[Contribution from the National Bureau of Standards]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXX. Photoisomerization of Azo Dyes in Aqueous Solution[1,2]

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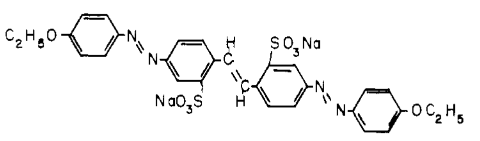
Although it has been possible to detect little or no phototropism in solutions of *p*-aminoazo and *p*-hydroxyazo compounds in hydroxylic solvents up to this time, it has been found that phototropic effects (which undoubtedly stem from photochemical *cis–trans* isomerization) can readily be observed with *p*-alkoxyazo compounds. A number of water-soluble methoxyazo compounds have been prepared. The *cis* isomers of these compounds are relatively stable in water, and all of the compounds show marked spectral changes when their aqueous solutions are irradiated. In contrast to the behavior of the corresponding hydroxyazo compounds, the rate of the thermal *cis* to *trans* reaction of some methoxy compounds is more rapid in alcohol or acetone than in water.

Introduction

Previous studies on the reversible photochemical *cis–trans* isomerization of *p*-hydroxyazo and *p*-aminoazo compounds have indicated that the phototropic effects are suppressed by ethanol.[3] The effect of this hydroxylic solvent would appear to be chiefly a result of an increase in the rate of the thermal *cis* to *trans* isomerization, for Hartley has shown that the addition of traces of methanol to benzene solutions of *p*-hydroxyazobenzene or *p*-aminoazobenzene greatly reduces the half-lives of the *cis* isomers.[4] It is therefore not surprising that aqueous solutions of most typical water-soluble azo dyes show no change in spectrum upon irradiation.[5]

However, one well-known dye, Chrysophenine (the sodium salt of 4,4′-bis-(4-ethoxyphenylazo)-stilbene-2,2′-disulfonic acid, C.I. 24895),[6] has been reported to show marked phototropic effects in aqueous solutions.[7] Studies with this dye indicate that these changes in spectrum are likewise a result of *cis–trans* isomerization about the azo linkages,[8] and that the ethylenic linkage is not involved. Chrysophenine differs from other common azo dyes by the presence of ethoxyl groups rather than the auxochromic hydroxyl or amine groups more commonly found in these dyes. Irradiation of water solutions of the dye Brilliant Yellow (C.I. 24890), which differs from Chrysophenine only by possessing hydroxyl groups in place of the ethoxyl groups, produces no spectral changes.[9]



Chrysophenine

Furthermore, in benzene or acetone solutions, the *cis* isomer of *p*-methoxyazobenzene has been reported to be very much more stable (the half-life is 600 times longer) than that of *p*-hydroxyazobenzene.[4] The relative stability of the *cis* isomers of *p*-alkoxyazo compounds (as compared to the corresponding hydroxy- or aminoazo derivatives) suggested the desirability of investigating aqueous solutions of a number of methoxyazo compounds for possible phototropic effects.

Experimental

(a) **Preparation of Methoxyazo Compounds.**—The hydroxyazo compounds used as starting materials were either commercial dyes of known composition or were prepared by conventional methods of diazotization and coupling. Methyl sulfate was used as the methylating agent, and the solvent was water, acetone or an acetone-water mixture. Small portions (1 to 2 ml.) of methyl sulfate and of a 20% sodium hydroxide solution were added alternately to a well-stirred solution of the hydroxyazo dye, keeping the mixture basic at all times. No external heating was required. After 5 or 10 minutes the reaction mixture became noticeably warmer, and in some cases precipitation of the methylated dye was observed. Addition of the methyl sulfate and sodium hydroxide was continued until no color change was observed when a small sample of the reaction mixture was diluted and acidified. The total reaction time varied from one to several hours, and a considerable excess of methyl sulfate was required. Stirring was continued for an hour after the reaction appeared to be complete. Additional sodium hydroxide then was put in and the reaction mixture was warmed to remove excess methyl sulfate. The crude product obtained by concentrating the reaction mixture was recrystallized several times from water or alcohol, the choice of solvent depending on the dye.

