

3. 4-*p*-Tolylthiosemicarbazide reacts readily with the above ketones to give easily purified solid derivatives having definite melting points.

CHAPEL HILL, NORTH CAROLINA

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF SWARTHMORE COLLEGE]
**THE INFLUENCE OF THE HALOGENS ON THE COLOR OF AZO
 DYES. THE SPECTRAL ABSORPTION OF CERTAIN
 MONO-AZO DYESTUFFS**

BY DUNCAN GRAHAM FOSTER

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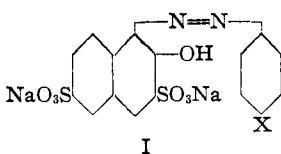
Introductory

Some years ago the author participated in one of a series of investigations on the relation of molecular structure to the color of azo dyes.¹ The influence of *o*-, *m*- and *p*-substitution of sulfur and oxygen was studied,^{2,3,4} and the preparation of dyes containing selenium is now under way.⁵

In all of this work color comparisons were made simply by the inspection of dyed samples. Recently the method of color analysis made possible by the development of the spectrophotometer has reached a stage where it is particularly valuable for this kind of study, and we hope that eventually all of the many dyes prepared in the investigations mentioned above may be quantitatively compared by means of this instrument.

This paper reports measurements of the spectra of dyes containing another group of the periodic system, the halogen family, with the spectrophotometer, to show the effect of *o*-, *m*- and *p*-substitution of chlorine, bromine and iodine. We attempted also to measure their absorption in the near ultraviolet with a quartz spectrograph and a densitometer, but because of the crudity of the apparatus were not able to obtain accurate results, and so have postponed this work until better instruments shall be available.

Preparation of the Dyes.—In order to preserve continuity with the dyes already studied, we selected dyes prepared by coupling an amine containing the halogen atom with R-salt. These compounds had the structure I, in which X is the halogen atom, shown here in the *p*-position. The *o*-, *m*- and *p*-chloro-, bromo- and iodo-anilines used were either bought on the market (Eastman Kodak Co.) or made by reduction of the corresponding halogeno nitrobenzene. In the latter case the amine was isolated as the hydrochloride.¹



¹ Foster and Reid, *THIS JOURNAL*, **46**, 1936 (1924).

² Waldron and Reid, *ibid.*, **45**, 2399 (1923).

³ Holt and Reid, *ibid.*, **46**, 2329; **46**, 2333 (1924).

⁴ Palmer and Reid, *ibid.*, **48**, 528 (1926).

⁵ See Foster and Brown, *ibid.*, **50**, 1182 (1928).

The purity of these compounds was established by the sharpness of the melting or boiling points. Solid compounds were recrystallized and liquid ones redistilled, if necessary, to melt or boil over a range of not more than one degree, and in most cases the melting or boiling range was less than this. Further purification was effected in the double (in some cases triple) recrystallization of the dyes themselves. There is, of course, no way of estimating the presence of a para compound in its ortho analog or *vice versa*, but this purification was felt to be amply sufficient to prevent the spectrum from being affected. Meta dyes, because of the different method of preparing the intermediate, could not be contaminated with the other isomers.

The amines were diazotized and coupled with R-salt by the standard method previously employed.² The dye made by coupling aniline with R-salt, which is the parent substance of the whole group, was prepared for use as a control. These compounds were all twice (at least) recrystallized from hot water. Because they were sodium salts and had no melting points, there was no criterion of purity, but sodium chloride, from the salting-out of the dye, is the only impurity likely to be present and this would not interfere with the spectral absorption. For purposes of making up standard solutions, the analyses gave us the amount of pure dyestuff present, and in point of fact it later developed that water was the chief contaminant of the solid dyes.

Analysis of the Dyes.—The dyes were analyzed both as dried samples and as indeterminate solutions made from the same samples. These indeterminate solutions were then used as stock solutions to make up the final solutions examined by the spectrophotometer. The method used was that of titration with titanous chloride, which is both rapid and accurate.⁶

Quantities sufficient to make 1 liter of $M/50$ solution were weighed roughly, dissolved in hot water and made up to 1 liter in a volumetric flask; 25-ml. titers were measured with a Bureau of Standards pipet and an excess of standard titanous chloride solution added from a buret. The excess was then determined with standard ferric ammonium sulfate solution, using ammonium thiocyanate as an indicator. This gave the amount of dyestuff in the solution and enabled us to calculate the volume that must be taken to make an exactly 5×10^{-5} molar solution, when diluted to one liter.

