RP-47

THE SPECTRAL ABSORPTION OF CERTAIN MONOAZO DYES

I. THE EFFECT OF POSITION ISOMERISM ON THE SPECTRAL ABSORPTION OF METHYL DERIVATIVES OF BENZENEAZOPHENOL

By Wallace R. Brode

ABSTRACT

Quantitative measurements of the spectral absorption of solutions of azobenzene, benzeneazophenol, and the mono- and dimethyl derivatives of benzeneazophenol in alcohol, aqueous hydrochloric acid, and aqueous sodium hydroxide are recorded and their relationships discussed. Although the differences found in the spectral absorption of alcohol solutions or of hydrochloric acid solutions of the position isomers studied are small, marked differences are found in the absorption of 3 per cent aqueous sodium hydroxide solutions.

CONTENTS

	Page
I. Introduction	501
1. Outline of investigation	501
2. Nomenclature	502
II. Spectrophotometric methods and apparatus	504
1. Photographic method	504
2. Visual method	507
III. Preparation of dyes and solutions	509
1. Preparation and purification of dyes	509
2. Analysis of dyes	509
3. Preparation of solutions	509
IV. Experimental data	511
V. Discussion of results	514
1. Alcohol solutions	514
2. Hydrochloric acid solutions	515
3. Sodium hydroxide solutions	518
VI. Summary	525

I. INTRODUCTION

1. OUTLINE OF INVESTIGATION

Probably no other single physical measurement is so characteristic of an organic compound as its spectral absorption. It is a means of identification and a measure of the purity and amount of the compound in the observed solution. The advantages of spectrophotometric analysis are particularly apparent in the examination of dyestuffs, where color is an important factor. The high molecular weight

of the average commercial dyestuff, together with its complex chemical structure and the presence of organic and inorganic impurities, renders more difficult the determination of either its chemical or its other physical properties.

It is natural, therefore, that the dye laboratory of the Bureau of Standards should include the measurement of spectral absorption among the observations which are being made in connection with the collection of accurate quantitative data on the physical and chemical properties of dyestuffs.[1] Through the cooperation of the colorimetry section of the Bureau of Standards, apparatus is available for the accurate measurement of spectral absorption. This apparatus, to a large extent, eliminates the instrumental and personal errors present in many of the earlier researches in this field.

The present paper is chiefly concerned with the relation between the spectral absorption and chemical constitution of the mono- and dimethyl derivatives of benzeneazophenol, in which but one methyl group is present in a benzene ring. These dyes have been prepared and purified, and accurate quantitative measurements have been made of their spectral absorption in three solvents. The solvents used were 95 per cent ethyl alcohol, concentrated hydrochloric acid (35 per cent), and a 3 per cent aqueous solution of sodium hydroxide. Since this work deals with only one type of substituting group, the methyl radical, no conclusions can be drawn on the general effect of substitution, and the discussion of the results will necessarily have to be limited to a recapitulation of the data presented without predicting the possible effects of other substituting groups.

In earlier papers data have been presented on the spectral absorption of azobenzene [2] and benzeneazophenol [3] in various solvents, and only such data on these compounds as may be essential to the clarity of the discussion and the correlation of the effects observed will be presented in this paper.

2. NOMENCLATURE

The nomenclature recommended in the report of a committee of the Optical Society of America [4] has in large part been followed. Scientific Paper No. 440 [5] and Technologic Paper No. 338 [6] of the Bureau of Standards have also been consulted in drawing up this set of definitions. The terms most used, symbolized by **T**, **t**, **k**, *c*, *b*,

[1] Appel, The Work of the Bureau of Standards on Dyes, Ind. and Eng. Chem., **18**, p. 1341; 1926.

[2] Brode, J. Am. Chem. Soc., **48**, p. 1984; 1926.

[3] Brode, J. Phys. Chem., **30**, p. 56; 1926.

[4] Progress Committee on Spectrophotometry, J. O. S. A. and R. S. I., **10**, p. 177, 1925.

[5] Gibson, McNicholas, Tyndall, Frehafer, and Mathewson, The Spectral Transmissive Properties of Dyes: 1. Seven Permitted Food Dyes, in the Visible, Ultra-violet, and Near Infra-red. B. S. Sci. Papers, **18**, No. 440; June, 1922.

[6] Peters and Phelps, Color in the Sugar Industry: 1. Color Nomenclature in the Sugar Industry. B. S. Tech. Papers, **21**, No. 338; March, 1927.

λ, and f, are few in number, but in order to precisely define them other terms are necessarily given.

The following terms relate to the rectilinear propagation of homogeneous radiant energy through a cell with plane, parallel sides (glass or quartz end plates) perpendicular to the direction of propagation, and containing a substance in homogeneous solution in a solvent:

$T_{sol.}$ = the *transmission* of this cell and its contents and is defined as the ratio of the radiant energy passing the last surface of the cell to that incident on the first surface.

$T_{sov.}$ = the transmission of the same or a duplicate cell containing solvent only.

$\mathsf{T}_{sol.}$ = the *transmittance* of the solution contained in the cell and is defined as the ratio of the radiant energy incident on the second inner surface of the cell to that passing the first inner surface.

$\mathsf{T}_{sov.}$ = the transmittance of the solvent only.

$\mathsf{T} = \frac{T_{sol.}}{T_{sov.}} = \frac{\mathsf{T}_{sol.}}{\mathsf{T}_{sov.}}$ = the transmittancy [7] of the dye in solution.

The transmittancy, T, of a dye solution is the quantity obtained from the actual measurements. Since the transmission of the cell containing the solution is always compared with that of a duplicate cell containing the solvent, losses by reflection from the ends of the cell and by absorption by the solvent are compensated. The negative logarithm of the transmittancy, $-\log \mathsf{T}$, is a quantity which is a direct measure of the absorption of the dissolved material. It is this quantity, often called the extinction coefficient in chemical papers, which is plotted in the graphs accompanying this paper.

$\mathbf{t}$ = *specific transmissivity;* that is, transmittancy reduced to unit conditions as regards thickness and concentration.

b = thickness of the absorbing solution. In the present paper 0.5 cm is taken as the unit of thickness, since all of the solutions reported were measured in a cell of that length.

c = concentration of the dissolved material. A concentration of 1.5×10^{-4} gram molecule per liter of solution has been used as the unit in this paper.

$\mathbf{t} = cb\sqrt{\mathsf{T}}$. This is an expression of Beer's law.

$\mathbf{k} = -\log \mathbf{t} = \frac{1}{cb}(-\log \mathsf{T})$ = the specific absorptive index.[8]

The specific absorptive index $\mathbf{k}$ is the characteristic quantity for any solution at any wave length or frequency in the spectrum.

---

[7] Transmittancy is generally designated in chemical publications as $\frac{I}{I_0}$, where I and I_0 correspond to $T_{sol.}$ and $T_{sov.}$

[8] The report on spectrophotometry, ref. 4, and B. S. Sci. Paper No. 440, ref. 5, call this specific transmissive index, but see B. S. Tech. Paper No. 338, ref. 6, p. 265.

As shown above, it is obtained from the observed transmittancy, T, by simply dividing the negative logarithm of this number by the product of the concentration and thickness of the solution measured.

λ = wave length, the unit of which in this paper is the millimicron, $m\mu = 10^{-9}$ m.

ν = frequency,[9] the unit of which in this paper is the fresnel, f = vibrations ÷ seconds $\times 10^{12}$.

The spectral absorption data are presented graphically and in tables. The graph form has $-\log_{10} T$ from 0.00 to 2.00 as ordinates and frequency from 350 f to 1,400 f as abscissas. It should be noted that $-\log_{10} T$ is plotted downward on the graph and, therefore, that the greater the absorption the farther a point will be from the top of the graph. The spectral absorption curve obtained by drawing a smooth curve through observed values plotted on the graph delimits narrow regions of relatively high absorption which are called absorption bands. An absorption band is located in the spectrum by its position of maximum absorption; that is, the frequency of a band is taken to be the frequency of maximum absorption. Similarly, the magnitude of a band is the value of the specific absorptive index at the frequency of maximum absorption. For purposes of discussion, the observed bands are numbered, starting with the one of lowest frequency. In case a band is composed of smaller ones, the components are lettered in order from the low-frequency to the high-frequency side. The principal band is the one of greatest magnitude.

II. SPECTROPHOTOMETRIC METHODS AND APPARATUS

1. PHOTOGRAPHIC METHOD

The observations in the ultra-violet and extending into the visible portion of the spectrum were made by the Hilger sector photometer method. This method requires the use of three distinct pieces of apparatus—a source of continuous radiant energy, a sector photometer, and a quartz spectrograph. (Fig. 1.)[10]

The source of radiant energy is a vertical high voltage spark under water, obtained by the use of a Tesla coil. The spark between the tungsten electrodes is approximately 12 mm in length and gives a continuous spectrum from the visible throughout the ultra-violet as far as the system will record. Distilled water is run through the spark chamber during operation.

The sector photometer consists essentially of two quartz wedge lenses, on one side of which are the rotating sectors and on the other

[9] This is the *true* frequency. The term wave number or oscillation frequency often used is defined as $\frac{10^5}{\lambda}$.

[10] The author is indebted to the colorimetry section of the Bureau of Standards for placing this entire apparatus at his disposal.

side a holder for the two absorption cells. The quartz spectrograph is a Fuess instrument, with lenses of 74 cm focal length giving a dispersion of 13.9 cm between 600 and 1,200 *f*. A slit width of 0.15

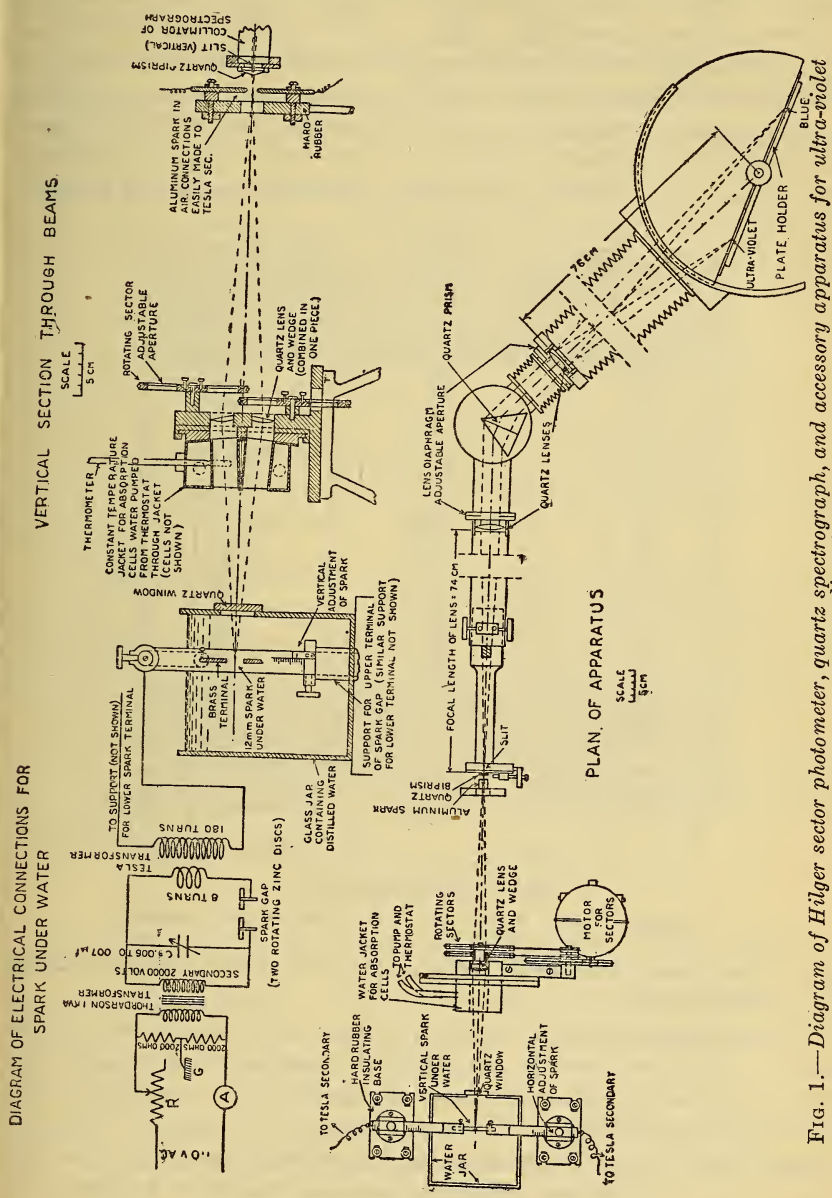


FIG. 1.—*Diagram of Hilger sector photometer, quartz spectrograph, and accessory apparatus for ultra-violet spectroradiometry.*

mm was used, corresponding to 3.7 *f* at a frequency of 1,200 *f*. A quartz biprism is placed directly in front of the slit of the spectrograph, with its refracting edge perpendicular to the slit, and serves to bring the two beams from the photometer adjacent to each other.

