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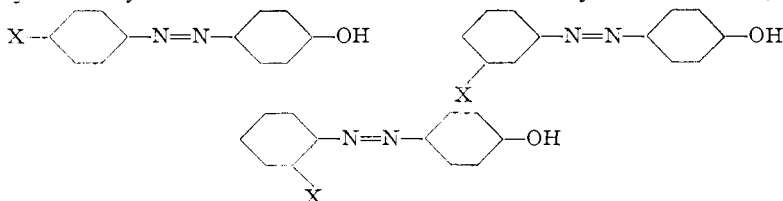
THE ABSORPTION SPECTRA OF PHENYLAZOPHENOL AND ITS DERIVATIVES

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In the electron theory of the absorption of light by organic substances¹ it is assumed that the valence electrons moving in orbits have the properties of electric currents and that the disturbance of one of these will affect those in the neighboring orbits in accordance with the laws of electrodynamics. The problem of interaction between neighboring molecules or groups of atoms then becomes one of mutual induction in neighboring circuits. According to this theory, selective absorption of light takes place when the frequency of light is the same as the natural period of the electron in its orbit. The introduction of new vibration centers will alter the original period of the electrons and produce a new characteristic frequency and thus change the absorption of the solution. From the point of view of this theory it then becomes of interest to consider the relation between the absorption spectra of organic substances in which the molecular structure can be varied through a known series of changes.

The derivatives of phenylazophenol lend themselves to such a study. They are easily obtained in several series of structurally isomeric forms, *i. e.*,



These substances form readily soluble metallic salts. The color, and hence the absorption in the visible region of the spectrum, are closely associated with the azo ($-\text{N}=\text{N}-$) group.

The absorption of phenylazophenol and its derivatives has been extensively studied^{2,3,4,5,6} and is characterized chiefly by a broad band lying in the ultra-violet and violet end of the visible spectrum. Salt formation either with alkalis or acids tends to shift the band toward the longer wave lengths, the displacement of the edge lying in the visible being roughly proportional to the displacement in the ultra-violet and in the same direction.

¹ McClelland, *Phil. Mag.*, [6] **29**, 192 (1915).

² Tuck, *J. Chem. Soc.*, **91**, 449 (1907).

³ Gorke, Köppe and Staiger, *Ber.*, **41**, 1156 (1908).

⁴ Hantzsch, *ibid.*, **42**, 2129 (1909).

⁵ Hantzsch and Robertson, *ibid.*, **43**, 106 (1910).

⁶ Robertson and Brady, *J. Chem. Soc.*, **103**, 1479 (1913).

It becomes possible, therefore, to follow the changes in the absorption by noting the progress of the displacement into the visible region as the molecule is loaded with various substituent atoms or groups.

Apparatus.—The observations were made by means of a Hilger constant deviation spectrometer (Fig. 1) to which was attached a Nutting polarization spectrophotometer,⁷

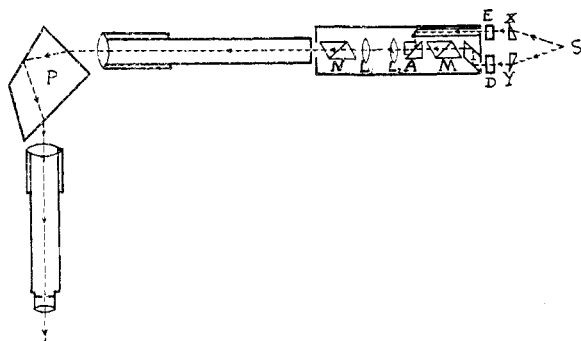


Fig. 1.—Hilger constant-deviaspectrometer and Nutting spectrophotometer.

and A , the extinction coefficient, was calculated from the usual equation, $I = I_0 e^{-cdA}$, where I_0 is the intensity of light received by absorption cell; I , the intensity of light after transmission by the cell; d , the thickness of absorption cell and c , the concentration of solution.

Preparation of Materials

Compounds.—The phenylazophenol derivatives were prepared by coupling the appropriate diazonium salt with phenol in sodium hydroxide solution. The dye was precipitated by acidifying with dil. hydrochloric acid, filtering and drying. Preliminary purification was effected by dissolving in aqueous ammonia or dil. sodium hydroxide solution and reprecipitating, usually with carbon dioxide. Final purification was made by repeated crystallizations from benzene or benzene-ligroin as the nature of the product required. The purity corresponded closely with the best given in the literature, as the following table of melting points will show.