When working with hydroxyazo compounds derived from salicylic acid, it was observed that some methylation of the carboxyl groups occurred. Before recrystallization, these methyl groups were removed by refluxing the product with 20% sodium hydroxide solution for an hour.

The dyes prepared for this investigation are listed in Table I.

(b) **Measurement of Absorption Spectra.**—The absorption spectra were determined by means of a Cary recording spectrophotometer (model 14) using matched fused quartz absorption cells with the solvent as the reference standard.

(c) **Irradiation of Solutions.**—For irradiation, a 500-watt projection lamp, placed between two concave mirrors, was used. Light from the source was condensed by one mirror,

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[1] Presented at the 134th National Meeting of the American Chemical Society, Chicago, Ill., September, 1958.

[2] This research was supported in part by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command under contract No. CS-680-57-3. Reproduction in whole or in part is permitted for any purpose of the United States Government.

[3] W. R. Brode, J. H. Gould and G. M. Wyman, This Journal, **75**, 1856 (1953).

[4] G. A. Hartley, *J. Chem. Soc.*, 633 (1938).

[5] G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955).

[6] C. I. numbers are taken from the "Colour Index," 2nd edition, The Society of Dyers and Colourists, Bradford, England, 1956.

[7] E. I. Stearns, *J. Opt. Soc. Amer.*, **32**, 282 (1942); H. F. Willis, J. O. Warwicker, H. A. Standing and A. R. Urquhart. *Trans. Faraday Soc.*, **41**, 506 (1945).

[8] E. Atherton and R. H. Peters, "Recent Advances in the Chemistry of Colouring Matters," Special Publication No. 4, The Chemical Society, London, p. 17 (1956).

[9] We have found this dye to be somewhat phototropic in acetone. The spectral changes obtained are very similar to those observed with Chrysophenine, but are not as extensive. We did not observe any increase in intensity above 450 mμ as reported for this dye in pyridine–water solution by A. S. Dunn ("Recent Advances in the Chemistry of Colouring Matters," Special Publication No. 4, The Chemical Society, London, p. 45 (1956)). Such an increase in intensity might be a result of an indicator change, for this dye has an absorption maximum at 475 mμ in basic solutions.

TABLE I

ABSORPTION SPECTRA DATA OF METHOXYAZO COMPOUNDS IN WATER

	trans Form[b]				Effect of irradiation		
Compound, acid[a]	λ_{max}	$\epsilon_{max} \times 10^{-3}$	λ_2	$\epsilon_2 \times 10^{-3}$	Filter used[c]	λ'[d]	Max. % de-crease[e]
m-(4-Methoxyphenylazo)-benzenesulfonic	348	25	241	13	348–386	365	91
p-(4-Methoxyphenylazo)-benzenesulfonic	352	26	241	11	348–386	367	91
p-(2,4-Dimethoxyphenylazo)-benzenesulfonic	375	16	240	8	352–415	385	80
4-Methoxy-3-(2,4-dimethoxyphenylazo)-benzenesulfonic	382	16	252	10	368–394	385	82
4,4'-Dimethoxyazobenzene-3,3'-dicarboxylic	362	21	253	11	342–395	370	90
5,5'-(4,4'-Biphenylenebisazo)-bis-(2-methoxybenzoic)	382	40	230	18	342–403	395	43
4,4'-Bis-(4-methoxy-3-carboxyphenylazo)-biphenyl-2,2'-disulfonic	358	58	250s[f]	(27)	348–396	370	78

[a] As sodium salt. [b] Wave length (in mμ) and molar absorption coefficient of most intense absorption band and of secondary absorption band. [c] Cut-offs (in mμ) of filter combination found to produce optimum conversion from the *trans* form. [d] Wave length (in mμ) at which maximum relative change in absorbance is observed. [e] Maximum percentage decrease in absorbance at λ' observed upon irradiation. [f] Shoulder.

while the second mirror projected the image of the source through a central hole in the first mirror. The light was passed through a water-filled cell and appropriate glass filters, and then into the dye solution contained in the absorption cell. The filters were air-cooled to prevent cracking.