All the data thus obtained are given in Table I, in which the figures are the average of three determinations in each case.

The low percentages of dyestuff in each dry sample were due to the fact that the dyes are highly hygroscopic and took up moisture perceptibly

⁶ Knecht and Hibbert, "New Reduction Methods in Volumetric Analysis," Longmans, Green and Co.

TABLE I
 ANALYTICAL DATA

Dye	Wt. of dye for 1 liter of $5 \times 10^{-5} M$ soln.	Dry dye found, %	Stock solution for 1 liter of 5×10^{-5} soln., ml.
Aniline	0.0229	87.20	23.20
<i>o</i> -Chloro	.0243	87.37	25.51
<i>m</i> -Chloro		90.80	23.15
<i>p</i> -Chloro		80.20	26.88
<i>o</i> -Bromo	.0266	92.40	20.78
<i>m</i> -Bromo		85.24	24.30
<i>p</i> -Bromo		90.28	26.92
<i>o</i> -Iodo	.0289	90.80	21.87
<i>m</i> -Iodo		97.10	22.52
<i>p</i> -Iodo		86.57	30.36

while being weighed. The *m*-iodo dye, for example, after drying for one hour at 85° and cooling in a desiccator, gained 4 mg. while weighing. The same sample, dried for one hour at 100°, cooled in a desiccator and rapidly weighed gave 97.10% of dye, the highest percentage obtained. All the others were exposed to the air for twenty-four hours to insure that their aqueous tension had reached that of the atmosphere. These samples were not used in making up our solutions for examination, so that the high moisture content has no effect on the final concentration.

Preparation of the Solutions.—Preliminary trials showed that a concentration of 5×10^{-5} molar was the most satisfactory to use in the spectroscopic examination. These solutions were made by measuring from a Bureau of Standards buret exactly (to 0.02 ml.) the quantity of the stock solutions described above required by the analysis to give this concentration when diluted to one liter. These quantities were diluted, with careful adjustment for temperature, in a Bureau of Standards volumetric flask, first adding from a pipet 10 ml. of a buffer solution of sodium acetate and acetic acid. This buffer was kept in stock in such concentration that 10 ml. would give a solution 0.01 *N* in both sodium acetate and acetic acid in the final volume of 1 liter. These solutions were freshly prepared within three to four hours before using.

That this method of analysis and preparation of solutions was of satisfactory accuracy was checked by repeating the spectral measurements in two cases with solutions made up freshly from dry dyestuff, analyzed separately and diluted to give the necessary concentration. These "repeat experiments" gave spectral absorption curves coincident with the originals, within the limitations of the instrument (see below).

Determination of the Spectral Absorption.—For the color analysis a Keuffel and Esser Color Analyzer was used,⁷ modified for use only with

⁷ This instrument and its accessories were put at the author's disposal through the kindness of the Technical Laboratory of the E. I. du Pont de Nemours Company, which the author hereby gratefully acknowledges.

solutions and reading directly the negative logarithm of the transmittancy. The cells were a special open-topped type made wholly of optical glass and were especially easily cleaned and filled. They offered a solution thickness of 10 mm. They were filled with a broad-tipped pipet and both pipet and cell were washed three times with solution before filling. Readings were taken at intervals of 10 millimicrons, first setting the wave length scale at the desired figure. Three readings agreeing within the limit of accuracy were made for each setting. This limit varies with the wave length and runs from about 0.002 of a unit at 700 millimicrons to about 0.1 of a unit at 450 millimicrons, the range over which determinations were made. Whenever it seemed necessary, particularly at the peaks and shoulders of the absorption bands, readings were taken at intervals of 5 millimicrons.

To check the accuracy and guard against personal error, a standard glass No. G. 586-A was measured and checked after measurement against figures published by the Bureau of Standards. The measurements were found to agree with the Bureau of Standards figures within the above limits. The instrument itself was also checked for adjustment at maximum and minimum transmittancy before each half-day's work.

Calculation of Results and Plotting of Graphs.—The values determined and plotted are the negative logarithms of the transmittancy of the dye solution at given wave lengths. The *transmittancy* is defined as the ratio of the *transmittance* of the solution to that of the solvent, or $T_{\text{sol.}}/T_{\text{sov.}} = \mathbf{T}$.⁸ The negative logarithm of this value represents as nearly as possible the way the color appears to the eye. In this paper these values are plotted from the top downward as abscissas, against the wave length as ordinates.

