of the given acid to the dissociation constant of cyclohexanecarboxylic acid against the reciprocal of the dielectric constant[5] of the solvent as shown in Fig. 2.

The fact that the dissociation constant of acrylic acid was found to be larger than those of the other carbocyclic carboxylic acids in each solvent may be attributed to stabilization of the anion of acrylic acid by resonance.

CHICAGO, ILLINOIS

[5] W. F. K. Wynne-Jones, *Proc. Roy. Soc.* (*London*), **A140**, 440 (1933).

[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXVI. Effect of Solvent and of Temperature on the *cis–trans* Isomerization of Azo Dyes

BY WALLACE R. BRODE, JOHN H. GOULD AND GEORGE M. WYMAN

RECEIVED NOVEMBER 1, 1952

The photochemical *trans* → *cis* isomerization of ten typical azo dyes was studied spectrophotometrically in five solvents of different polarities. In general, hydrocarbon solvents favored isomerization, whereas ethanol appeared to suppress it most extensively. Upon heating benzene solutions of more than 20 azo dyes to 65° the isomerization equilibrium was shifted toward the stable (*trans*) form, whenever possible. The main absorption band of the dye at 65° appeared at a slightly shorter wave length than at room temperature. Spectral absorption data are presented for 12 typical azo dyes at 65°, together with suggested explanation for this hypsochromic shift.

Introduction

The rapid photochemical isomerization of a number of azo dyes in benzene solutions was described in an earlier paper in this series.[1] This work has been extended to include a study of the effect of solvent on the photochemical isomerization of dyes of this type, by determining the spectra in four additional common solvents of widely different polarities. In addition, the effect of heat on the isomerization equilibria of some azo dyes in benzene solutions was evaluated.

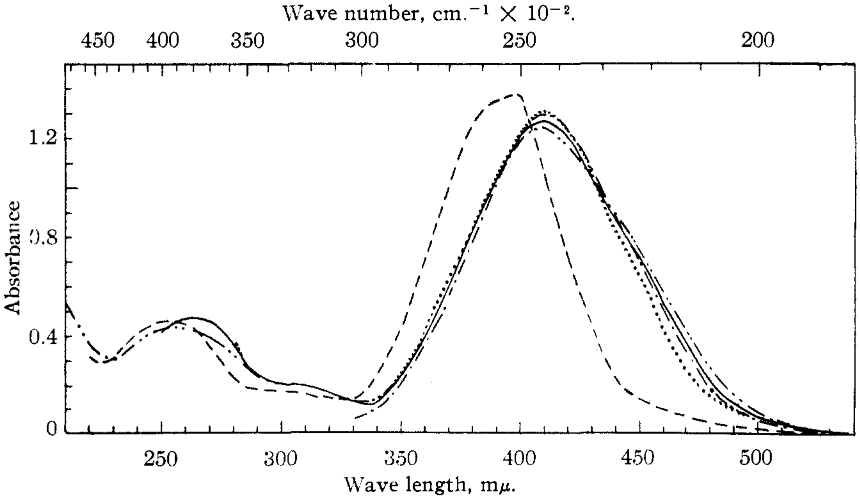

Fig. 1.—Absorption spectra of 4-dimethylaminoazobenzene in five solvents: - - -, in isoöctane; -·-·-·-·, in alcohol; ------, in chloroform; ......, in benzene; -----, in methyl ethyl ketone after storage in darkness. Concentration, 0.0052 g./l.; cell length, 2.00 cm.

I. Solvent Effect

Experimental. Preparation of Solutions.—The technique employed in the preparation of solutions and the physical properties of the dyes used have been described in the previous paper.[1]

Apparatus.—Irradiation of the solutions during the measurement was effected by means of the rotating shutter described in an earlier paper.[2]

Measurement of Spectra.—The absorption spectra were determined by means of a Cary recording quartz spectrophotometer with the appropriate solvent as reference standard.

Discussion of Results

Results.—The absorption spectra of the stable form of a typical strongly phototropic azo dye, 4-dimethylaminoazobenzene, in five solvents are shown in Fig. 1.