The cells used in this work were a special modification of those described in Scientific Paper No. 440 [11] of the Bureau of Standards. The essential difference is the use of half centimeter rings, and cover pieces of quartz which were of the same diameter as the outside diameter of the glass rings. (Fig. 2.) The advantage of the half centimeter rings and the smaller quartz cover is that they may be used in a 1 cm holder to give a half centimeter cell, in a 2 cm holder by the use of a 1 cm ring to give a 1.5 cm cell, and similarly with a 4 cm holder to produce a 2.5, 3, or 3.5 cm cell. A 0.5 cm cell was used in the work reported in this paper because it permitted a reduc-

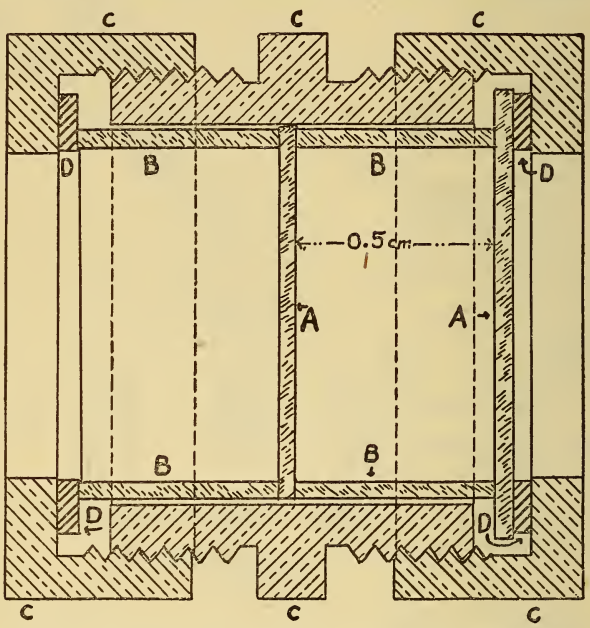


FIG. 2.—*Diagram of absorption cell used with the Hilger sector photometer method*

A, Quartz end plates; *B*, glass rings; *C*, brass parts; *D*, rubber washers

tion in the time of exposure necessary in obtaining the data at the higher frequencies.

In measuring the spectral absorption of a dye an exposure of 20 seconds is first made on the photographic plate of an aluminum spark in air to give the necessary lines for locating the frequency scale used in reading the plate. Next an exposure of 10 seconds, duration is made with the underwater spark, but without the cells in the cell rack of the photometer. This exposure is made to compare the intensities of the two beams, which must be the same throughout the observed spectrum. The cell containing the solvent is now placed in one of the openings in the holder and the cell containing

[11] See footnote 5, p. 502.

the solution in the other. A series of exposures is then made, varying the ratio of the apertures for each exposure.

There results on the photographic plate a series of pairs of contiguous spectra. One member of each pair has undergone absorption in certain regions and the other member has been reduced in density throughout its whole length. At certain frequencies the photographic densities of the spectra may be equal, and at these frequencies the transmittancy is known from the relative apertures of the sectors.

When enough exposures have been made, the cells are interchanged in the holder and the series repeated, thus giving data from which the possible instrumental error has been very largely eliminated.[12] The next to the last exposure is another comparison without the cells in the holder, and the last exposure is the aluminum spark in air to give the necessary reference lines for the reading of the plates. In general, 25 exposures were made on each plate and two plates were required for each solution. The observations were repeated for each dye, so that four plates were obtained for each different type of solvent. The plates known as "Eastman 36" (prepared by the Eastman Kodak Co.) were used in this work and proved quite satisfactory.

The plates were read by superimposing an accurately ruled frequency scale and observing them over an illuminated milk glass. The frequencies of equal densities were then located, the values plotted in the curves being the average of several readings of each of the four exposures.

In general, the data may be considered accurate within $\pm 3\ f$ in frequency and within ± 0.03 unit in $-\log_{10}$ transmittancy, although the accuracy is somewhat dependent on the shape, size, and position in the spectrum of the bands.

2. VISUAL METHOD

The determination of the spectral absorption of these compounds in the visible portion of the spectrum was made on a Keuffel and Esser "Color Analyzer." This apparatus, like the ultra-violet apparatus, uses rotating sectors for the variation of intensity. These are rotated with sufficient rapidity to eliminate flicker, and the opening of one of these sectors may be varied while they are in motion. The cells were for the most part the same as those used with the ultra-violet apparatus, although in some cases another type, previously described by the author,[13] was used.

---

[12] See B. S. Sci. Paper No. 440, ref. 5, and also note R. Davis, Experimental Study of the Relation Between Intermittent and Nonintermittent Sector-Wheel Photographic Exposures, B. S. Sci. Papers, **21**, No. 528, pp. 95–140; 1926.

[13] Brode, J. Am. Chem. Soc., **46**, p. 584; 1924.

The visual method was used for the alkaline and acid solutions, but not for the alcohol solutions. The visual observations for the most part supplement the photographic observations, as the majority of the bands observed have their maxima in the ultra-violet. The points recorded on the graphs in this paper are the average of all the observations for that particular value of $-\log_{10} T$, including the photographic and visual results when data were obtained for the same point by both methods. The maxima of all the curves were

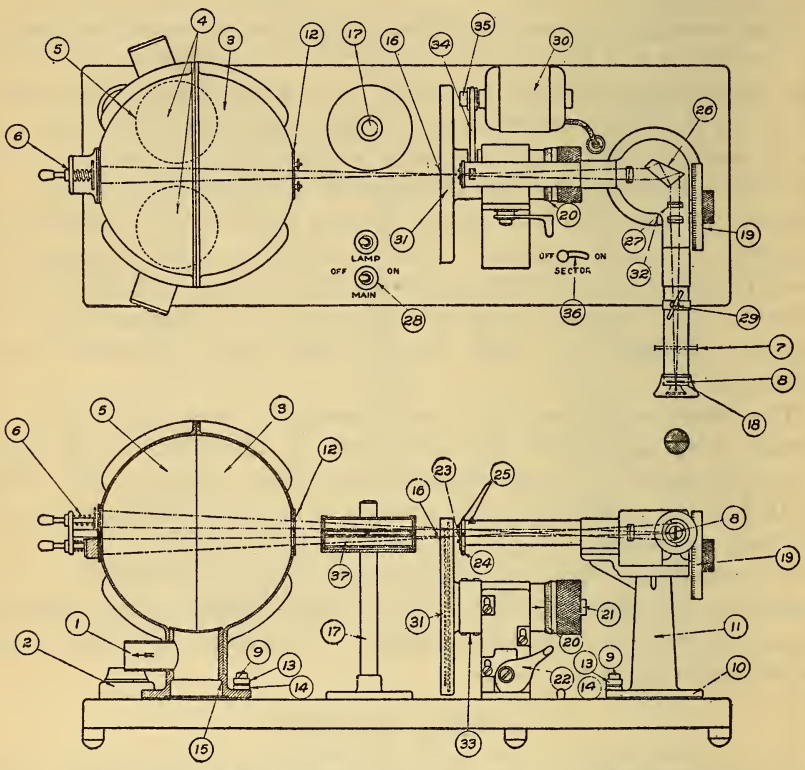


FIG. 3.—*The Keuffel & Esser "Color Analyzer"*

A complete description of this apparatus is given in a booklet issued by the company

determined solely by the photographic method. The visual method was essential, however, in determining the shape of the first absorption band near its base, where it was often beyond the range of the photographic method.

The method used was to set the rotating sectors at values of $-\log_{10} T$ and then to adjust the wave-length scale of the constant deviation prism until a match was obtained. The accuracy of this method is dependent on the shape, magnitude, and position of the band, the uncertainty being between ± 2 to 4 mμ in wave length (2 to 4 f) and within ± 0.04 unit in $-\log_{10} T$.

III. PREPARATION OF DYES AND SOLUTIONS

1. PREPARATION AND PURIFICATION OF DYES

The dyes were prepared from materials of a chemically pure grade and were crystallized from alcohol. In general, one-sixth molar quantities and the same methods of diazotization and coupling were used for all of the dyes. The directions given by Fierz [14] for the diazotizing of aniline were used for all of the amines. The couplings were made according to the general directions for basic coupling given by Fierz and by Cain.[15] Mechanical stirring was used throughout the diazotization and coupling to insure complete reactions. The dyes were prepared separately at different times, and no general observations were made as to the relative ease of diazotization or coupling. In all cases coupling was effected without difficulty. The dyes were purified by at least three separate crystallizations from alcohol. The structural formulas of the dyes prepared are given in Figure 4.

2. ANALYSIS OF DYES

The dyes were analyzed according to the Kolthoff [16] modification of the Knecht and Hibbert [17] titanous chloride method. The titration results and the observed melting points, together with the melting points given in the literature [18] for these dyes, are recorded in the accompanying table. (Table 1.)

TABLE 1.—*Analysis and melting points*

Dye	Analysis by $TiCl_3$	Melting points	
		Observed	Literature
	Per cent	° *C.*	° *C.*
Azobenzene	100.0	68	68
Benzeneazophenol	99.6	152	152
Benzeneazo-o-cresol	99.2	128	128–130
Benzeneazo-*m*-cresol	98.5	107	109
o-Tolueneazophenol	99.5	102	102–3
m-Tolueneazophenol	98.3	140	144–5
p-Tolueneazophenol	100.8	151	151
o-Tolueneazo-*o*-cresol	99.6	132	132
o-Tolueneazo-*m*-cresol	100.5	113	111
m-Tolueneazo-*o*-cresol	98.0	114	115
m-Tolueneazo-*m*-cresol	99.5	106	106–7
p-Tolueneazo-*o*-cresol	100.2	162	163
p-Tolueneazo-*m*-cresol	99.7	135	135

3. PREPARATION OF SOLUTIONS

All of the dyes are soluble in alcohol and were measured in this solvent, in strong hydrochloric acid, and in dilute sodium hydroxide

[14] Fierz, Farbenchemie, Schulthess, Zürich; 1920.
[15] Cain, Synthetic Dyestuffs, Griffin & Co., London; 1923.
[16] Kolthoff, Rec. Trav. Chim., 45, p. 169; 1926.
[17] Knecht and Hibbert, New Reduction Methods in Volumetric Analysis, Longmans, New York; 1925.
[18] Beilstein, Handbuch der Organischen Chemie, 4; 1899; Ergänzungsband, 4; 3d ed.; 1906.

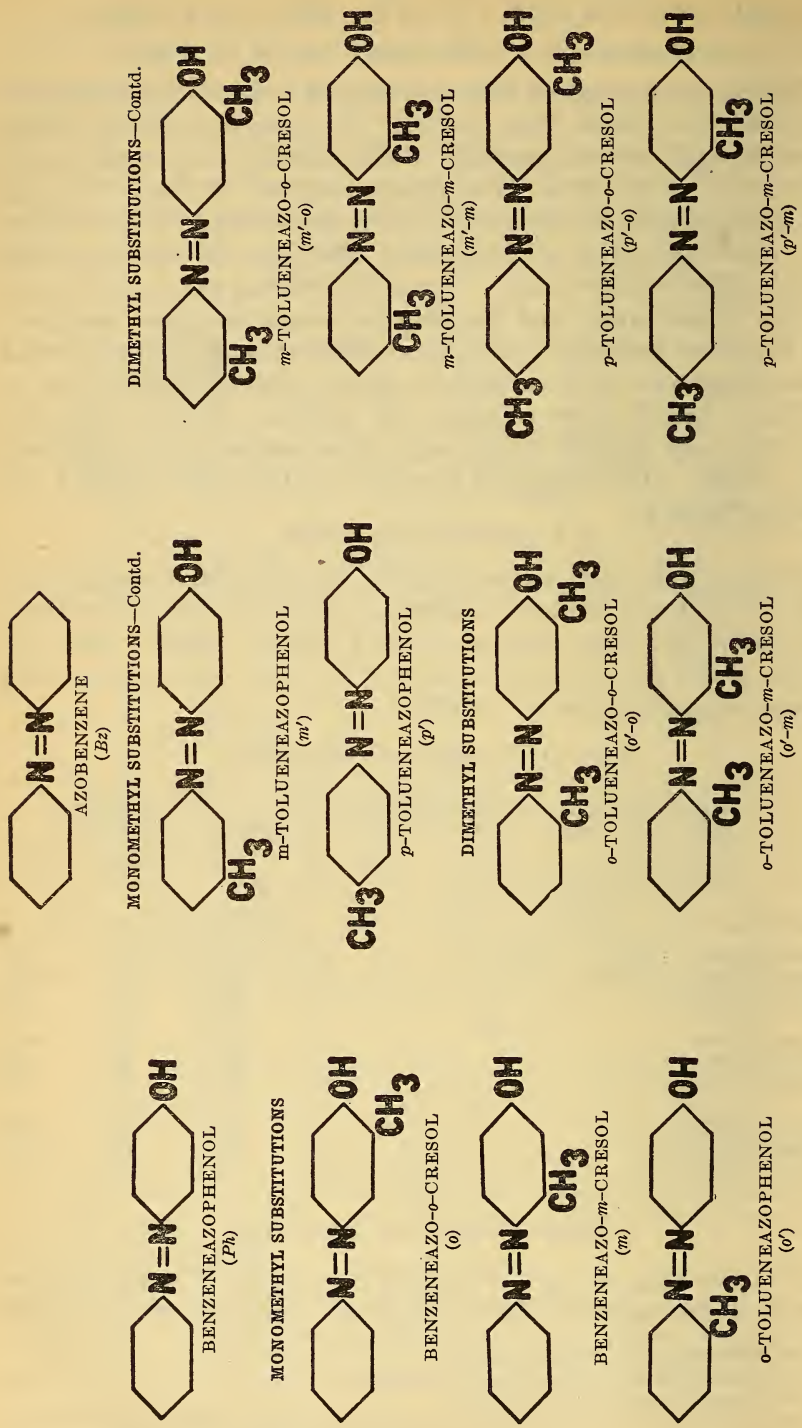


FIG. 4.—*Structural formulas of the compounds studied*

The symbols in parentheses are used in this paper in place of the longer names under which they are placed

solution, with the exception of azobenzene, which could be measured in alcohol and hydrochloric acid solutions only. The alcohol solutions were prepared as follows: 0.7200 g of benzeneazophenol or 0.8450 g of its various methyl and dimethyl derivatives was dissolved in 95 per cent ethyl alcohol at room temperature and diluted to 500 ml at 20° C. (solution A). The alcohol was of good commercial quality and showed practically no selective absorption in the spectral regions studied. Fifty ml of solution A was diluted with alcohol to 250 ml (solution B) and 25 ml of solution B diluted to 250 ml (solution C). Thus solution C, which was measured, contained 2.88 cg per liter of benzeneazophenol, or 3.38 cg per liter of the mono- and dimethyl dyes.