Discussion of Results

Examples of the spectral absorption curves obtained are given in the figures. Because no striking differences were observed, we are publishing one set of curves only and one "analyzed" curve, in order to economize space. In Fig. 1 the isomeric *o*-, *m*- and *p*-chloro derivatives are plotted together to show the difference between them. The color of all the dyes was red, with the chief absorption band in the violet portion of the spectrum, at almost the same wave length in every case. When dyed to 2% dyeings on wool flock they showed differences in shade easily visible to the naked eye, in the same directions but of a lesser magnitude than had been shown by the corresponding dyes containing sulfur.

It was obvious from the graphs that the color difference is a complex phenomenon, not due to a simple change in the magnitude or position of the chief absorption band. Thus a color that appears deeper red to the

⁸ For detailed definitions see Brode, *Bureau of Standards Journal of Research*, **2**, 502 (1929).

eye than another may have a lesser absorption in the red portion of the spectrum *or* a deeper absorption in the violet, or both. It may also have quite different characteristics in the yellow or green or even a uniform difference throughout the entire range preceding the chief absorption band. This last effect is shown most strikingly by the three bromo dyes, which exhibit absorption curves parallel but of slightly different depth throughout the whole of this range.

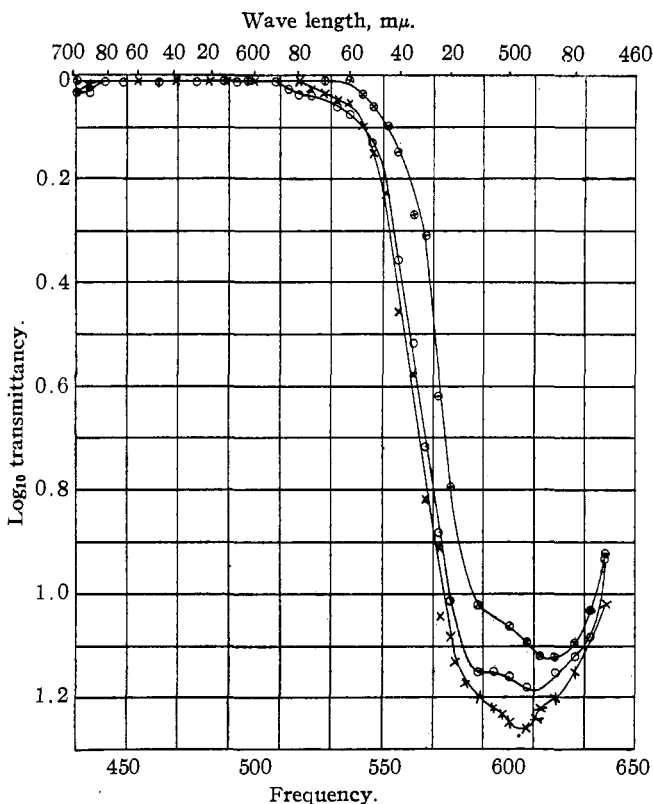


Fig. 1.—Chlorine dyes: ○, ortho; ⊕, meta; ×, para.

There is no uniformity even in the influences of position isomerism, for the depth of the absorption band for the chloro and bromo dyes increases in the order meta, ortho, para; while with the iodo dyes this sequence is ortho, meta, para. From the data obtained it is extremely difficult to make any generalizations.

The irregularities appearing near the peaks of the absorption bands appear as well in all the other dyes not shown in the figures. The iodine dyes, in fact, show two of them, one on either side of the peak of the band. We do not believe that these are accidental, since repetitions of the meas-

urements in two instances, made two days apart with fresh solutions, gave the same results.

