-cresol; dye 4, *p*-phenylazodimethylaniline; dyes 16 to 20 as indicated in Table I.

In general the partial acetylation was accomplished by the reaction of acetic anhydride with dilute solutions of the amines in alcohol. The monoacetyl derivatives were recrystallized from xylene, diazotized and coupled to di-

Discussion of Results.—The absorption spectra curves of five unsymmetrical disazo dyes at

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(3) Brode, *J. Research Natl. Bur. Standards*, **2**, 501 (1929).

0.0001 molar concentration in a 0.4-cm. cell, as observed in alcohol, 3% aqueous sodium hydroxide, and dilute and concentrated hydrochloric acid given in Figs. 1–4. The heavy line curves in each figure represent the added absorption band of what might be termed component dyes. In the figures these (component) dyes are phenylazo-*p*-cresol (dye no. 1) and phenylazodimethylaniline (dye no. 4). Other component dyes such as nos. 2 or 3 and 5 or 6 (described in the previous paper[1]) could have been used in place of nos. 1 and 4. The experimental points have been omitted to avoid confusion.

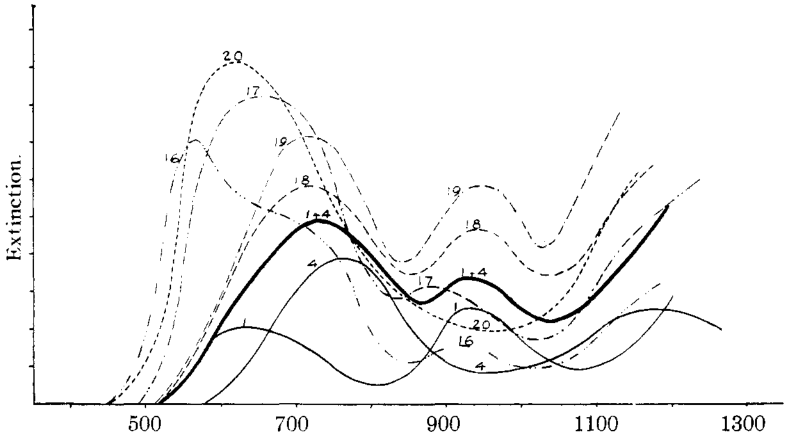

Fig. 4.—Absorption spectra of disazo dyes in 3% sodium hydroxide in 95% ethyl alcohol: dye 1, *o*-phenylazo-*p*-cresol; dye 4, *p*-phenylazodimethylaniline; dyes 16 to 20 as indicated in Table I.

The separation of the aromatic center and the chromophores by $—CH_2—$ of $—CH_2—CH_2—$ (dyes 18 and 19) produces the same effect in the unsymmetrical as in the symmetrical disazo dyes, in that both chromophores act independently of each other. The increase in absorption intensity of the unsymmetrical dyes (18 and 19) in alkaline solution is easily explained on the basis that the dimethylaniline component dye (no. 4) in 3% sodium hydroxide is not in true solution but is essentially colloidal in character, whereas in the unsymmetrical dye the phenolic group permits true solution and hence a greater extinction value.

The general conclusions observed in the symmetrical disazo dyes apply to the data presented here; *i. e.*, a methylene or ethylene linkage acts as an effective insulation between resonators, an ethenylene linkage acts as a coupler to convert the two resonators into a single resonator and the close

TABLE I

THE DISAZO DYES

Compound	M. p., °C.	Formula	Nitrogen, % Calcd.	Nitrogen, % Found
	Monoacetyl = R			
R-*p*,*p*′-diaminobiphenylmethane	121 –122	$C_{15}H_{16}ON_2$	11.66	11.92
R-*p*,*p*′-diaminobibenzyl	146 –147	$C_{16}H_{18}ON_2$	11.02	11.42
R-*p*,*p*′-diaminostilbene	238 –238.5	$C_{16}H_{16}ON_2$	11.11	11.33
	4-Dimethylaminophenylazo = R			
1-(R)-4-acetylaminobenzene	227 –227.5 (lit. 217)[16]			
4-(R)-4′-acetylaminobiphenyl	278 –281	$C_{21}H_{22}ON_4$	15.63	15.89
4-(R)-4′-acetylaminobiphenylmethane	158 –159	$C_{22}H_{24}ON_4$	15.05	14.98
4-(R)-4′-acetylaminobibenzyl	248 –249	$C_{23}H_{26}ON_4$	14.50	14.85
4-(R)-4′-acetylaminostilbene	282 –285	$C_{23}H_{24}ON_4$	14.58	14.74
	4-Dimethylaminophenylazo = R			
1-(R)-4-aminobenzene	191 –191.3 (lit. 186–187)[17]			
4-(R)-4-aminobiphenyl	226 –227	$C_{19}H_{20}N_4$	17.71	17.28
4-(R)-4-aminobiphenylmethane	132 –139	$C_{20}H_{22}N_4$	16.96	16.85
4-(R)-4-aminobibenzyl	155.5–156.5	$C_{21}H_{24}N_4$	16.27	16.00
4-(R)-4-aminostilbene	242 –246	$C_{21}H_{22}N_4$	16.37	16.57
4-Dimethylaminophenylazo = R; 2-Hydroxy-5-methylphenylazo = R′				
1-(R)-4-(R′)-benzene (Dye no. 16)	185 –186	$C_{21}H_{21}ON_5$	19.49	19.39
4-(R)-4′-(R′)-biphenyl (Dye no. 17)	219.5–220	$C_{27}H_{25}ON_5$	16.08	16.15
4-(R)-4′-(R′)-biphenylmethane (Dye no. 18)	166 –167	$C_{28}H_{27}ON_5$	15.59	15.52
4-(R)-4′-(R′)-bibenzyl (Dye no. 19)	199.5–200.5	$C_{29}H_{29}ON_5$	15.12	15.12
4-(R)-4′-(R′)-stilbene (Dye no. 20)	251 –254	$C_{29}H_{27}ON_5$	15.18	15.18

