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

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. VI. The Influence of Chromophore Position in Disazo Dyes

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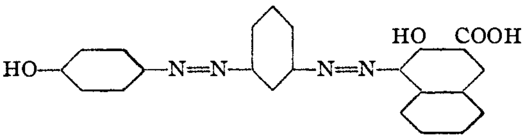
The previous papers of this series[1] have dealt with position isomers of monoazo dyes. In this paper there has been an attempt made to correlate the absorption spectra and structure of disazo dyes in which both of the azo groups are attached to the same aromatic nucleus. The observations have been confined for the most part to a study of dyes in which the two azo groups occupy either meta or para positions with respect to each other.[2]

The dyes listed in Table I were prepared, purified, analyzed and their absorption spectra determined according to methods previously described.[1] The three solvents used for absorption spectra determinations were 30% alcohol, 3% aqueous sodium hydroxide and concentrated hydrochloric acid. Due to the presence of sulfonic acid groups which reduced the solubility of some of the dyes in alcohol, a water–alcohol mixture (30% alcohol) was used in place of the 95% alcohol solvent which had been used previously.

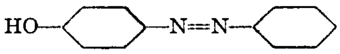
The positions of the band maxima of the dyes studied have been arranged in tabular form (Table I) and from these data and an examination of the absorption spectra curves it has been possible to draw the following conclusions with regard to structure and absorption.

In the isomeric disazo dyes, in which the two forms differ by meta and para positions of the two azo groups attached to a central benzene ring, and in which an auxochrome (OH) is attached to each of the outer aromatic nuclei, the dyes with the azo groups para to each other produce more intense and better defined absorption bands than the corresponding meta substituted derivatives. The introduction of a carboxyl group on one of the outer aromatic nuclei produces broader absorption bands with a decrease in their intensity.

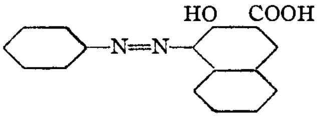
In comparison with monoazo dyes of similar structure the disazo dyes have broader and less sharply defined bands with a slight decrease in the equivalent absorption intensity, although on a gram-molecule basis there is a marked increase in the absorption intensity over the corresponding absorption of a molecular concentration of the monoazo dye. The absorption spectra of disazo dyes with the azo groups meta to each other are quite similar to the absorption spectra obtained by addition of the absorption bands of what might be termed the component dyes. For example the dye



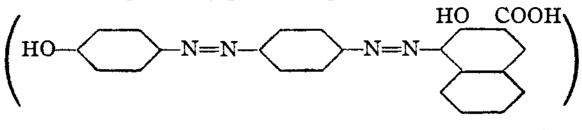
may be considered as composed of



and



The corresponding para coupled dye



shows a distinct shift in the intensity distribution in its absorption spectra, with intensified bands (hyperchromic effect) at lower frequencies (hypsochromic effect). From the data presented in this paper it appears that coupling of azo groups in the para position promotes an effect similar to conjugation of chromophores to form a single chromophore in the molecule, whereas the meta substituted chromophores do not appreciably influence each other. The inactive character of the meta substitution effect on a chromophore has been noted in earlier papers in this series,[1c,e] with regard to the influence of non-chromophoric substituents.

The production of both hyperchromic and hypsochromic effects by conjugated (para coupled) azo groups is not in complete agreement with the effects determined by Henri[3] for simple chromophores, *e. g.*, C=O, when conjugated

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[1] (a) Brode, THIS JOURNAL, **48**, 1984 (1926); (b) *J. Phys. Chem.*, **30**, 56 (1926); (c) *Bureau of Standards J. of Research*, **2**, 501 (1929); (d) THIS JOURNAL, **51**, 1204 (1929); (e) *Ber.*, **61**, 1722 (1928).

[2] Riggli [*Helv. Chim. Acta*, **15**, 75–110 (1932)] has compared isomeric ortho and para disazo dyes and has shown their visible absorption spectra to be quite similar.

[3] Henri and Bielecki, *Ber.*, **47**, 1690 (1914).