Brode has observed the same effect with other dyes and has suggested that it is due to the presence of two or more component bands partly superimposed upon each other.⁹ According to him these component bands are

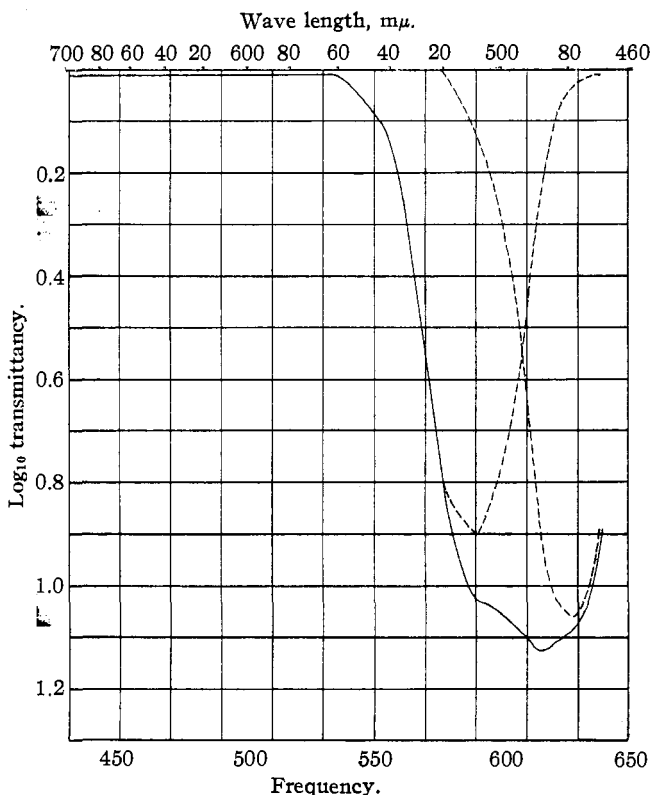


Fig. 2.—Analysis of the spectral curve of the *m*-chloro dye into its components. The solid curve is the experimental curve, the dotted curves the components, so drawn that the sum of the abscissas of the component curves at any point equals the abscissa of the experimental curve at the same point.

caused by two or more color-absorbing constituents of the dye molecule in equilibrium with each other, and the absorption curves can be analyzed to show their position and shape. Such an analysis for the *m*-chloro dye is shown in Fig. 2.

In general, the shift in the magnitude of the chief absorption bands due to position isomerism is in accord with the observations to be found in the literature. *p*-Substitution brings about a marked increase in depth, *o*-

⁹ Reference 8 above, p. 520.

substitution a decrease and *m*-substitution a less marked decrease. The only exception to these rules are our *m*-chloro and *m*-bromo dyes, which show a greater decrease than the corresponding *o*-compounds.

Summary

1. A series of dyes containing the three halogens in the *o*-, *m*- and *p*-positions have been prepared, their spectral absorptions in water solution determined and compared with that of a parent dye containing no halogen.

2. The results show no simple relationship between the dyes attributable to variations in molecular weight but a complicated effect distributed in different portions of the spectrum.

3. The effect of position isomerism is for the most part the same as that observed by other workers.

4. The chief absorption bands appear to be composed of two or more constituent bands. These have in one instance been calculated.

SWARTHMORE, PENNSYLVANIA

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES OF COLUMBIA UNIVERSITY No. 650]

RESEARCHES ON THIAZOLES. XVI. THE SYNTHESIS AND STUDY OF NEW AMINOTOLUTHIAZOLES AND DERIVATIVES FROM 2,5-DIAMINOTOLUENE-4-THIOSULFURIC ACID

BY MARSTON TAYLOR BOGERT AND MANASSEH G. SEVAG

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Following up the work already reported¹ from these laboratories on benzothiazole dyes, incidental and related compounds, it seemed to us desirable to ascertain the tinctorial properties of such dyes when they carried also free amino groups in the molecule, and the present paper is a contribution to the solution of the problem, in that it describes a method by which the necessary intermediates may be synthesized and records some preliminary experiments in the preparation therefrom of dyes of the Columbia Yellow (Colour Index No. 814) class.

The initial material was the 2,5-diaminotoluene, which was converted into a monothiosulfuric acid by the method of Bernthsen.² Theoretically, such a derivative might possess any one of the structures I, II or III, all of which are capable of yielding benzothiazoles. Thus, if condensed with *o*-nitrobenzaldehyde, they should give the thiazoles IV, V and VI, respectively, elimination of whose amino groups should result in the production of VII, VIII and IX.

¹ (a) Bogert and Bergeim, *Color Trade J.*, **15**, 63 (1924); (b) Bogert and Allen, *Ind. Eng. Chem.*, **18**, 532 (1926); (c) Bogert and Allen, *THIS JOURNAL*, **49**, 1315 (1927).

² Bernthsen, *Ann.*, **251**, 61 (1889).