The acid solutions were made by diluting 5 ml of solution B to 100 ml with the usual laboratory 35 per cent C. P. hydrochloric acid. The concentration of the dye in these solutions was then 1.44 cg per liter of solution in the case of benzeneazophenol and 1.69 cg per liter of the other dyes. It should be noted that these solutions and the alkaline solutions described below contained a small amount of alcohol.

The alkaline solutions were made by diluting 10 ml of solution B and 10 ml of a 30 per cent solution of C. P. stick sodium hydroxide in distilled water to 100 ml with distilled water. The concentration of the dye in the alkaline solutions was the same as in the alcohol solutions. The concentration of the sodium hydroxide in the solutions measured was 3 per cent.

The alcohol and hydrochloric acid solutions of azobenzene were prepared in the same manner as the above solutions, using 0.825 g of the pure compound. The measured solutions contained 3.30 cg of dye per liter in alcohol and 1.65 cg per liter in hydrochloric acid.

IV. EXPERIMENTAL DATA

The experimental data obtained in the determination of the spectral absorption of azobenzene, benzeneazophenol, and all the mono- and dimethyl derivatives of benzeneazophenol, in which there is not more than one methyl substitution in a benzene ring, dissolved in alcohol, concentrated hydrochloric acid, and 3 per cent aqueous sodium hydroxide, are given graphically in Figures 12 to 37 and numerically in Tables 2 to 6. The data in the graphs are plotted on a form previously described, and in each case the name of the compound, the solvent, the concentration of the dye, and the cell length are given. The points on the graphs are the average of all the observations made. The spectral absorptions of the dyes in alcohol and in hydrochloric acid are presented on the same graphs. In all cases the band of lower frequency is the principal one of the curve for the hydrochloric acid solution. It should be noted that the concentration of the dye in

hydrochloric acid is one-half the concentration of the same dye in alcohol. The spectral absorption of the dyes in an aqueous solution of sodium hydroxide, as well as that of benzeneazophenol in an alcoholic solution of sodium hydroxide, are plotted on separate graphs because of the unusual behavior of the dyes in these solvents. As an aid in the general comparison of the various curves, most of them are given on a greatly reduced scale in Figures 5, 6, 7, and 8. In comparing the curves in these figures it should be remembered that only with compounds having the same molecular weight is the concentration the same.

TABLE 2.—*Frequencies of the absorption bands of solutions of compounds in 95 per cent ethyl alcohol*

[Values given in vibrations per 10^{-12} second]

Compound [1]	Band I [2]	Band II	Band III	$\frac{f_I}{f_{II}}$	$\frac{f_{III}}{f_{II}}$
Bz	670	947	1,410	0.71	1.49
Ph	635	855	1,280	.74	1.50
o	627	843	1,257	.74	1.49
m	655	840	1,265	.78	1.51
o'	667	847	1,260	.78	1.48
m'	635	855	1,274	.74	1.49
p'	655	850	1,255	.77	1.48
o'-o	605	839	1,240	.72	1.48
o'-m	650	833	1,240	.78	1.49
m'-o	650	843	1,260	.77	1.48
m'-m	650	836	1,255	.78	1.50
p'-o	652	838	1,245	.78	1.48
p'-m	670	831	1,250	.81	1.50

[1] The names of the compounds represented by these abbreviations are given in Figure 4.
[2] The accuracy of these values is considerably lower than in the other cases, because of the size and shape of the bands.

TABLE 3.—*Specific absorptive indices of the absorption bands; that is, at the frequencies given in Tables 2 and 4, of solutions of the compounds studied in 95 per cent ethyl alcohol and in concentrated hydrochloric acid*

Compound [1]	Centigrams per liter	Solvents					
		Alcohol			Hydrochloric acid		
		Bands					
		I [2]	II	III	I	II [2]	III
Bz	2.731	0.06	1.28	1.10	2.20	0.82	(1.10)
Ph	2.971	.12	1.91	1.00	2.96	.16	.51
o	3.182	.11	1.82	.89	2.77	----------	.62
m	3.182	.09	1.76	.80	2.82	.13	.61
o'	3.182	.09	1.75	.89	2.71	.22	.64
m'	3.182	.08	1.83	.95	2.80	.17	.81
p'	3.182	.07	1.95	.98	3.12	.16	.65
o'-o	3.392	.09	1.78	.84	2.75	.16	.54
o'-m	3.392	.13	1.76	.84	2.76	.22	.63
m'-o	3.392	.10	1.87	.98	3.02	.27	.80
m'-m	3.392	.10	1.77	.79	2.94	.18	.74
p'-o	3.392	.08	1.95	.99	3.12	----------	.84
p'-m	3.392	.09	1.97	.84	3.32	----------	.66

[1] The names of the compounds represented by these abbreviations are given in Figure 4.
[2] The accuracy of these values is considerably lower than in the other cases, because of the size and shape of this band.

TABLE 4.—*Frequencies of the absorption bands of solutions of the compounds in concentrated hydrochloric acid*

[Values given in vibrations per 10^{-12} second]

Compound [1]	Band I	Band II [2]	Band III [2]	$\frac{f\,II}{f\,I}$	$\frac{f\,III}{f\,I}$
Bz	725	1,070	----------	1.48	----------
Ph	644	922	1,207	1.43	1.87
o	628	----------	1,185	----------	1.89
m	636	927	1,172	1.46	1.84
o'	628	890	1,176	1.42	1.87
m'	632	920	1,185	1.46	1.88
p'	625	910	1,185	1.46	1.90
o'-o	619	870	1,160	1.41	1.87
o'-m	628	927	1,195	1.48	1.90
m'-o	630	922	1,190	1.46	1.89
m'-m	629	900	1,210	1.43	1.92
p'-o	617	----------	1,172	----------	1.90
p'-m	613	----------	1,187	----------	1.94

[1] The names of the compounds represented by these abbreviations are given in Figure 4.
[2] The accuracy of these values is considerably lower than in the other cases, because of the size and shape of the bands.

TABLE 5.—*Frequencies of the absorption bands of solutions of the compounds studied in a 3 per cent aqueous solution of sodium hydroxide*

[Values given in vibrations per 10^{-12} second]

Compound [1]	Band I				Band II
	A		B		
	A (observed)	A' (analysis)	B (observed)	B' (analysis)	Observed [2]
Ph	697	676	760	778	1,140
o	673	672	763	770	1,107
m	675	672	737	760	1,110
o'	695	672	743	764	1,170
m'	698	672	765	770	1,150
p'	698	672	773	770	1,181
o'-o	[3] (690)	668	----------	755	1,128
o'-m	665	665	729	752	1,150
m'-o	670	667	745	750	1,110
m'-m	670	666	738	755	1,120
p'-o	661	664	757	748	1,110
p'-m	668	664	735	752	1,138

[1] The names of the compounds represented by these abbreviations are given in Figure 4.
[2] The accuracy of these values is considerably lower than in the other observed cases, because of the flat shape of this band and its position in the far ultra-violet near the limit of observation.
[3] Approximate values.

TABLE 6.—*Specific absorptive indices of the absorption bands; that is, at the frequencies given in Table 5, of solutions of the compounds studied in a 3 per cent aqueous solution of sodium hydroxide*

Compound [1]	Bands						
	I						II
	A (observed)	B (observed)	A′ (analysis)	B′ (analysis)	A′+B′	$\frac{A'}{A'+B'}$	
Ph	1.70	1.56	1.53	1.29	2.82	0.543	0.60
o	1.84	1.38	1.82	.85	2.67	.682	.68
m	1.55	1.67	1.38	1.29	2.67	.518	.65
o′	1.48	1.63	1.18	1.40	2.58	.457	.61
m′	1.69	1.55	1.50	1.26	2.76	.543	.66
p′	1.77	1.60	1.57	1.32	2.89	.542	.66
o′–o	[2](1.63)	[2](1.51)	1.47	1.06	2.53	.581	.65
o′–m	1.14	1.63	1.06	1.34	2.40	.442	.61
m′–o	1.96	1.50	1.92	.90	2.82	.680	.71
m′–m	1.53	1.71	1.40	1.31	2.71	.517	.61
p′–o	2.05	1.26	2.05	1.02	3.07	.668	.72
p′–m	1.64	1.86	1.52	1.42	2.94	.517	.73

[1] The names of the compounds represented by these abbreviations are given in Figure 4.
[2] Approximate values.

In Tables 2, 4, and 5 are given the observed values for the frequencies of the absorption bands.

In Tables 3 and 6 are given the specific absorptive indices, **k**, of the compounds studied at the frequencies of the bands. (See Tables 2, 4, and 5.) These values of **k** are the corresponding values of $-\log_{10}\mathbf{T}$ taken from the graphs reduced to unit thickness and concentration. For convenience, the measured thickness 0.5 cm has been taken as the unit of thickness and 1.5×10^{-4} g molecule per liter of solution as the unit of concentration. The latter is equivalent to 2.731 cg of azobenzene, 2.971 cg of benzeneazophenol, 3.182 cg of the monomethyl-benzeneazophenols, and 3.392 cg of the dimethyl-benzeneazophenols per liter of solution. With this unit of concentration the calculated values, **k**, are usually rather near the observed values, $-\log_{10}\mathbf{T}$. However, Beer's law was found to be applicable to the solutions over a much wider range of concentrations than are involved in the calculations of **k**. The values of **k**, Tables 3 and 6, represent then the absorption of molecular equivalents of the dyes in the different solvents at the frequencies of maximum absorption.

V. DISCUSSION OF RESULTS

1. ALCOHOL SOLUTIONS

The spectral absorptions of azobenzene and benzeneazophenol have been discussed in previous articles [19] and will be referred to only in relation to the absorption of the derivatives with which this paper is concerned.

[19] See footnotes 2 and 3, p. 502.

Table 2 gives the positions of the absorption bands of the solutions of the dyes in 95 per cent ethyl alcohol. There are three bands which are similar in character for all the compounds. The first band is small, the second prominent and narrow, and the third intermediate in size and shape between the other two. The numerical relationship between the positions of the bands of the individual compounds is given in the table. It will be seen that the frequency of the first band is 0.76 ± 0.05 time that of the second and the frequency of the third 1.49 ± 0.02 times that of the second. This gives a whole number relationship between the frequencies of the bands of very nearly 3, 4, and 6 times some fundamental frequency. The introduction of the OH group into azobenzene, of the CH_3 group into benzeneazophenol, and of the CH_3 group into methylbenzeneazophenol is accompanied by a shift in the position of the bands to lower frequencies in most but not all cases. The relationship between the positions of the bands is apparently not altered by these changes in constitution.

The specific absorptive indices of the absorption bands shown by the alcohol solutions are listed in Table 3. The introduction of OH into azobenzene is accompanied by an increase in the index of the second band and a decrease in that of the third band. The specific absorptive indices of the second and third bands of the methyl and dimethyl derivatives are all smaller than the corresponding values of benzeneazophenol with the exception of the p'-substituted compounds, whose indices for the second band are larger than those of benzeneazophenol. The ratio of the index of the third band to that of the second is 0.86 for azobenzene, 0.52 for benzeneazophenol, and varies between 0.46 and 0.52 for the methyl and dimethyl derivatives. Thus, there is no decided shift in the relative absorption of the second and third bands in going from benzeneazophenol to its methyl derivatives, although there are variations in the absorptive indices. The variations in the specific absorptive indices of the first band are not significant, because the band is too small to be accurately measured.

2. HYDROCHLORIC ACID SOLUTIONS

Hydrochloric acid may behave not only as a solvent, but as a reagent. Addition compounds of this acid with some of the dyes discussed in this paper have been isolated, and it is probable that similar compounds may exist in the solutions measured. No attempt has been made to study the formation of such compounds, but a comparison of the spectral absorption of the hydrochloric acid solutions with that of the corresponding alcohol solutions indicates that the effect of the acid is not merely one of a solution, but is chemical in nature, and is not directly associated with the hydroxyl group.