The filters were commercial glass type, and in many cases a combination of two filters was employed to obtain a narrower transmission range. The cut-offs recorded for the filters or filter combinations are the wave lengths at which the transmission becomes less than 1%.

The time required to reach photoequilibrium varied from 5 minutes to 2 hours, depending on the filters and the nature of the compound irradiated. After equilibrium was attained, the cell was transferred rapidly to the sample compartment of the spectrophotometer and the spectrum recorded. Some dyes reverted to the *trans* form so rapidly after irradiation that extensive changes occurred in the absorption bands during the time required for the recording of the spectrum. In obtaining the spectra of such dye solutions, it was necessary to interrupt the recording every few seconds for additional illumination of the sample.

Results and Discussion

Water solutions of all of the methoxyazo compounds investigated were found to undergo changes in spectrum on irradiation. The results are summarized in Table I. Typical spectral absorption curves obtained for three of these dyes under different conditions of illumination are shown in Figs. 1, 2 and 4.

The extent of the maximum change in spectrum obtained for the various dyes depends on the differences between the spectra of the *cis* and *trans* forms and also on the rate of the thermal *cis* to *trans* reaction.[10] As the rate of the thermal reaction increases, the maximum concentration of the *cis* isomer obtained during illumination decreases.

The effective filter combinations for optimum conversion are those transmitting light of a wave length where there is the greatest percentage difference between the absorbance of the two forms. It has been shown[11] that in the absence of thermal isomerization the concentration of the two isomers of various azo compounds at photochemical equilibrium is largely determined by the relative absorbancies of the two forms at the wave length of illumination used. If the *cis* isomer is relatively stable toward thermal isomerization, the intensity of illumination has little effect on the concentration of the *cis* isomer present when the photostationary state is reached. In such cases filter combinations transmitting in a narrow wave length range can be used, even if the transmission of the combination is low. However, for compounds where the thermal back-reaction is rapid, the amount of the *cis* isomer which can be obtained is greatly influenced by the intensity of the illumination. With such compounds, it is desirable to use filter combinations having maximum transmission at the desired wave length, even though this necessitates the use of filters transmitting over a wider range of wave lengths.

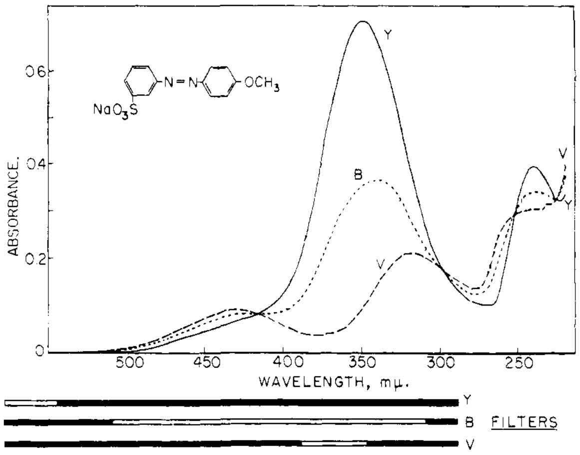

Fig. 1.—Absorption spectra of sodium *m*-(4-methoxyphenylazo)-benzenesulfonate in water, irradiated with light transmitted by different filter combinations: Y (———), λ > 545 mμ; B (. . . . .), 305–513 mμ; V (– – – –), 348–386 mμ; concentration, 5.1 mg./l.; cell length 2.00 cm. The open portions of the bar graphs indicate the regions in which the transmission of the filters is greater than 1%.

In Figs. 1 to 4, the curves obtained with the yellow filters (Y) are very nearly the same as those obtained when the solutions are allowed to reach equilibrium in the dark. They are therefore essentially the spectra of the *trans* forms. Since the rate of the *cis* to *trans* isomerization in the dark was often quite slow, exposure of the solutions using such yellow filters was used as a rapid means of

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[10] See the discussion on the photodimerization of anthracene; S. Glasstone "Textbook of Physical Chemistry," D. Van Nostrand Co., Inc., New York, N. Y., 1946, p. 1184.