TABLE I
SUBSTANCES AND MELTING POINTS

Substance	M. p. recorded °C.	M. p. found °C.
Phenylazophenol ⁸	152	154
<i>o</i> -Tolylazophenol ^{9,10}	102-103	101
<i>m</i> -Tolylazophenol ¹¹	144-145	144
<i>p</i> -Tolylazophenol ¹²	151	149.5

⁷ Bureau of Standards, *Bull.*, **2**, 317 (1906).

⁸ Heumann and Paganini, *Ber.*, **23**, 3550 (1890).

⁹ Noeltig and Werner, *ibid.*, **23**, 3257 (1890).

¹⁰ Hewitt and Pope, *ibid.*, **30**, 1628 (1897).

¹¹ Jacobson, *Ann.*, **287**, 161 (1895).

¹² Heumann and Oeconomides, *Ber.*, **20**, 905 (1887).

TABLE I (continued)

Substance	M. p. recorded °C.	M. p. found °C.
<i>o</i> -Chloro-phenylazophenol $\frac{1}{2}$ H ₂ O ¹³	96	95.7
<i>m</i> -Chloro-phenylazophenol $\frac{1}{2}$ H ₂ O ¹³	135	135
<i>p</i> -Chloro-phenylazophenol ¹³	154	154
<i>o</i> -Nitro-phenylazophenol ^{14,15}	155-157	155.6
<i>m</i> -Nitro-phenylazophenol ^{14,16}	159	158.8
<i>p</i> -Nitro-phenylazophenol ^{15,17}	212-213	213

Dilutions.—The stock solutions were in every case 0.002 *M*. The solvent for these stock solutions was 60% alcohol in all cases except for the glacial acetic acid solutions discussed below. One mg. mol of the pure dye was dissolved and diluted to exactly 500 cc. with the same solvent. Other dilutions were prepared from the stock solutions as indicated in the following table.

TABLE II
DILUTIONS USED

Conc. <i>M</i>	Ratio dye, alkali	Volume stock soln. Cc.	Volume standard Cc.	Alkali <i>N</i>	Diluent to make 100 cc.
0.001	{ 1 : 0 1 : 1 1 : 10 1 : 100 }	50	0.0		60% alc.
			10	0.01	Water
			10	0.1	Water
			10	1.0	Water
0.0002	{ 1 : 0 1 : 10 }	10	0.0		60% alc.
			20	0.01	Water

Solutions of phenylazophenol in glacial acetic acid were prepared from a 0.002 *M* stock solution in this solvent by an analogous method.

Results

Fig. 2 shows the absorption of *p*-tolylazophenol and its sodium, potassium and barium salts in 0.0002 *M* solution. The absorption band is shifted toward the red end of the spectrum by the substitution of the metal for the hydrogen atom of the phenol group. The shift in the barium salt is least and that in the sodium salt, greatest. The curves, however, lie close together for equal normality of alkali. It thus appears that this substitution produces a marked change in the characteristic frequency of the center of vibration which is responsible for the absorption. This change, which is such as would follow from a decrease in the frequency of the center of vibration producing the absorption band, can be thought

¹³ Hewitt, *Ber.*, **26**, 2975 (1893).

¹⁴ Noelting, *ibid.*, **20**, 2998 (1887).

¹⁵ Hewitt, Moore and Pitt, *ibid.*, **31**, 2121 (1898).

¹⁶ Meldola, *J. Chem. Soc.*, **10**, 143 (1894).

¹⁷ Bamberger, *Ber.*, **28**, 845 (1895).

of as arising from the mutual induction between electronic circuits in the original vibration center and those in the added substituent.

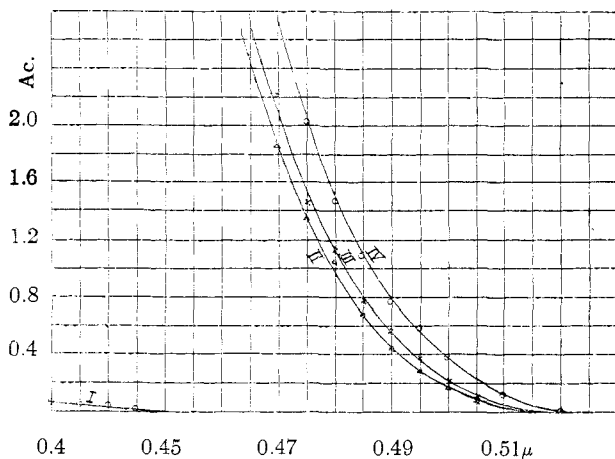


Fig. 2.—All solutions 0.0002 *M*. (I) *p*-Tolylazophenol; (II) *p*-tolylazophenol + 5Ba(OH)₂; (III) *p*-tolylazophenol + 10 KOH; (IV) *p*-tolylazophenol + 10 NaOH.