Table 4 gives the positions of the absorption bands of the solutions of the dyes in concentrated hydrochloric acid. There are three bands, similar in character for all of the compounds studied but entirely different from those of the compounds dissolved in alcohol. The first

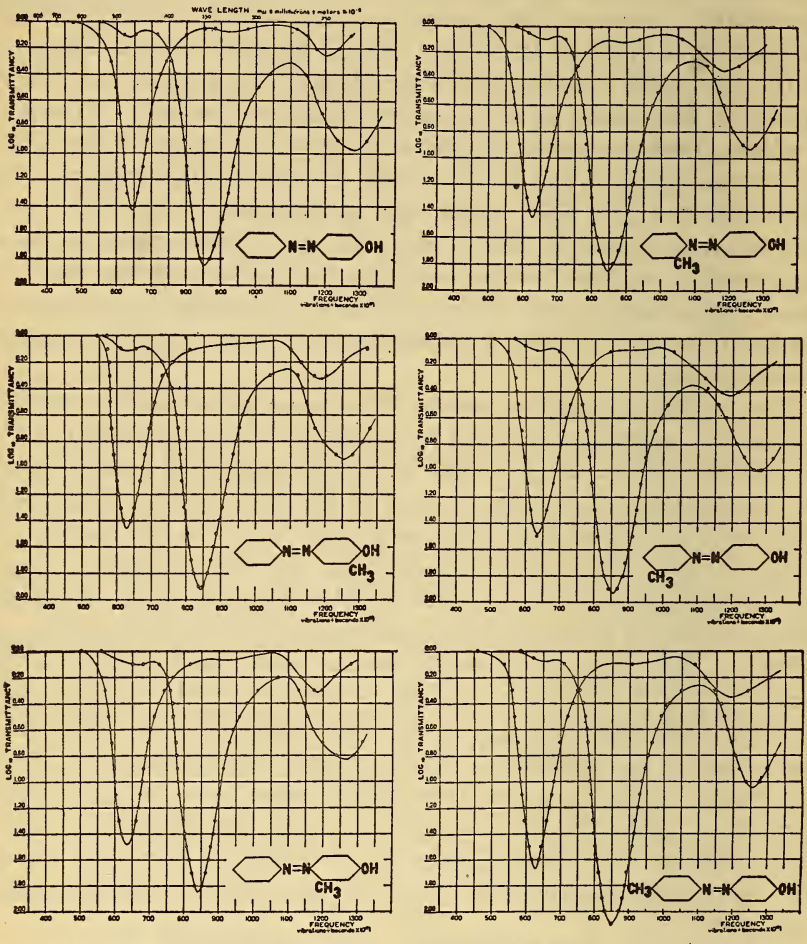


FIG. 5.—*The spectral absorption of solutions of benzeneazophenol and its monomethyl derivatives in 95 per cent ethyl alcohol (the right-hand principal bands) and in concentrated hydrochloric acid (the left-hand principal bands)*

The names of the compounds, the formulas of which are shown in the above graphs, are given in Figure 4. For data on these compounds plotted on a larger scale, giving cell thickness and concentration, see Figures 13, 16, 18, 20, 22, and 24

band is prominent and narrow, the second band is very small, and the third intermediate between the other two. The second band is located at a frequency approximately 1.45 times that of the first. The third band is located at a frequency 1.89 ± 0.06 times that of the first.

Substitution is accompanied by a shift in the position of the bands to lower frequencies except in three of the dimethyl derivatives.

The specific absorptive indices of the bands are listed in Table 3. The indices of the first band are considerably larger than those of the

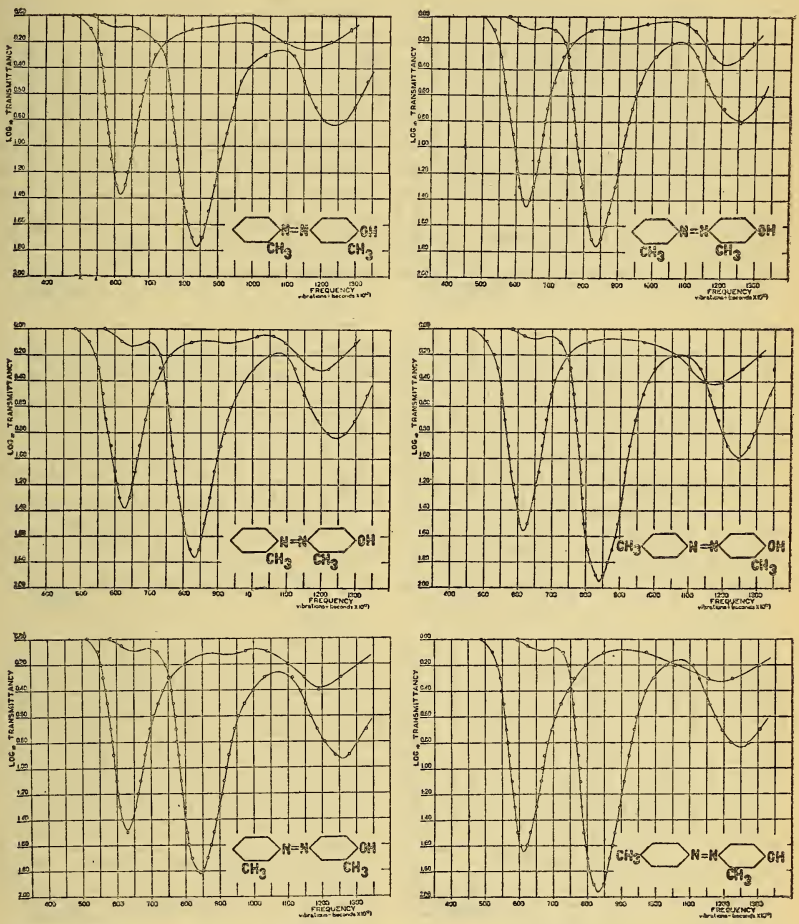


FIG. 6.—*The spectral absorption of solutions of the dimethyl derivatives of benzeneazophenol, in which but one methyl substitution occurs in a benzene ring, in 95 per cent ethyl alcohol (the right-hand principal bands) and in concentrated hydrochloric acid (left-hand principal bands)*

The names of the compounds, the formulas of which are shown in the above graphs, are given in Figure 4. For data on these compounds, plotted on a larger scale, giving concentration and cell thickness, see Figures 26, 28, 30, 32, 34, and 36

principal band of the alcohol solution in each instance. The introduction of the OH group into azobenzene and of the methyl groups into benzeneazophenol is accompanied by changes in the specific absorptive index of the first band analogous to those of the second band of the corresponding alcohol solutions.

3. SODIUM HYDROXIDE SOLUTIONS[20]

The action of a solution of sodium hydroxide is chemical in nature and is directly connected with the hydroxyl group in the molecule, so that data on azobenzene can not be obtained.

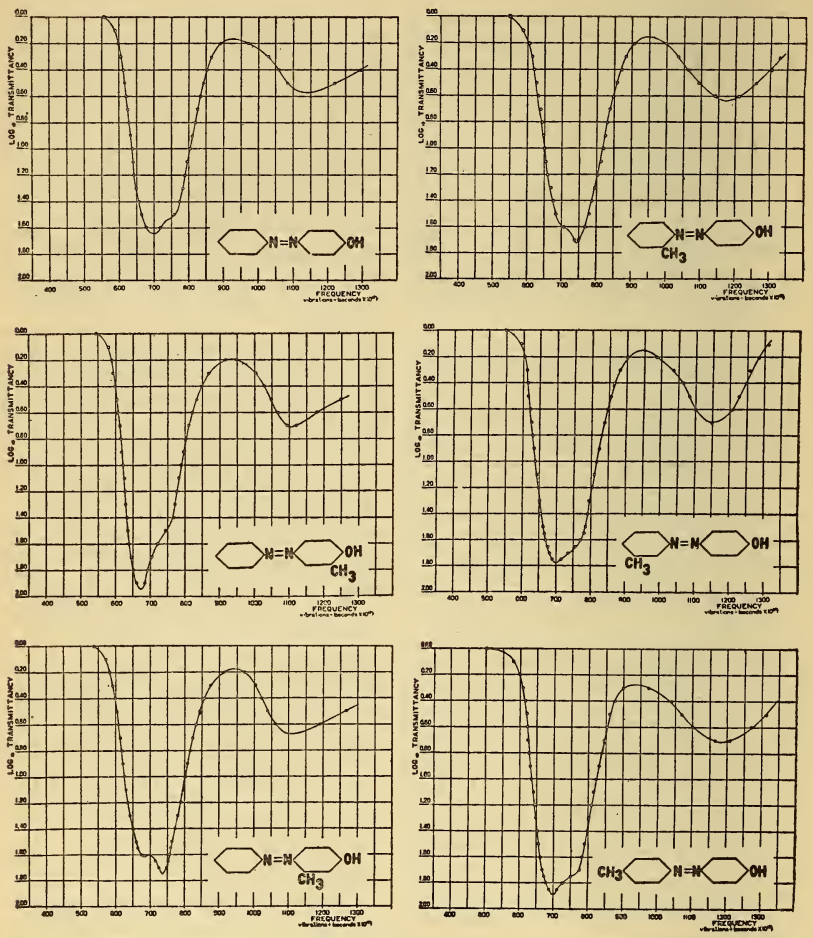


FIG. 7.—*The spectral absorption of solutions of benzeneazophenol and its monomethyl derivatives in a 3 per cent aqueous sodium hydroxide solution*

The names of the compounds, the formulas of which are shown in the above graphs, are given in Figure 4. For data on these compounds, plotted on a larger scale, giving cell thickness and concentration, see Figures 14, 17, 19, 21, 23, and 25

The absorption spectrum of benezeneazophenol in a 3 per cent aqueous solution of sodium hydroxide has two principal bands. The first band is more than twice as strong as the second and, like those already described in this paper, is asymmetric with a larger portion of the base on the high-frequency side. It differs, however, from

[20] A portion of this section was presented before the Philadelphia meeting of the American Chemical Society, September, 1926.

the other bands studied in that it is broad at the peak and unsymmetrical, with an indication of being composed of two bands close together, the component of lower frequency being slightly stronger than the other. Confirmation of the presence of two overlapping bands is to be found in the data for the methyl derivatives of the dye

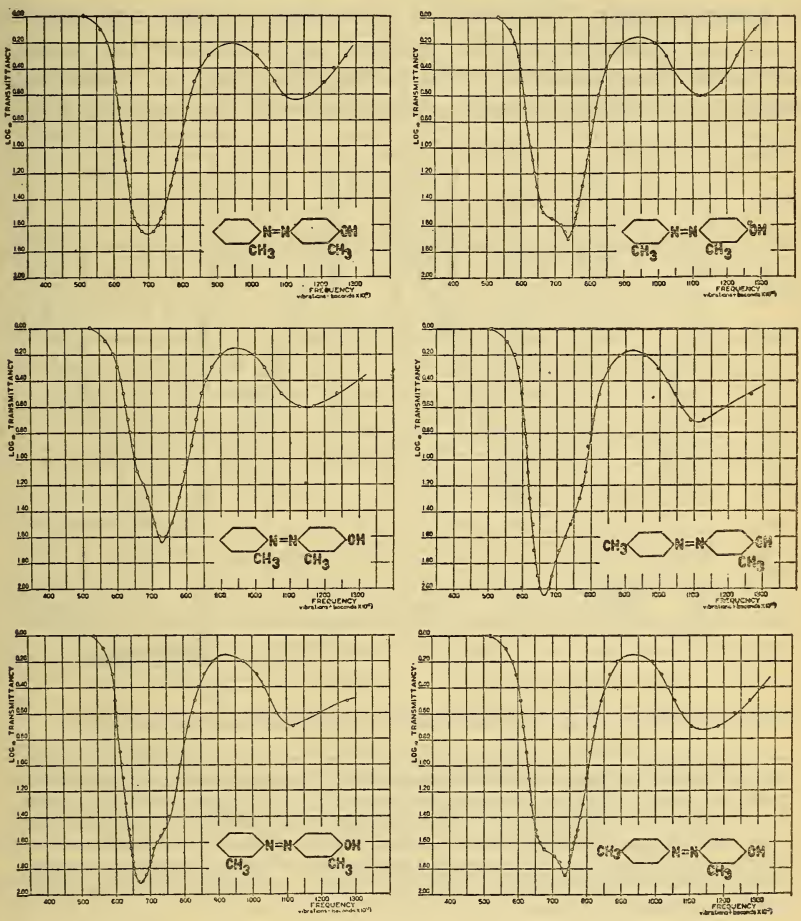


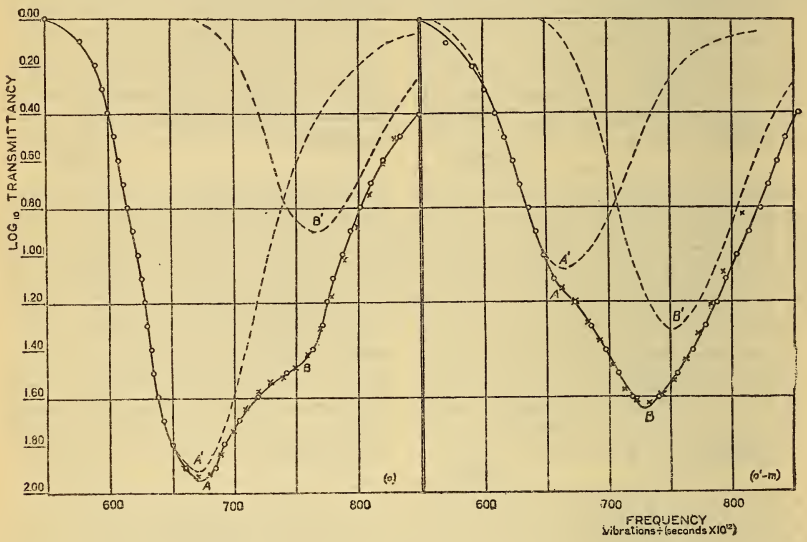
FIG. 8.—*The spectral absorption of solutions of the dimethyl derivatives of benzeneazophenol, in which but one methyl substitution occurs in a benzene ring, in a 3 per cent aqueous solution of sodium hydroxide*

The names of the compounds, the formulas of which are shown in the above graphs, are given in Figure 4. For data on these compounds, plotted on a larger scale, giving cell thickness and concentration, see Figures 27, 29, 31, 33, 35, and 37

described below. The second principal band is located at 1,140 *f* and is broad and flat in character.