[11] M. Frankel, R. Wolovsky and E. Fischer, *J. Chem. Soc.*, 3441 (1955); E. Fischer and Y. Frei, *J. Chem. Phys.*, **27**, 328 (1957).

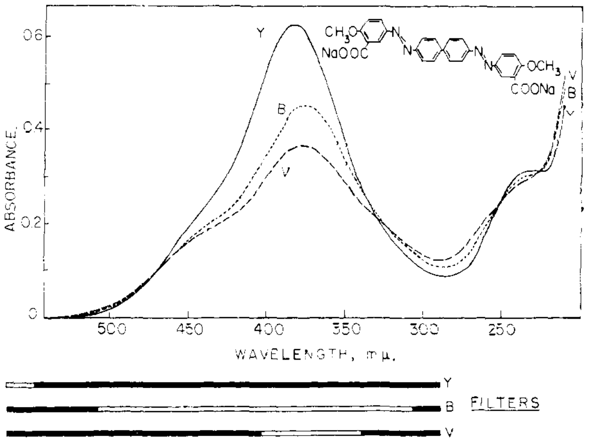

Fig. 2.—Absorption spectra of the sodium salt of 5,5′-(4,4′-biphenylenebisazo)-bis-(2-methoxybenzoic acid) in water, irradiated with light transmitted by different filter combinations: Y (———), $\lambda > 545$ mμ; B (. . . .), 305–513 mμ; V (– – – –), 342–403 mμ; concentration, 4.4 mg./l.; cell length, 2.00 cm.

obtaining reproducible spectra not significantly different from those of the pure *trans* forms.

The series of curves obtained with sodium *m*-(4-methoxyphenylazo)-benzenesulfonate in water (see Fig. 1) resembles that obtained previously with a typical *p*-hydroxyazo compound in benzene,[12] as do the spectra obtained by irradiating solutions of the other monoazo dyes listed in Table I. A number of well-defined isosbestic points, where the curves intersect at a common point, can be seen in Fig. 1. In general such points are found at wave lengths where two interconvertible species have the same specific absorbance and are therefore commonly taken as evidence for equilibrium between two forms. The curve in Fig. 1 obtained using the violet filter combination (V) corresponds very closely to that calculated in the earlier work for the *cis* isomer. Calculations using the absorbance values at 365 mμ indicate that not more than 9% of the *trans* isomer is present in the equilibrium mixture represented by curve V.

The *cis* isomer of this compound is quite stable; from the rate of change of the spectrum in the dark, the half-life for the thermal *cis* to *trans* conversion in water at room temperature was found to be about one week. It is interesting to note that this conversion is faster in acetone or in ethanol than in water. The half-life in acetone at room temperature is about 36 hours. This behavior resembles that of the *cis* isomer of azobenzene, which is more stable in water than in acetone.[4]

An opposite effect is observed with *p*-hydroxyazo compounds. The sodium salt of *m*-(4-hydroxyphenylazo)-benzenesulfonic acid was found to be phototropic in acetone. The addition of small amounts of water to the acetone solution caused a marked increase in the rate of the thermal isomerization (see Table II).

At concentrations of water greater than 2%, the thermal reaction was so rapid that no isomerization could be detected at room temperature under the experimental conditions used. These observations strongly suggest that the apparent suppression of the phototropism of *p*-hydroxyazo and *p*-aminoazo compounds by hydroxylic solvents is a result of the increased rate of the thermal isomerization in these solvents.

TABLE II

EFFECT OF WATER ON ISOMERIZATION OF SODIUM *m*-(4-HYDROXYPHENYLAZO)-BENZENESULFONATE IN ACETONE[a]

Water concn., %	Half-life of *cis* isomer, sec.
0	21
0.25	14
0.5	10
0.75	7
1.25	5

[a] At room temperature.