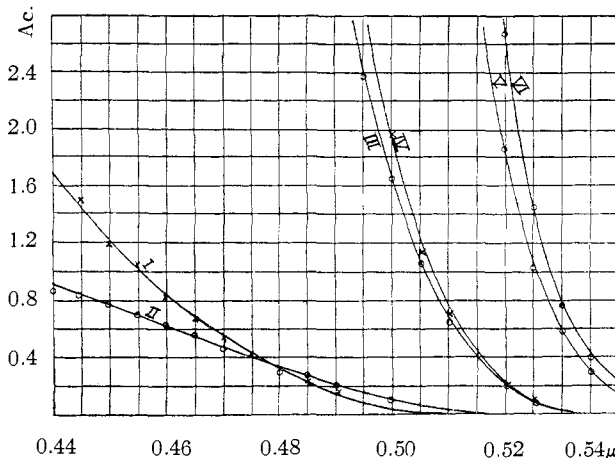


Fig. 3.—All solutions 0.001 *M*. (I) Phenylazophenol; (II) phenylazophenol + glacial acetic acid; (III) phenylazophenol + 10 NaOH; (IV) phenylazophenol + 100 NaOH; (V) phenylazophenol + 1 cc. HCl; (VI) phenylazophenol + 10 cc. HCl.

In Fig. 3, is shown the absorption of phenylazophenol in 0.001 *M* solutions. Curve I, shows the absorption of the free dye in 30% alcohol. Curve II is for the same substance in glacial acetic acid. Curves III

and IV are for phenylazophenol with 10 and 100 equivalents of sodium hydroxide, respectively, and lie very close together. Curves V and VI represent the absorption by phenylazophenol of concentration 0.001 *M* in glacial acetic acid to which 1 cc. and 10 cc., respectively, of conc. hydrochloric acid solution had been added. These curves lie in the same general region as those for the alkali salts, but are farther displaced toward the red end of the spectrum.

From the structural point of view, phenylazophenol and its alkali salts have the true azo structure¹⁸ while the hydrochlorides are represented

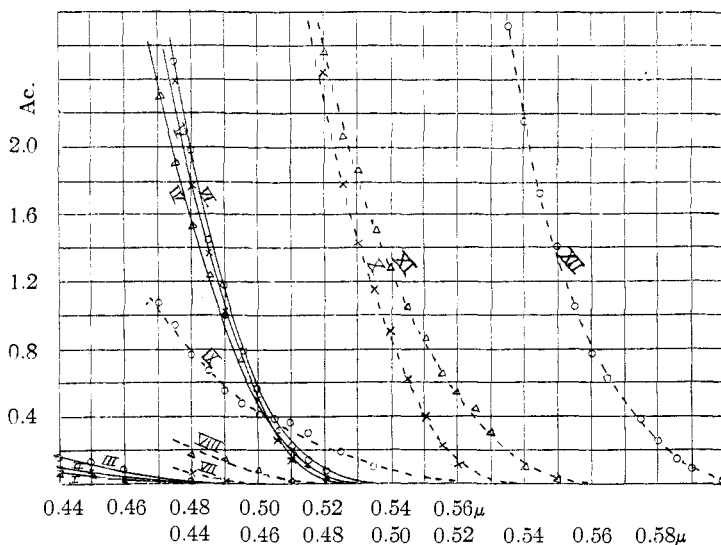


Fig. 4.—All solutions 0.0002 *M*. (I) *o*-Chloro-phenylazophenol; (II) *m*-chloro-phenylazophenol; (III) *p*-chloro-phenylazophenol; (IV) *o*-chloro-phenylazophenol + 10 NaOH; (V) *m*-chloro-phenylazophenol + 10 NaOH; (VI) *p*-chloro-phenylazophenol + 10 NaOH. (VII) *m*-nitro-phenylazophenol; (VIII) *o*-nitro-phenylazophenol; (IX) *p*-nitro-phenylazophenol; (X) *m*-nitro-phenylazophenol + 10 NaOH; (XI) *o*-nitro-phenylazophenol + 10 NaOH; (XII) *p*-nitro-phenylazophenol + 10 NaOH.

as the salts of the *p*-benzoquinone phenylhydrazone.⁴ The shifts of the absorption bands are of the same character, but differ in magnitude. Evidently, the change of frequency in the centers of vibration produced by the formation of the alkali salt is less than the changes which arise in the formation of the hydrochloride.