The general characteristics of the spectral absorption of the mono- and dimethyl derivatives of benzeneazophenol are the same as those of the parent substance; that is, (1) two principal bands, the first being more intense than the second; and (2) the first band appears to

be composed of two components which together produce the observed band. Since this principal band appears to be composed of two parts and varies considerably in shape with different compounds, it is difficult to draw any conclusions with regard to the relation between either frequency or amount of absorption and chemical constitution. The general relation between the substitution effects and the frequency and magnitude of the bands is approximately the same as observed in other solvents. The average frequency of these bands appears to be shifted toward lower values with increasing molecular



(*a*) (*b*)

FIG. 9.—*The analysis of two observed curves into component curves*

Note that in the above curves, which show the greatest observed difference in the ratio of A′ to B′, the frequency differences of A′ and B′ is approximately the same in both cases. The shift in frequency of both components in case (*b*), as compared with the frequency of the same components in case (*a*), is approximately the same as that observed in alcohol and in hydrochloric acid solutions, when a second methyl radical is introduced into the molecule. The above curves represent the spectral absorption of (*a*) benzeneazo-*o*-cresol, and (*b*) *o*-toluneneazo-*m*-cresol in a 3 per cent aqueous solution of sodium hydroxide. (See figs. 17 and 29.) The *x* marks on the graphs indicate values calculated from A′ and B′

weight. The spectral absorption of compounds with *p*′-substitutions is greater than that with the other substitutions or of the unsubstituted parent compound. By a method of analysis [21] it has been

[21] The analysis of these curves into their elements is based on two assumptions—(1) that each composite curve has but two components and (2) that these two components have the same shape when calculated to the same height of band. The basis of the first assumption is that the general characteristics of all of these bands are such as to indicate but two main components. The observed bands may be composed of a large number of lesser components or even lines, but, for the purposes of analysis and study, it may be assumed that these lesser components are equivalent in their aggregate to only two effective bands. The second assumption is based on the following facts. In the other solvents studied the general shape of each curve and the frequency relations between the bands were the same for all of the compounds. It is therefore reasonable to expect the same general relationships when an aqueous solution of sodium hydroxide s used as a solvent.

If these assumptions are accepted, then each of the observed composite curves can be analyzed into two component curves definite in shape and position. It does not follow, however, that all composite curves

possible to determine approximately the frequency and magnitude of the component bands which constitute the observed principal band. These data are given in Tables 5 and 6, together with approximate values obtained directly from the compound curves. The smaller band observed in the neighborhood of 1,150 f is extremely flat and varies considerably in shape with the particular compound, which indicates the possibility that it also is a compound band.

In Table 6 are given the specific absorptive indices of the components A and B of the principal bands. These values include observations made directly on the curves at the apparent maxima (A and B), and the data obtained by the analysis of the compound curves into their components (A′ and B′). Comparing these two sets of values, it may be seen that, while the apparent deviations in the data are of the same type and direction in both sets of values, the analytical values furnish a better estimate of the actual magnitudes of the two bands which compose the principal absorption bands. The general indications from both groups of data and from the varied shapes of the original curves are that there is an apparent equilibrium between two forms of vibration of the molecule, representing, possibly, slightly different molecular states, and that this equilibrium is influenced by the position of the substituting group in the benzene rings of the parent substance.

Figure 10 gives the sum of the specific absorptive indices of the components (A′+B′). It has been noted in other solvents that substitution in the the p'-position causes an increase in absorption. This generalization holds equally true in the case of an aqueous solution of sodium hydroxide as the solvent. Substitution in the o'-position tends to decrease absorption as well as influence the relative magnitudes of A′ and B′.

The spectral absorption of benzeneazophenol, the parent substance, in an aqueous solution of sodium hydroxide represents what we may call a neutral equilibrium in which band A is of slightly greater magnitude than band B. This neutral equilibrium does not represent an equal amount of the two forms and may undoubtedly be influenced by changes in the character of either the basic substance or the solvent. For example, in the absorption spectrum of benzeneazophenol in an alcoholic solution of sodium hydroxide (fig. 15) the equilibrium has been shifted with an increase in B and a corresponding decrease in A. Two other curves closely resemble the neutral curve of benzene-

can be so analyzed. The fact that all of the curves studied may be so analyzed lends additional weight to the assumptions. The suitability of the theory is further attested by the facts that (1) the frequency differences of the component bands in all cases are approximately the same, (2) there is an apparent equilibrium between the two component bands, dependent on the position of the substitution, so that as one band is increased the other band is decreased a corresponding amount. The general relations between the magnitudes of the bands, both observed and calculated (Table 6), are of the same general type. The analytical data, however, show more clearly the relative proportions of the two components in any one band.

azophenol, namely, those of the spectral absorption of the *m'*- (fig. 23) and *p'*- (fig. 25) substituted compounds. These two, together with the unsubstituted parent substance, constitute the neutral group or series. In the case of the *m'*-substituted compounds there appears to be practically no effect of any kind on either the equilibrium between A and B or the specific absorptive indices of these bands. In the case of the *p'*-substituted compounds there is an increase in absorption, but the relative shapes of the bands and the ratio between A and B are the same as in the original compound without the *p'*-substitution.

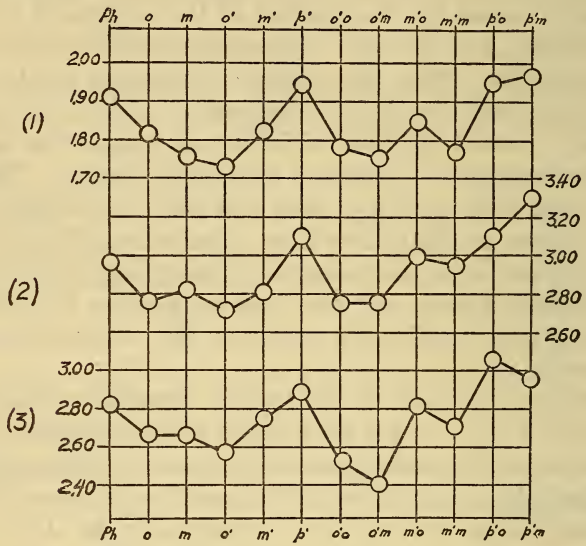


FIG. 10.—*Specific absorptive indices at the frequencies of maximum absorption of the principal bands of solutions of the compounds studied in (1) ethyl alcohol, (2) concentrated hydrochloric acid, and (3) a 3 per cent aqueous solution of sodium hydroxide* ($A'+B'$)

(The abbreviated symbols for the compounds are explained in fig. 4)

Substitution in the *o*-position (*o* to the hydroxyl group) (fig. 17) causes a marked increase in the A band and a corresponding decrease in the B band, or, in other words, a shift of the equilibrium toward the A state.

Substitution in the *m*-position (fig. 19) causes a shift of the equilibrium in the opposite direction; that is, an increase in the B band with a corresponding decrease in the A band. The degree of shift of this equilibrium from the neutral state, however, is not as great as in the case of the *o*-substitution.

Substitution in the *o'*-position (fig. 21) causes an increase in the B band with a decrease in the A band of about the same difference from the neutral ratio, but in the opposite direction to that caused

by the *o*-substitution. In addition, there is a suppression of both of the bands, so that the sum of the specific absorptive indices of bands A and B is considerably smaller than in the other cases. (Fig. 10.)

The general effect of di-substitution on the specific absorptive indices of the two component bands is a combination of two separate directing forces. In the case of the *o'*, *o*-substituted compound (fig. 27) the effects are opposite in character and to a large extent neutralize each other. The *o*-substitution appears to have a slightly stronger influence than the *o'*-substitution, as the percentage of A present is slightly greater than in the neutral equilibrium. (Fig. 11.) How-

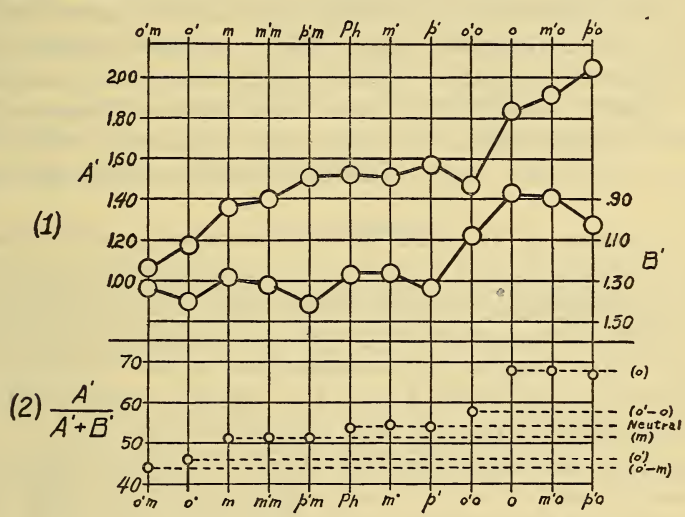


FIG. 11.—(*1*) *Specific absorptive indices of the components of the principal bands of solutions of the compounds studied in a 3 per cent aqueous solution of sodium hydroxide. A'=upper series, B'=lower series.* (*2*) *Percentage of the A' component,* $\frac{A'}{A'+B'}$, *of the principal bands of solutions of the compounds studied in a 3 per cent aqueous solution of sodium hydroxide*

(The abbreviated symbols for the compounds are explained in fig. 4)

ever, the effect of the *o'*-substitution on the suppression of the bands seems to be only slightly influenced by the oppositely directed force of the *o*-substitution. In the *o'*, *m*-substituted compound (fig. 29) the substituting positions influence in the same direction from the neutral equilibrium or level, so that there is an addition of the two effects and a slightly greater suppression of the bands due to the *o'*-substitution. The effect of the introduction of the second substitution in the *m'*-position on the spectral absorption of the compound is practically nil within the accuracy of the observations. There is possibly a slight increase in the specific absorptive indices of the bands of the *m'*, *o*-substituted compound over that of the *o*-substi-

tuted compound alone, and a slight lowering of the ratio of A to B. In the spectral absorption of the *m′*, *m*-substituted compound there is an indication of the same effect, although it is less prominent than in the *m′*, *o*-substituted compound. The influence of substitution in the *p′*-position, as mentioned before, seems to be merely to increase the absorption, an effect quite independent of the solvent used.

In the graph (fig. 11) giving the specific absorptive indices of components A′ and B′, those of B′ are plotted on an inverted scale, since from general observation it may be seen that as one band increases the other decreases. It is to be noticed that in cases which are normal, such as the unsubstituted, *m*-substituted, and *m′*-substituted compounds, approximately the same differences exist between the A′ and B′ values in the graph. Cases in which there is an intensification of the bands, *p′*-substituted compounds, show a difference greater than the normal values, and cases with suppressed bands, *o′*-substituted compounds, show differences smaller than the normal values.

A comparison of the sum of the calculated specific absorptive indices of bands A′ and B′ for each compound with the indices of the principal bands of the same compounds in other solvents (fig. 10) lends confirmation to the theory that, in any particular compound, the equilibrium between the concentration of the tautomeric forms represented by the bands A and B is directly proportional to the specific absorptive indices of their respective bands.

It appears that the sum of the specific absorptive indices of the component bands A′ and B′ bears approximately the same relation to the indices of the principal bands of the same compounds in other solvents. Hence, for each compound the ratio of A′/A′+B′ should give approximately the percentage of the A compound present and at the same time make the necessary corrections or allowances for the *p′*- and *o′*-substitution effects on the specific absorptive indices of both the bands. Table 6 gives these percentage values which, as may be observed, can be arranged in groups (fig. 11) representing different stages or levels in the equilibrium.

Reference should be made to the works of earlier investigators which are closely related to the principal objects of this investigation. The methods and apparatus used by many of these investigators have limited the possible accuracy of their observations to such an extent as to preclude the detection of variations in the shape of the curves of the order observed in the study of the series of compounds described in this paper. Baly,[22] Purvis,[23] and Klingstedt[24] have observed the effect of *p*-substitution on the increase in the magnitude

[22] Baly, J. Chem. Soc., **107**, p. 1058; 1915.
[23] Purvis, J. Chem. Soc., **103**, p. 1088; 1913.
[24] Klingstedt, Compt. rend., **175**, p. 365; 1922.

of the band. This same effect, although not always mentioned, can be noted in the data of other observers. Among the series of data on the absorption spectra of isomeric compounds, where the isomerism consists of the change of the position of substitution in a benzene ring, may be mentioned the following: *o*-, *m*-, and *p*-xylene, *o*-, *m*-, and *p*-nitrotoluene, *o*-, *m*-, and *p*-cresol, and a number of other derivatives, which are for the most part given in the list of references to the absorption spectra of organic compounds published by the British Association for the Advancement of Science.[25] With the exception of the general increase in magnitude of the bands of the *p*-substituted compounds, these data are of little aid in the prediction of the effect of substitution on the absorption bands. Recent work by Henri [26] and his coworkers on the absorption spectra of position isomers, in particular the xylenes, dichlorobenzenes, and toluidines in the vapor state, promises to be of considerable value in the determination of the relation between absorption and chemical constitution.

VI. SUMMARY

1. The spectral absorption of solutions of azobenzene in 95 per cent ethyl alcohol and in concentrated hydrochloric acid has been measured in the visible and in the ultra-violet to a frequency between 1,250 and 1,450 *f*.

2. The spectral absorption of solutions of benzeneazophenol in 95 per cent ethyl alcohol, concentrated hydrochloric acid, and a 3 per cent aqueous solution of sodium hydroxide has been measured in the same regions of the spectrum.

3. The 11 possible mono- and dimethyl derivatives of benzeneazophenol, in which there is but one methyl substitution in a benzene ring, have been prepared, and the spectral absorption of their solutions in the same solvents in the same regions of the spectrum as in the case of the parent compound, benzeneazophenol, has been measured.

4. The spectral absorption of a solution of benzeneazophenol in a 3 per cent alcoholic solution of sodium hydroxide has also been measured.

From the data obtained the following generalizations may be made:

1. An increase in molecular weight is, in most instances, accompanied by a decrease in the frequency of the absorption band of these similarly constituted compounds.

2. In any one solvent there appears to be a definite mathematical relationship between the frequencies of the observed bands. In the various solvents used the mathematical relationships between the

[25] Annual Report of the British Association for the Advancement of Science; 1916.