coupling produced by a common benzene linkage results in a repression of the absorption band.

Summary

Measurements of the absorption spectra of a number of disazo dyes in various solvents have been made and their correlation with the chemical constitution of the dyes has been discussed.

COLUMBUS, OHIO RECEIVED OCTOBER 19, 1940

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

Adsorption at Crystal–Solution Interfaces. XII. A Study of the Adsorption of Isomeric Dyes by Crystals of Cupric Acetate during their Growth from Solution*

BY WESLEY G. FRANCE AND KATHRYN M. WOLFE

This paper like the preceding two, X and XI,[1] of this series on the adsorption at crystal–solution interfaces is concerned primarily with the effect of certain polar groups in the foreign molecules. In those studies it was found that the dyes containing sterically hindered groups were in general not adsorbed by the crystals. It was thought desirable in order to obtain further information on this steric adsorption effect to extend this investigation to include a crystal belonging to a system as yet not studied. Cupric acetate monohydrate was selected. At 30° it crystallizes in dark green rhombohedra. It belongs to the holohedral class of the monoclinic system. No data appear to have been published concerning the unit cell of this crystal. Few colored crystals have previously been used in similar investigations. However, Buckley[2] in studying the growth and variation of the crystal of pure potassium chlorate used certain permanganate and chromate salts as impurity. These were used as impurity rather than as the substance undergoing modification.

The same dyes were employed in this study as by Rigterink and France[1] and by France and Wolfe[1] in their investigations of potassium sulfate, sodium nitrate, sodium bromate and sodium chlorate. These dyes are members of two series of isomers prepared by coupling aniline and the ortho-, meta- and para-sulfonated anilines by the usual diazotization method with a series of mono- and di-sulfonic acid derivatives of α- and β-naphthols and α- and β-naphthylamines. The abbreviations in the tables are derived from the intermediates used in their preparation. These intermediates are: aniline (A), ortho-sulfonated aniline (O), meta-sulfonated aniline (M), para-sulfonated aniline (P), α-naphthol (α-OH), β-naphthol (β-OH), α-naphthylamine (α-NH_2) and β-naphthylamine (β-NH_2). The numbers given in the tables after the abbreviations refer to the positions of the —SO_3Na groups attached to the naphthalene rings.

Experimental

The solutions in which the crystals were grown were made by heating enough dye with the saturated solution of the salt so that upon subsequent cooling in the constant temperature room for twenty-four hours at 30 ± 0.2° some of the dye precipitated. The solutions were then filtered into 20-cc. vials, two for each dye used and single seed crystals were suspended in the solutions by copper wire attached by de Khotinsky cement. The crystals were allowed to grow for ten days.

Results.—The results are summarized in Tables I, II, III and IV. All of the eighty-six dyes recorded in the paper by Rigterink and France[1] were used. However, only those which modified the cupric acetate are recorded in the tables. The types referred to in the tables are as follows.

Type 1.—The growth rate between a pair of parallel orthodome faces was retarded, thus developing this pair of faces shown in Fig. 1.

Type 2.—A stair-step-like formation of planes was formed parallel to the faces of the crystal.

Of the forty-two dyes which modified the crystal habit of cupric acetate forming type 1 there were

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* Presented to the Colloid Division of the American Chemical Society, Detroit Meeting, September, 1940.

[1] McBurney and France, THIS JOURNAL, **46**, 540 (1924); Eckert and France, *J. Am. Ceram. Soc.*, **10**, 579 (1927); Keenen and France, *ibid.*, **10**, 821 (1927); Bennett and France, *ibid.*, **11**, 571 (1928); France, *Colloid Symposium Annual*, **7**, 59 (1930); Lash and France, *J. Phys. Chem.*, **34**, 724 (1930); Foote, Blake and France, *ibid.*, **34**, 2236 (1930); Weinland and France, *ibid.*, **36**, 2832 (1932); Starr, Master's Thesis, O. S. U., 1933; Paine and France, *J. Phys. Chem.*, **39**, 425–429 (1935); Davis and France, *ibid.*, **40**, 81–87 (1936); Rigterink and France, X, *ibid.*, **42**, 1079 (1938); Wolfe and France, XI, a paper presented at the Colloid Division of the American Chemical Society Meeting, Cincinnati, Ohio, April 8–12, 1940.

[2] Buckley, *Z. Krist.*, **82**, 31–36, 37–46, 47–49 (1932).