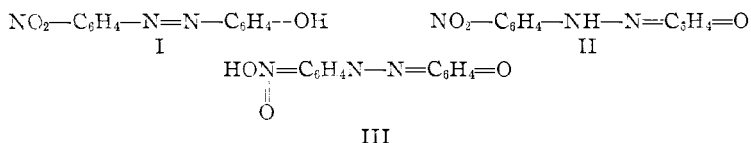
The absorption of the three chloro-phenylazophenols in 0.001 *M* solutions in 60% alcohol, and in the presence of aqueous caustic soda is represented by the continuous curves on the left hand side of Fig. 4. In each case as in *p*-tolylazophenol the presence of the alkali shifts the absorption

¹⁸ McPherson, *Am. Chem. J.*, **22**, 364 (1899).

band toward the red end of the spectrum. The *ortho* isomer absorbs least and the *para* most, and this same order is maintained in the alkaline solutions.¹⁹

The dotted curves of Fig. 4 show the absorption of the three nitro-phenylazophenols both in 60% alcohol and in aqueous sodium hydroxide. In this case the free *meta* compound absorbs least and the *para* most. The same order is again maintained in the alkaline solutions.

Structurally *o*- and *p*-nitro-phenylazophenols may be represented by three possible formulas.



Formula I represents them as true azophenols, II as the nitro-phenylhydrazones of *p*-benzoquinone, and III as the mononitronic acid analogs of *p*-benzoquinone-azine. Borsche²⁰ has shown that these two isomers, but not the *meta*, are formed by the action of *o*- and *p*-nitro-phenylhydrazine upon *p*-benzoquinone, a method of synthesis which should yield products with the structure II. This author, however, from the properties of the compounds regarded them as true azophenols, I.

Hewitt and Mitchell²¹ and also Baly, Tuck, and Marsden²² have studied the absorption of the nitro-phenylazophenols. From the results obtained the former workers concluded that the alkali salts should be regarded as having Structure III. Baly and his co-workers were equally convinced that all the derivatives should be regarded as true azophenols.

The curves in Fig. 4 show that the absorption in the visible is much more pronounced in the case of the *para* isomer. In this respect the behavior of this isomer resembles that of phenylazophenol hydrochloride in glacial acetic acid (Fig. 3) which according to Hantzsch has a hydrazone structure, $\text{C}_6\text{H}_5\text{—N(HCl)H—N=C}_6\text{H}_4\text{=O}$. Consequently, from the point of view of the interaction of neighboring electronic circuits in the molecules or atomic groupings, it might be expected that these derivatives would give rise to similar selective absorption.

The shifts of the absorption bands toward the red observed in these azophenols are such as would follow from the electron theory of selective absorption. The electronic currents in new centers of vibration would according to the laws of electrodynamics change the frequency of the elec-

¹⁹ An extension of this work, covering some 60 substitution derivatives of azobenzene and now nearing completion, has developed the fact that the order is not the same in solutions of higher concentration. This shift will be fully discussed in a later paper.

²⁰ Borsche, *Ann.*, **357**, 171 (1907).

²¹ Hewitt and Michell, *J. Chem. Soc.*, **91**, 1264 (1907).

²² Baly, Tuck and Marsden, *ibid.*, **97**, 1494 (1910).

trons in the neighboring centers. This change would be such as to decrease the natural period of vibration of the molecular species by an increase in its effective inductance. Since selective absorption occurs where the natural frequency of the electrons in the molecular species approaches the frequency of the incident light, selective absorption takes place for lower frequencies and longer wave length in the salts than in the free substance. This seems a more intimate, though not necessarily a different explanation from that suggested by Baly.²³ According to his theory, when groups of atoms are united to form molecules, there will be a certain condensation of the magnetic and electric fields about them to make the system as nearly as possible closed. If such a system is opened up as in the formation of salts of these azophenols, the chemical reactivity is increased and the absorption band shifted toward the red end of the spectrum. Thus, the mutual influence of two centers of vibrations is to shift the absorption band toward the red end of the spectrum. McClelland thinks of this as due to mutual induction between the electronic circuits, while Baly does not clearly specify the nature of the interaction between the centers of vibration.

Summary

1. The absorption spectra of phenylazophenol, and each of the three isomeric tolylazophenols, chloro-phenylazophenols and nitro-phenylazophenols, respectively, have been studied by the visual method.
2. The substitution products absorb light more strongly in the visible than does phenylazophenol, and the alkali salts more strongly than the free dyes.
3. The order of absorption for the isomers in the dilutions studied is $p > m > o$, excepting for the nitro derivatives, when it becomes $p > o > m$. The deviation of the latter derivatives may be due to a difference in structure.
4. These changes in absorption by substitution are discussed briefly in the light of McClelland's mutual induction theory of light absorption.

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²³ Baly, "Spectroscopy," Longmans, Green and Co., 1912 p. 483.