[26] Henri, Structure des Molécules, Herman, Paris; 1925.

observed absorption bands are quite different, indicating a considerable change in the molecular states of the compounds.

3. The introduction of a hydroxyl group into the *p*-position of the azobenzene molecule, forming benzeneazophenol, results, in addition to a decided shift in the frequency of the bands, in an increase in the magnitude and a narrowing of the principal band and a decrease in magnitude and flattening of the other observed bands. This would indicate a shift of the vibrational intensity of the molecule to the frequency of the principal band.

4. Substitution of a methyl group in the *p'*-position in benzeneazophenol results in an increase in the magnitude of the absorption bands, irrespective of the type of solvent.

5. Substitution of a methyl group in the *o'*-position in benzeneazophenol results in a general decrease in the magnitude of the absorption bands.

6. The principal absorption bands of solutions of benzeneazophenol and its methyl derivatives in a 3 per cent aqueous solution of sodium hydroxide appear to consist of two overlapping bands.

7. The equilibrium which seems to exist between these two components is dependent on the nature of the solvent and the position of the substituting group. An *o*-substitution of the methyl group in the benzeneazophenol molecule causes an increase in the lower frequency component, with a corresponding decrease in the higher frequency component. A *m'*- or *o'*- substitution produces a reverse effect, while the equilibrium is not affected by either a *m'*- or *p'*-substitution.

The data presented in this paper suggest the possibility of a method of structural analysis for the determination of the position of a substituting group in a complex organic molecule and a reverse of this process in the prediction of the spectral absorption of a compound of known structure. Additional data on the effect of substituting groups, including those of nitro, chlorine, bromine, carboxy, and sulphonic acid substitutions, are now being collected with this object in view.

Fundamental data have been presented on the relation between spectral absorption and chemical constitution.

Acknowledgement is made to W. D. Appel, of the dye laboratory of the chemistry division, for his assistance and advice in this work.

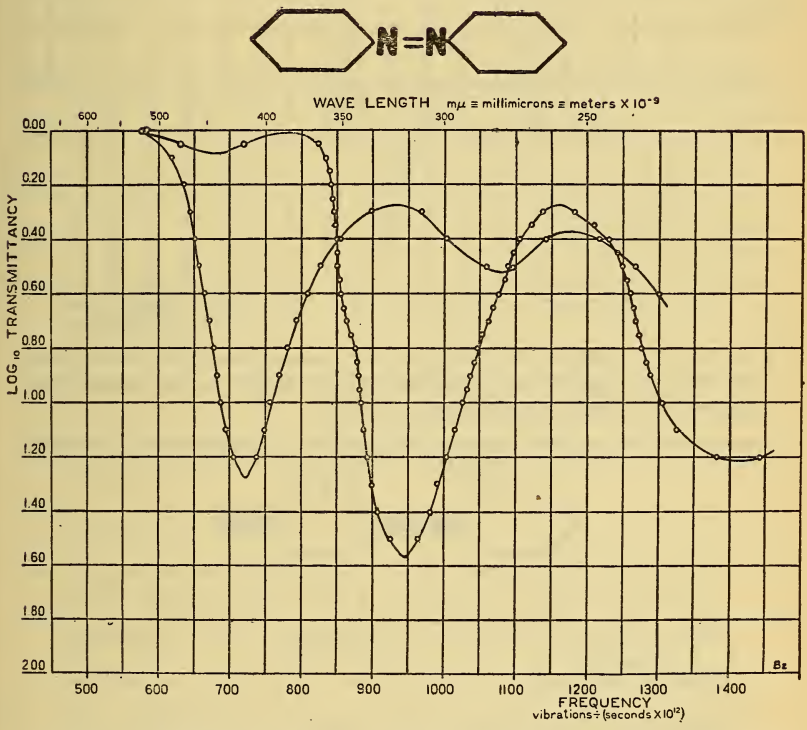


FIG. 12.—*The spectral absorption of azobenzene (Bz) dissolved in 95 per cent ethyl alcohol (principal band at 947 f) and in concentrated hydrochloric acid (principal band at 725 f)*

Concentration, 3.300 cg per liter in alcohol; 1.650 cg per liter in hydrochloric acid. Cell thickness 0.5 cm in both cases

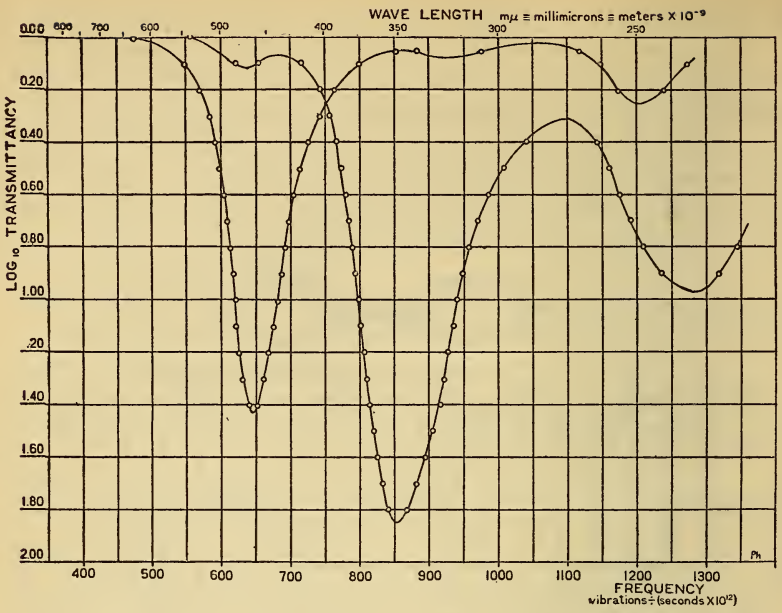
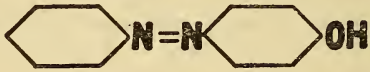


FIG. 13.—*The spectral absorption of benzeneazophenol (Ph) dissolved in 95 per cent ethyl alcohol (principal band at 855 f) and in concentrated hydrochloric acid (principal band at 644 f)*

Concentration, 2.880 cg per liter in alcohol; 1.440 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



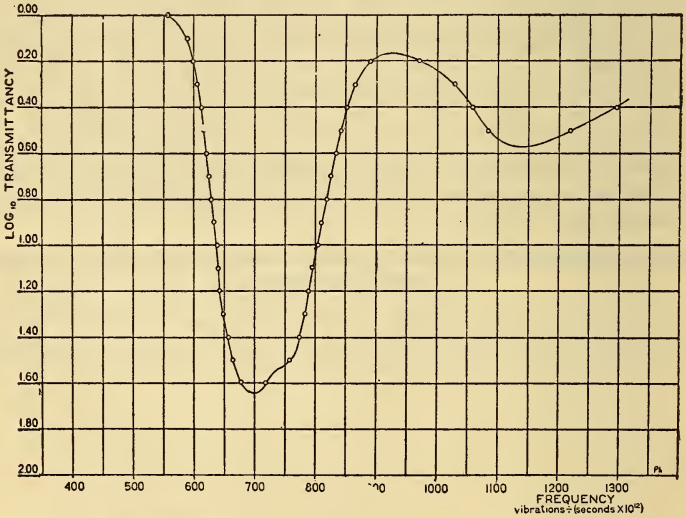


FIG. 14.—*The spectral absorption of benzeneazophenol (Ph) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 2.880 cg per liter. Cell thickness, 0.5 cm

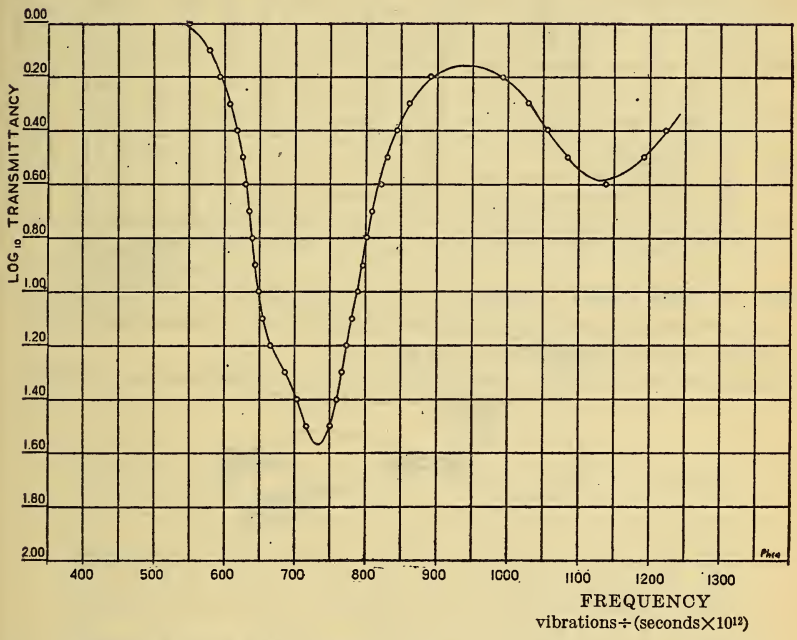


FIG. 15.—*The spectral absorption of benzeneazophenol (Ph) dissolved in a 3 per cent solution of sodium hydroxide in 95 per cent ethyl alcohol*

Concentration, 2.292 cg per liter. Cell thickness, 0.5 cm

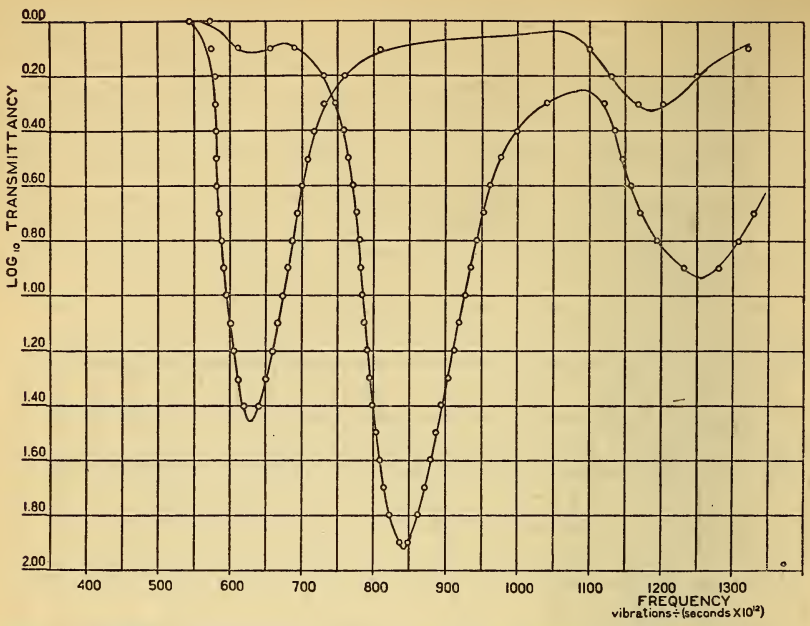
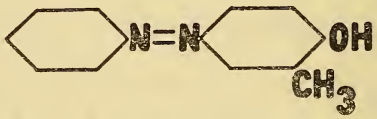


FIG. 16.—*The spectral absorption of benzeneazo-o-cresol (o) dissolved in 95 per cent ethyl alcohol (principal band at 843 f) and in concentrated hydrochloric acid (principal band at 628 f)*

Concentration 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



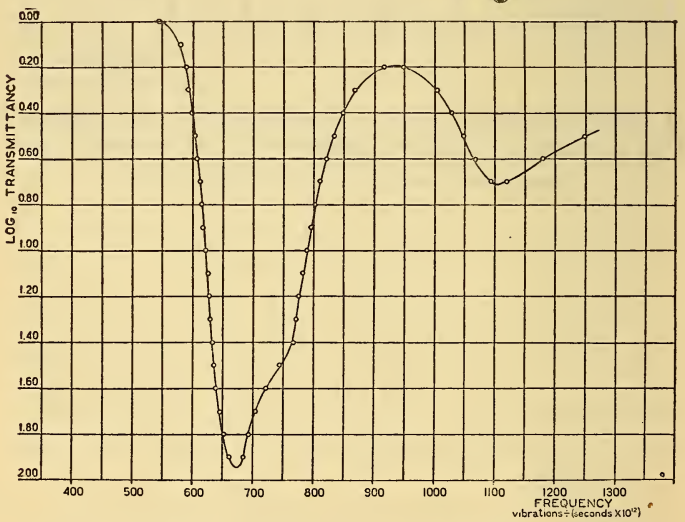


FIG. 17.—*The spectral absorption of benzeneazo-o-cresol (o) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

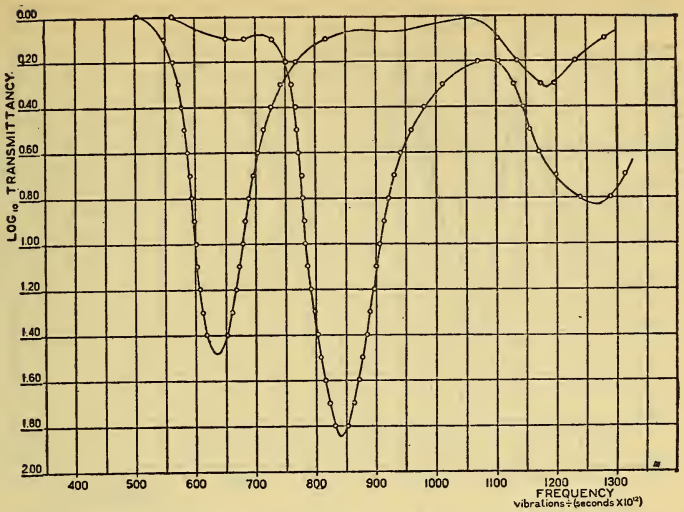
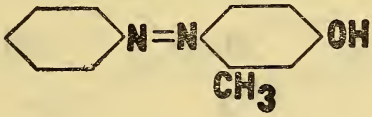