With disazo compounds there is the possibility of isomerization about either of two azo groups. When there is conjugation between the two azo groups of a symmetrical disazo compound, the two chromophoric groups cannot act independently, and equilibrium exists between three isomeric forms—*trans–trans*, *trans–cis* and *cis–cis*. Since it is highly improbable that all three forms should have the same specific absorbance at any given wave length, the spectra of such compounds will usually contain no isosbestic points, but rather a series of crossing points as the relative concentrations of the various species are charged. This effect may be seen in Fig. 2, particularly in the 325–335 mμ region.

It had been thought[8] that the bulky sulfonic acid groups *ortho* to the ethylenic linkage in Chrysophenine would prevent coplanarity of the molecule and would therefore result in insulation between the two chromophoric azo groups. If there is insulation between the two halves of the molecule in a symmetrical disazo dye, the two chromophoric groups are forced to function independently, and the spectrum is essentially the same as that of the monoazo dye which corresponds to the half-molecule.[13] The spectral changes observed on irradiating solutions of such a dye should also be similar to those observed with monoazo dyes, for only two spectrally distinguishable absorbing species will be present—the *trans*-half-molecule and the *cis*-half-molecule. The absence of well-defined isosbestic points in the spectra of Chrysophenine (see Fig. 3) clearly indicates that more than two forms are in equilibrium. This would suggest that there is conjugation over the whole molecule.

Sulfonic acid groups *ortho* to the connecting linkage in biphenyl are known to prevent coplanarity of the two halves of the molecule.[14] This steric hindrance should be sufficient to produce insulation between the two chromophoric centers of the compound shown in Fig. 4. As expected, the position of the main absorption peak of this compound is found to be very close to that of corresponding monomethoxy monoazo dyes, and irradiation produces changes in spectrum very like those occurring with the monoazo dyes, with several

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[12] W. R. Brode, J. H. Gould and G. M. Wyman, THIS JOURNAL, **74**, 4641 (1952).

[13] J. D. Piper and W. R. Brode, *ibid.*, **57**, 135 (1935); R. J. Morris and W. R. Brode, *ibid.*, **70**, 2485 (1948).

[14] M. S. Lesslie and E. E. Turner, *J. Chem. Soc.*, 2394 (1932); B. Williamson and W. H. Rodebush, THIS JOURNAL, **63**, 3018 (1941).

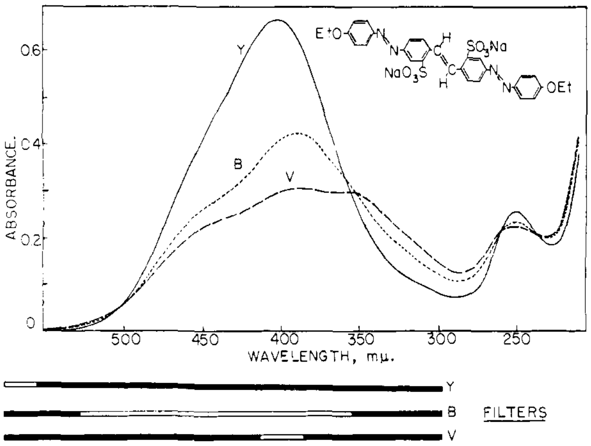

Fig. 3.—Absorption spectra of Chrysophenine in water, irradiated with light transmitted by different filter combinations: Y (———), λ > 567 mμ; B (. . . .), 354–527 mμ; V (- - - -), 370–413 mμ; concentration 4.3 mg./l.; cell length, 2.00 cm.