TABLE I

		Frequency (vibrations ÷ (seconds × 10^{12}))								
		Bands in alcohol (30%)			Bands in 3% NaOH			Bands in concd. HCl		
Monoazo dyes	Compounds	I	II	III	I	II	III	I	II	III
1	*p*-Phenylazophenol	698	865	1280	(740)		1115	644	922	1207
2	5-Phenylazosalicylic acid		862	>1200		715	1072		657	1000
3	1-Phenylazo-2-naphthol	612	(718)	968	590	690	895	595	750	968 1145
4	1-Phenylazo-2-naphthol-7-sulfonic acid	612	761	920	600	725	882	593	714	920
Disazo dyes										
5	1-*p*-(*p*-Hydroxyphenylazo)-phenylazo-2-oxy-3-naphthoic acid (Na salt)	580	822	1210	535	666	1152	610	915	1120
6	1-*m*-(*p*-Hydroxyphenylazo)-phenylazo-2-oxy-3-naphthoic acid (Na salt)	610	910			682		615		1140
7	1-*p*-(*p*-Hydroxyphenylazo)-phenylazo-2-naphthol-7-sulfonic acid (Na salt)	577	825	(1300)	555	625 (728)	1135	612		1171
8	1-*m*-(*p*-Hydroxyphenylazo)-phenylazo-2-naphthol-7-sulfonic acid (Na salt)	612	920		590	680		600	890	
9	5-*p*-(3-Carboxy-2-hydroxy-1-naphthylazo)-phenylazo-salicylic acid (Na salt)	577	810	(1300)	540	625 (731)	1170	616	843	1150
10	5-*m*-(3-Carboxy-2-hydroxy-1-naphthylazo)-phenylazo-salicylic acid (Na salt)	600	840			698	1100	625	857	
11	5-*p*-(2-Hydroxy-7-sulfonic-1-naphthylazo)-phenylazo-salicylic acid (Na salt)	580	870	(1300)	555	644	1030	608	850	
12	5-*m*-(2-Hydroxy-7-sulfonic-1-naphthylazo)-phenylazo-salicylic acid (Na salt)	610	850	(1250)		700	1090	610	868	
13	4-*p*-(*p*-Sulfophenylazo)-phenylazo-phenol (Na salt)	590	810		593	682	915	605	900	
14	5-*p*-(*p*-Sulfophenylazo)-phenylazo-salicylic acid (Na salt)		780	(1300)	590		909	620	860	(1070)
15	1-*p*-(*p*-Sulfophenylazo)-phenylazo-2-naphthol (Na salt)	588	852	1138	535	867	1070	480	555 857	1080
16	1-*p*-(*p*-Sulfophenylazo)-phenylazo-2-naphthol-7-sulfonic acid (Na salt)	577	833	(1300)	545	857	1150	485	575 857	1110
17	5-*p*-(Phenylazophenylazo)-salicylic acid (Na salt)	715	790	(1300)	670	790	1050	600	925	
18	2-Hydroxy-1-(*p*-phenylazophenylazo)-3-naphthoic acid (Na salt)	588	810		650	802	1170	600	914	
19	2-Hydroxy-1-4-(*p*-hydroxyphenylazo)-6-sulfo-1-naphthylazo-3-naphthoic acid (Na salt)	665	857	(1100)	625	845	(1050)	530	834	1034
20	1-4-(*p*-Hydroxyphenylazo)-6-sulfo-1-naphthylazo-2-naphthol-7-sulfonic acid (Na salt)	652	750	1145	625	(790)	1070	525	857	

Values in parentheses indicate inflections or poorly defined maxima.

together. Recent data on the conjugated ethylene chromophore[4] and directly coupled ring systems[5] are in accordance with our observations that both strong hyperchromic and hypsochromic effects are produced in compounds containing conjugated chromophores.

Summary

The absorption spectra of solutions of eight disazo dyes have been measured in 30% alcohol, 3% sodium hydroxide and in concd. hydrochloric acid. Four of these dyes had the two azo groups attached para to each other and the other four were the corresponding meta isomers. The absorption spectra of eight other disazo and four monoazo dyes were measured for purposes of comparison. It has been possible to draw some conclusions concerning the influence of position substitution on the absorption spectra of disazo dyes.

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[4] Kuhn, *Helv. Chim. Acta*, **11**, 151 (1928); Karrer, *ibid.*, **15**, 507 (1932); Ramart-Lucas, *Bull. soc. chim.*, **51**, 301 (1932).

[5] Clar, *Ber.*, **66**, 202 (1933).