FIG. 18.—*The spectral absorption of benzeneazo-m-cresol (m) dissolved in 95 per cent ethyl alcohol (principal band at 840 f) and in concentrated hydrochloric acid (principal band at 636 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



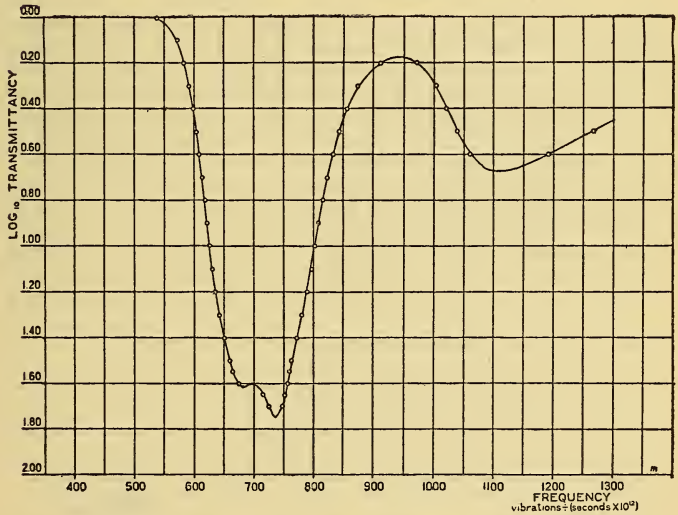


FIG. 19.—*The spectral absorption of benzeneazo-m-cresol (m) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

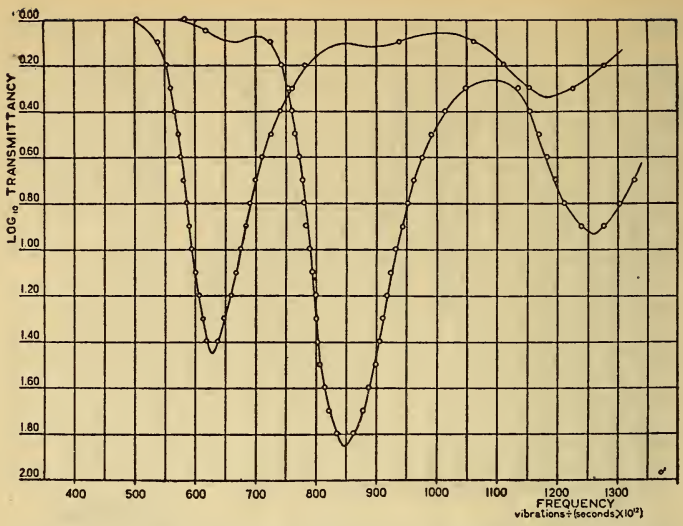
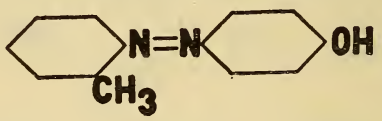


FIG. 20.—*The spectral absorption of o-tolueneazophenol (o′) dissolved in 95 per cent ethyl alcohol (principal band at 847 f) and in concentrated hydrochloric acid (principal band at 628 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



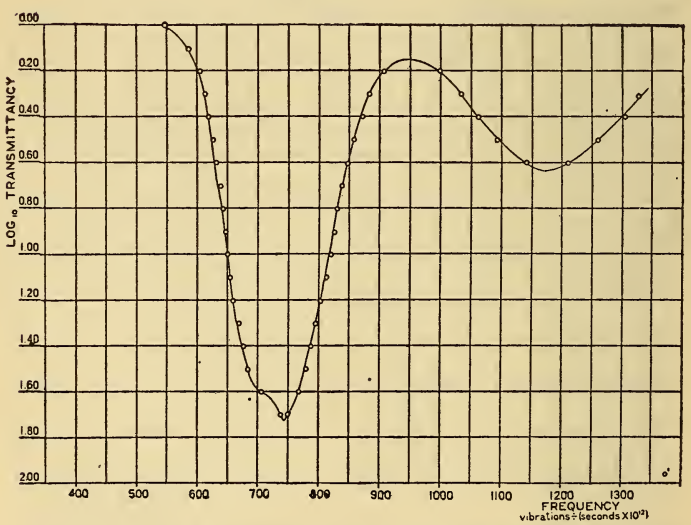


FIG. 21.—*The spectral absorption of o-tolueneazophenol (o′) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

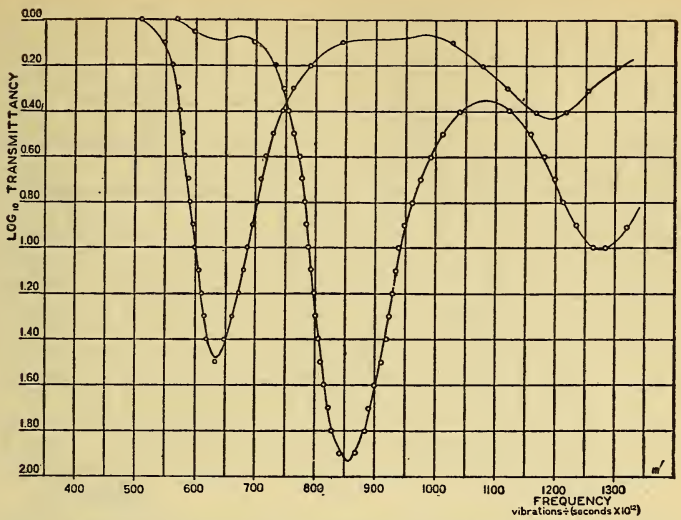
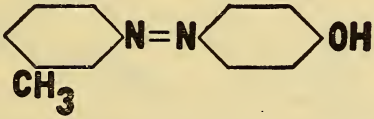


FIG. 22.—*The spectral absorption of m-tolueneazophenol (m') dissolved in 95 per cent ethyl alcohol (principal band at 855 f) and in concentrated hydrochloric acid (principal band at 632 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



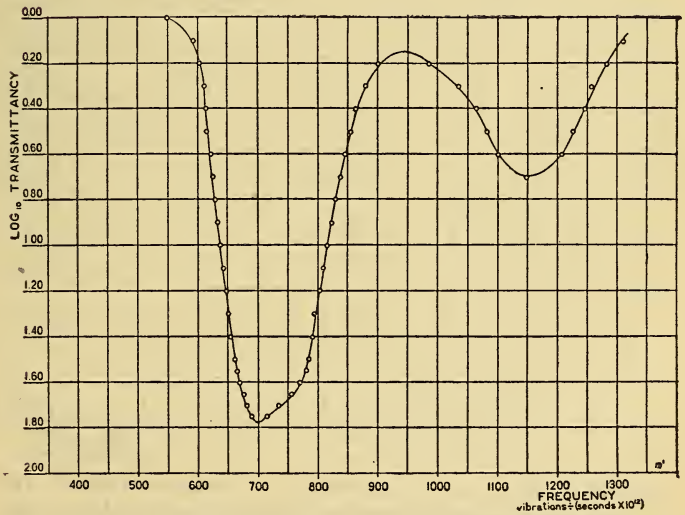


FIG. 23.—*The spectral absorption of m-tolueneazophenol (m') dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

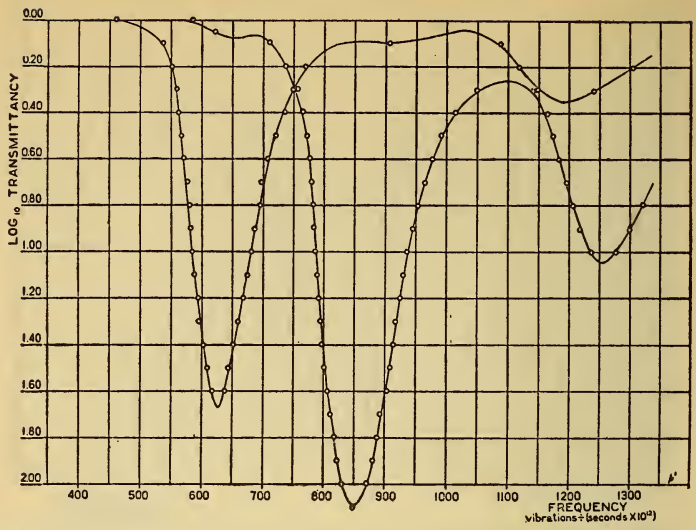
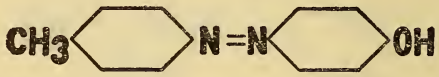


FIG. 24.—*The spectral absorption of p-tolueneazophenol (p′) dissolved in 95 per cent ethyl alcohol (principal band at 850 f) and in concentrated hydrochloric acid (principal band at 625 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



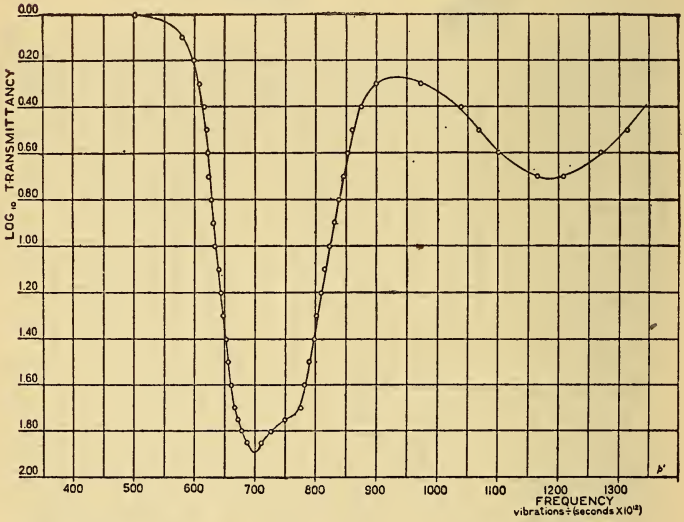


FIG. 25.—*The spectral absorption of p-tolueneazophenol (p′) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

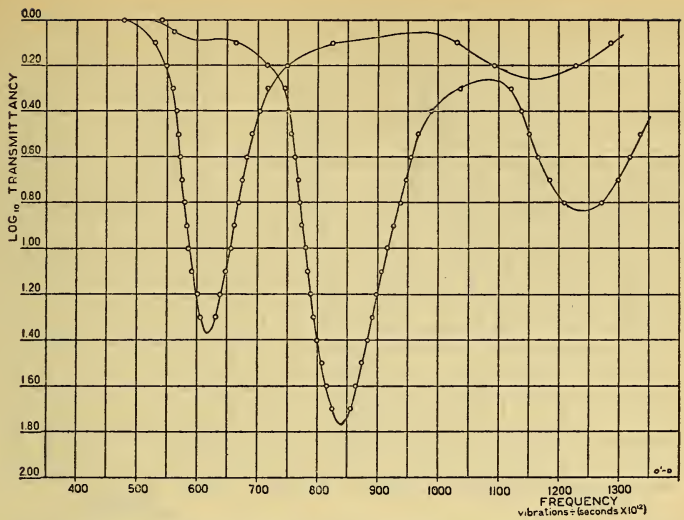
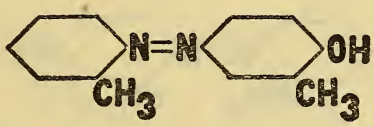


FIG. 26.—*The spectral absorption of o-tolueneazo-o-cresol (o′, o) dissolved in 95 per cent ethyl alcohol (principal band at 839 f) and in concentrated hydrochloric acid (principal band at 619 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



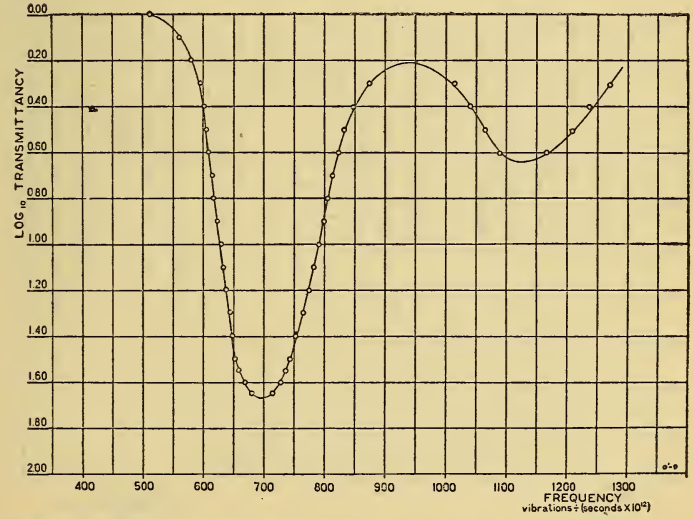


FIG. 27.—*The spectral absorption of o-tolueneazo-o-cresol (o′, o) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

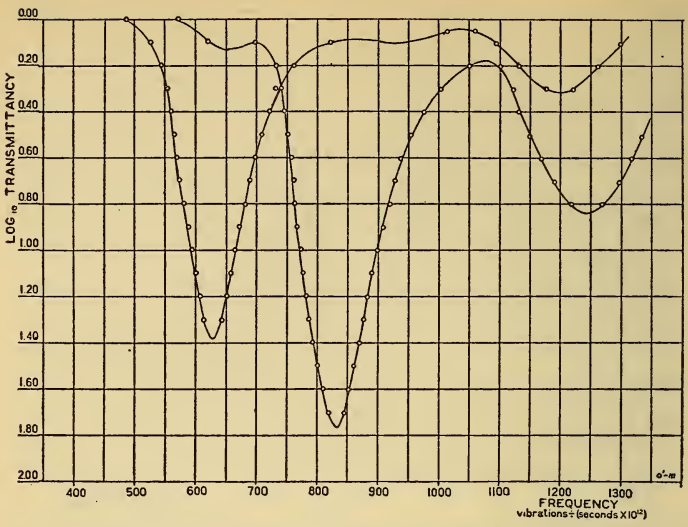
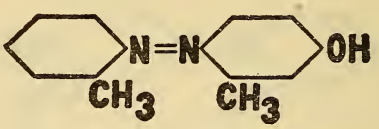