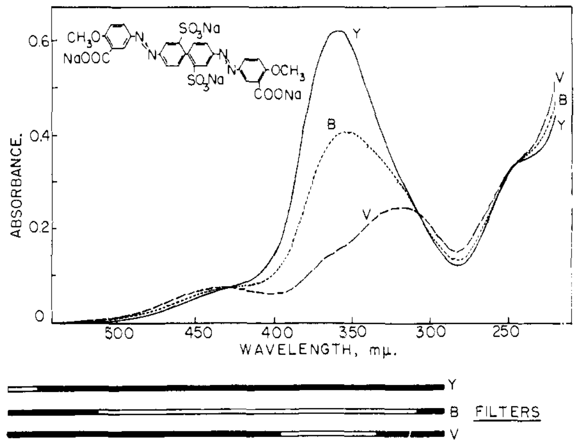

Fig. 4.—Absorption spectra of the sodium salt of 4,4′-bis-(4-methoxy-3-carboxyphenylazo)-biphenyl-2,2′-disulfonic acid in water, irradiated with light transmitted by different filter combinations: Y (———), λ > 545 mμ; B (. . . .), 305–513 mμ; V (- - - -), 348–386 mμ; concentration, 7.3 mg./l.; cell length, 2.00 cm.

apparent isosbestic points. However, closer examination of the spectra in the 300–315 mμ region, using a more concentrated solution and a slower scanning speed, reveals the absence of a well-defined isosbestic point, thus showing that even in this compound the insulation between the two halves of the molecule is not complete.

On the basis of the findings reported here, it appears that the *cis* isomers of alkoxyazo compounds are sufficiently more stable than those of the corresponding hydroxyazo compounds to permit observation of reversible phototropic *cis–trans* isomerization in aqueous solutions. Further investigation is being conducted on the nature of the solvent effects in the thermal *cis* to *trans* isomerization of these compounds.

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[Contribution from the Organic Chemical Research Section and the Biochemistry Research Section, Lederle Laboratories Division, American Cyanamid Co.]

The Preparation and Identification of the Isomeric 1-Aryl-3(and 5)-methyl-5(and 3)-(4-pyridyl)-pyrazoles

By William B. Wright, Jr., Herbert J. Brabander, Robert A. Hardy, Jr., and William Fulmor

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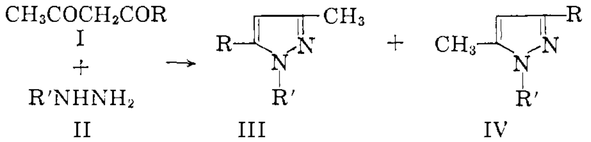
Several pairs of isomeric 1-aryl-3(and 5)-methyl-5(and 3)-(4-pyridyl)-pyrazoles have been prepared by the acid-catalyzed condensation of isonicotinoylacetone with phenylhydrazines. The ultraviolet absorption curves of these isomers are characterized by a hypsochromic shift of λ_{max} and a lower molar extinction coefficient of one member of each pair. This effect may be explained by steric inhibition of resonance and has been used as a basis of structural assignments. The differences in ultraviolet absorption curves of three isomeric pairs of substituted 3(and 5)-methyl-5(and 3)-phenyl-pyrazoles of unequivocal structure may be explained by the same reasoning. A series of 1-aryl-3-methyl-5-(2 and 3-pyridyl)-pyrazoles is also described.

The preparation of pyrazoles from unsymmetrical β-diketones (I) and monosubstituted hydrazines (II) is complicated by the possible formation of two isomers (III and IV).

R′ = substituted phenyl



a, R = 4-pyridyl
b, R = 3-pyridyl
c, R = 2-pyridyl

a, R = 4-pyridyl

Jacobs[1] has reviewed and more recently Finar and Simmonds[2] have further investigated this type of reaction. A number of examples exist in which only one isomer was isolated and the structural assignment was equivocal or arbitrary. In other examples two isomeric pyrazoles have been isolated from the same reaction mixture, but the proper structure has not been investigated. Relatively few examples are known in which two isomers have been obtained from the same reaction and the structural assignments investigated. We have iso-

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(1) T. L. Jacobs in R. C. Elderfield, Ed., "Heterocyclic Compounds," Vol. 5, J. Wiley and Sons, Inc., New York, N. Y., 1957, pp. 50–55.

(2) I. L. Finar and A. B. Simmonds, *J. Chem. Soc.*, 200 (1958).