These absorption curves are very similar in shape and differ but slightly with respect to the position and the intensity of the main absorption band, as is usually the case when no new molecular species are formed in the different solvents.[3,4] The curve obtained in isoöctane (2,2,4-trimethylpentane) differs most from the spectra obtained in the other solvents, in that the main absorption band appears at a shorter wave length (by about 10 mμ). This effect is in accordance with earlier observations on the spectra of benzeneazophenol in various solvents[3] and the results of Sheppard and Newsome on the effect of solvents on the spectrum of 4-dimethylamino-4′-nitroazobenzene.[5] Although the reasons for this relation between the position of an absorption band

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

[2] J. H. Gould and W. R. Brode, *J. Opt. Soc. Am.*, **42**, 380 (1952).

[3] W. R. Brode, *J. Phys. Chem.*, **30**, 56 (1926).

[4] C. D. Mason and F. F. Nord, *J. Org. Chem.*, **17**, 778 (1952).

[5] S. E. Sheppard and P. T. Newsome, THIS JOURNAL, **64**, 2937 (1942).

TABLE I

ABSORPTION SPECTRA DATA OF AZO DYES IN VARIOUS SOLVENTS (AFTER STANDING IN DARKNESS FOR 2–3 HOURS)

Symbol	Dye	Isoöctane[a]		$CH_3COC_2H_5$[b]		C_6H_6[c]		$CHCl_3$[d]		C_2H_5OH[e]	
		λ	$\epsilon \times 10^{-2}$	λ	$\epsilon \times 10^{-2}$	λ	$\epsilon \times 10^{-2}$	λ	$\epsilon \times 10^{-2}$	λ	$\epsilon \times 10^{-2}$
I	4-Aminoazobenzene	362	280	389	269	377	259	370	250	387	237
II	4-Dimethylaminoazobenzene	398	298	411	281	410	283	410	271	410	270
III	4-Dimethylamino-4′-phenylazobenzene	406	362	414	350	423	346	422	335	422	336
IV	4-Chloro-4′-hydroxyazobenzene	345	277	344[g]	286[g]	350	266	350	262	356	272
V	4-Hydroxy-4′-methylazobenzene	340	256	340[g]	277[g]	347	256	347	250	351	264
VI	4-Hydroxy-2,2′,4′,6,6′-pentamethylazobenzene	335	123	332[g]	206[g]	340	181	336	180	341	202
VII	4-Benzeneazo-1-naphthol	383	150	406	163	410	133	464	179	410	151
		396	150			450	129				
VIII	4-Benzeneazo-1-naphthylamine	416	226	429	240	426	218	422	222	440	216
IX	2-Hydroxyazobenzene	321	180	332[g]	165[g]	325	180	325	175	323	182
X	1-(2-Hydroxybenzeneazo)-2-naphthol	476	173	486	169	480	174	478	169	495	194

[a] Spectro-grade, made by Phillips Petroleum Co. [b] Technical. [c] A.C.S. grade. [d] U.S.P. grade. [e] 95%. [f] Wave length of main absorption band. [g] Data only approximate due to high solvent absorption in this wave length region.

and the nature of the solvent are not fully understood, possible explanations therefore were given in reference 5.

The spectra of these same solutions irradiated with blue light are plotted in Fig. 2. Corning Filter No. 585 (transmitting light of λ < 495 mμ) was used, because light of this wave length range was found to be effective in causing *trans* → *cis* isomerization for this dye. Inspection of these absorption curves discloses that the extent of phototropic change, with the apparatus used, is a function of the solvent used: the solution in ethanol exhibits practically no change upon irradiation, while solutions in isoöctane, methyl ethyl ketone and benzene are strongly phototropic. Furthermore, since the curves for the irradiated solutions in isoöctane and methyl ethyl ketone are similar in shape to the curve in benzene and the curve for the irradiated solution in chloroform appears intermediate between the irradiated and stable curves in benzene, it is reasonable to assume that the absorption curves of the unstable *cis* form are probably similar in shape in all these solvents. (A probable absorption curve for *cis*-4-dimethylaminoazobenzene in benzene was plotted in Fig. 1 of reference 1.) The absorption spectra of the stable forms of the other dyes that comprised this investigation were found to differ but slightly in the various solvents used, with the sole exception of 4-benzeneazo-1-naphthol. The strong solvent dependence of the absorption spectrum of this dye had been reported previously,[6] and their results were essentially confirmed in the present work (*cf.* Table I). They attributed this phenomenon to the existence of a tautomeric equilibrium between the azoid and quinoid forms of this dye. The absorption spectra data for the ten dyes are given in Table I.