FIG. 28.—*The spectral absorption of o-tolueneazo-m-cresol (o′, m) dissolved in 95 per cent ethyl alcohol (principal band at 833 f) and in concentrated hydrochloric acid (principal band at 628 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



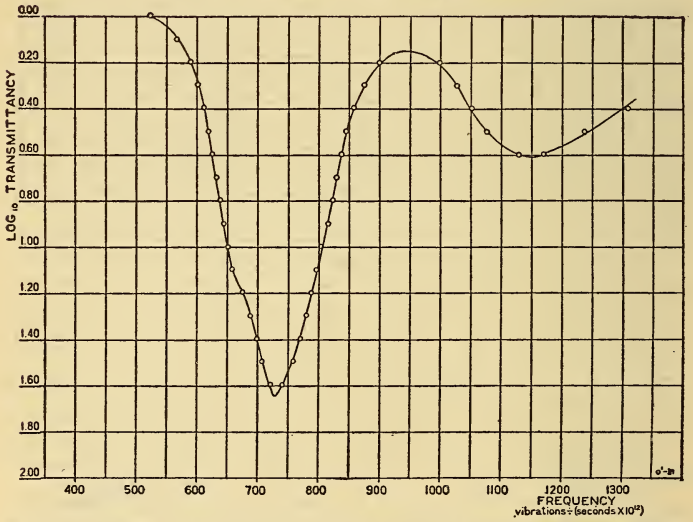


FIG. 29.—*The spectral absorption of o-tolueneazo-m-cresol (o′, m) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

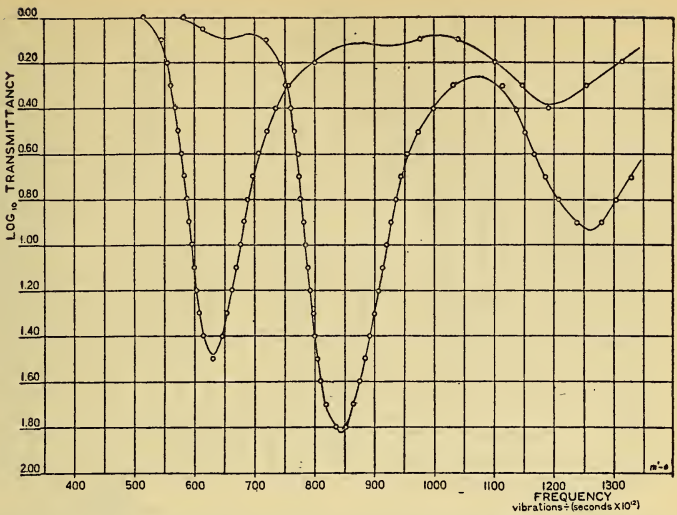
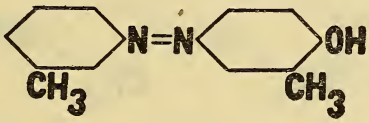


FIG. 30.—*The spectral absorption of m-tolueneazo-o-cresol (m′, o) dissolved in 95 per cent ethyl alcohol (principal band at 843 f) and in concentrated hydrochloric acid (principal band at 630 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



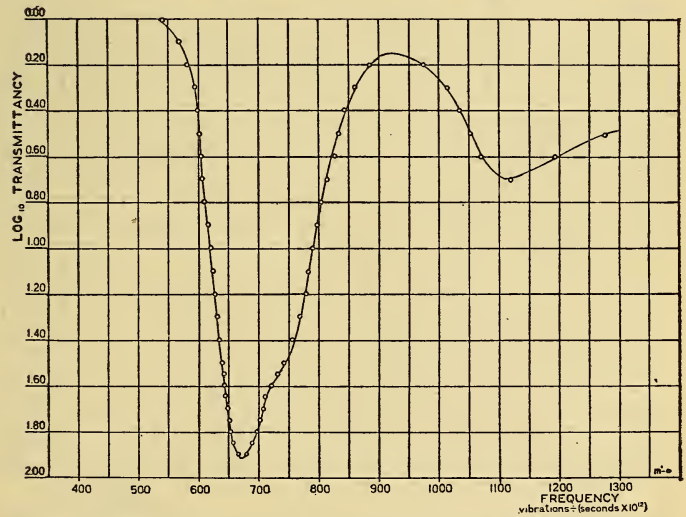


FIG. 31.—*The spectral absorption of m-tolueneazo-o-cresol (m′, o) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

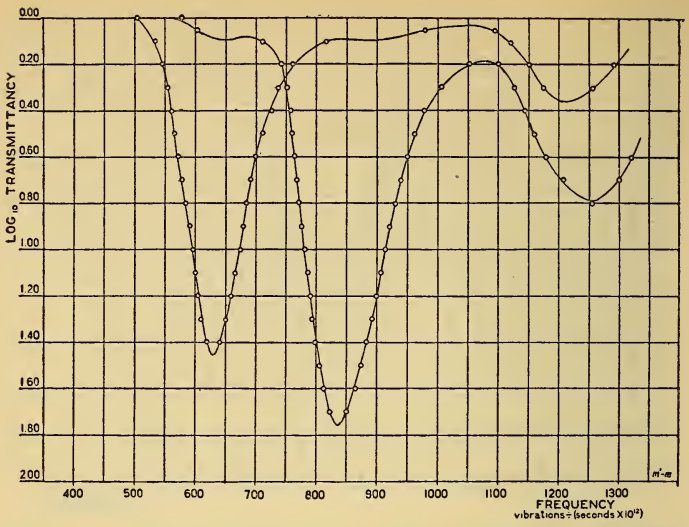
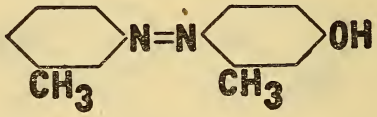


FIG. 32.—*The spectral absorption of m-tolueneazo-m-cresol (m′, m) dissolved in 95 per cent ethyl alcohol (principal band at 836 f) and in concentrated hydrochloric acid (principal band at 629 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid
Cell thickness, 0.5 cm in both cases



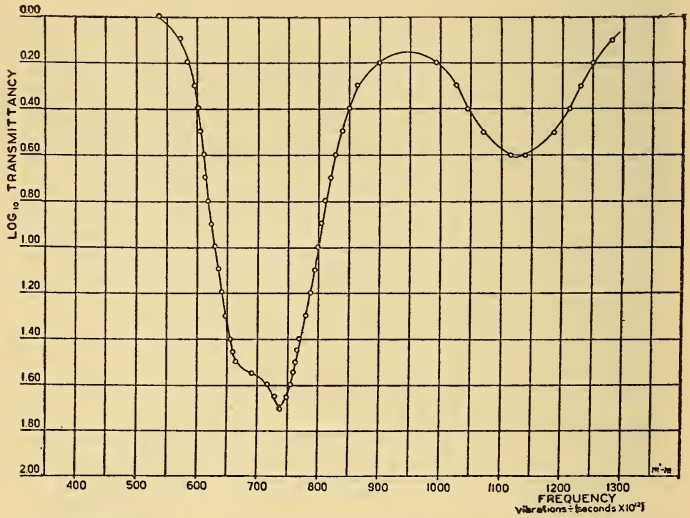


FIG. 33.—*The spectral absorption of m-tolueneazo-m-cresol (m′, m) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

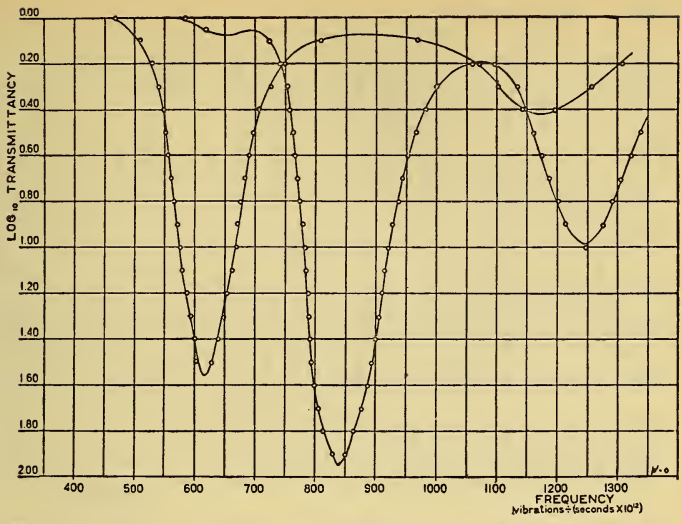
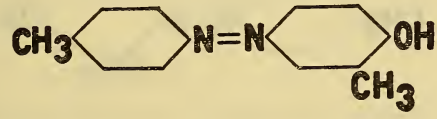


Fig. 34.—*The spectral absorption of p-tolueneazo-o-cresol (p′, o) dissolved in 95 per cent ethyl alcohol (principal band at 838 f) and in concentrated hydrochloric acid (principal band at 617 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



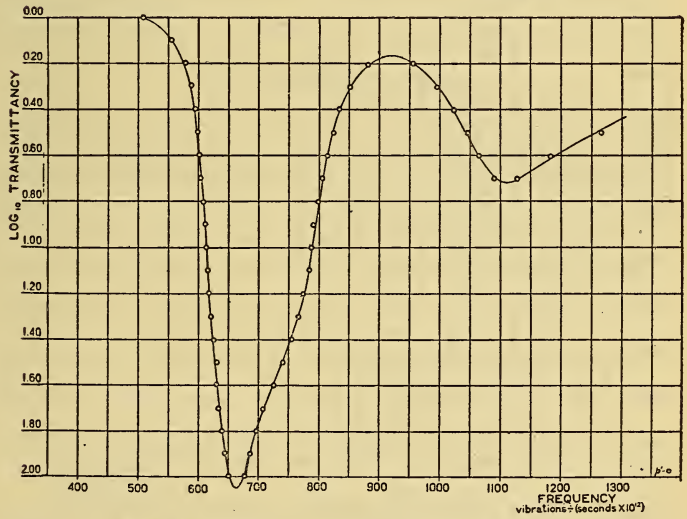


Fig. 35.—*The spectral absorption of p-tolueneazo-o-cresol (p′, o) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

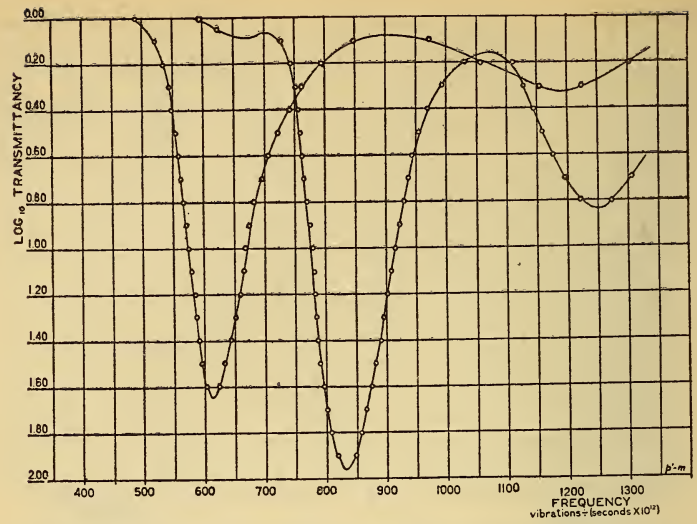
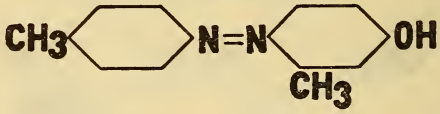


FIG. 36.—*The spectral absorption of p-tolueneazo-m-cresol (p′, m) dissolved in 95 per cent ethyl alcohol (principal band at 831 f) and in concentrated hydrochloric acid (principal band at 613 f)*

Concentration, 3.380 cg per liter in alcohol; 1.690 cg per liter in hydrochloric acid. Cell thickness, 0.5 cm in both cases



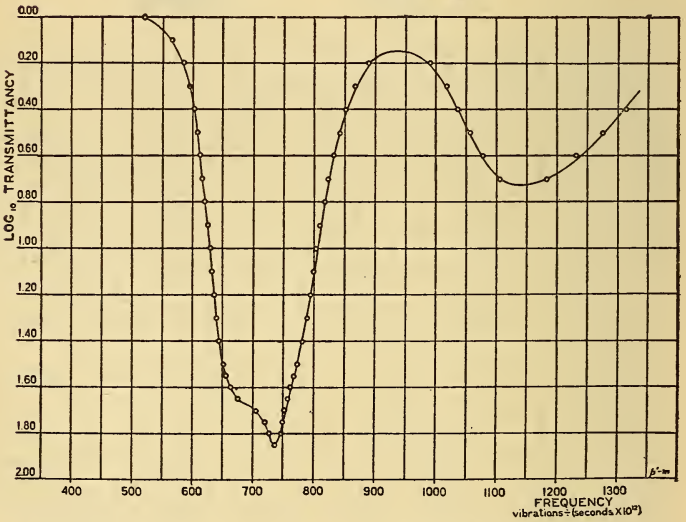


FIG. 37.—*The spectral absorption of p-tolueneazo-m-cresol (p′, m) dissolved in a 3 per cent aqueous solution of sodium hydroxide*

Concentration, 3.380 cg per liter. Cell thickness, 0.5 cm

WASHINGTON, September, 1926.