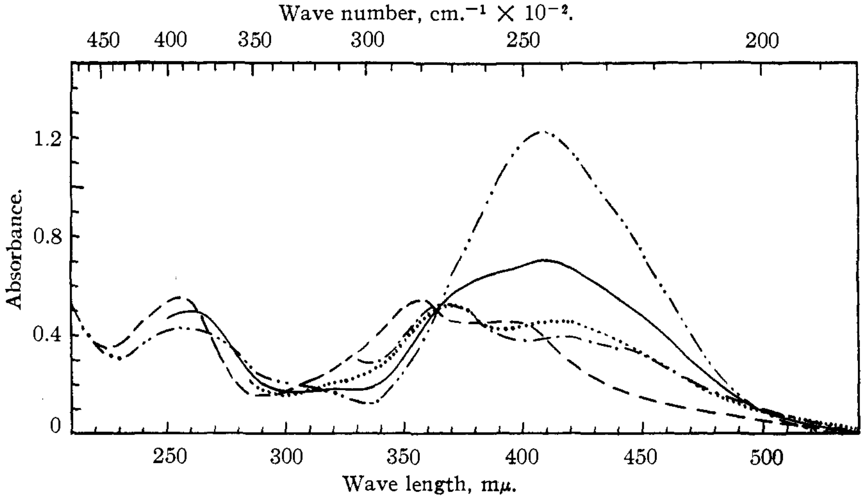

Fig. 2.—Absorption spectra of 4-dimethylaminoazobenzene in five solvents: - - -, in isoöctane; -·-·-·-·-, in alcohol; ------, in chloroform; ......, in benzene; -··-··-, in methyl ethyl ketone, after irradiation with blue light (λ < 495 mμ). Concentration, 0.0052 mg./l.; cell length, 2.00 cm.

Since, in the case of each of these phototropic dyes, the *cis* isomer appears to have relatively little absorption in the wave length region of the main absorption band of the *trans* form, the decrease in the intensity of the absorption band upon irradiation may be considered to be an approximate indication of the degree of *trans* to *cis* isomerization. This tendency for isomerization has been given in Table II, for the different dyes in the five solvents tested.

These data show that hydrocarbon solvents favor isomerization while ethanol inhibits it to the greatest extent. The order in which the solvents inhibit isomerization is the same as the order of increasing eluting power in chromatographic adsorptions.[7] Thus only the strongly phototropic azo dyes exhibit phototropism in ethanol solution, whereas in isoöctane even the absorption band of 2-hydroxyazobenzene, for which compound the *trans* configuration is stabilized by hydrogen-bonding,[8] is slightly depressed by irradiation. Apparently, of all the dyes studied, only *trans*-1-

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(6) R. Kuhn and R. Baer, *Ann.*, **516**, 143 (1935).

(7) C&EN Staff Report, *Chem. Eng. News*, **30**, 4248 (1952).

(8) S. B. Hendricks, *et al.*, THIS JOURNAL, **58**, 1991 (1936).

TABLE II

EFFECT OF SOLVENT ON PHOTOTROPISM^{a,b}

Dye^c	Iso-öctane	$CH_3COC_2H_5$	C_6H_6	$CHCl_3$	C_2H_5OH
III	0.31	0.38	0.30	0.87	1.00^d
II	.34	.31	.36	.58	0.96
I	.56	.30	.33	.91	1.00^d
VIII	.72	.75	.63	1.00	1.00^d
VI	.81	.75	.67	0.97	1.00^d
V	.89	.98	.50	.94	1.00
IV	.92	.97	.48	.87	1.00
VII	.97	.95	.95	.97	1.00
IX	.96	.98	1.00	1.00	1.00
X	1.00	1.00	1.00	1.00	1.00

[a] Fractions indicate the intensity of absorption at the wave length of the main band, after irradiation, relative to the absorption intensity of the stable form at the same wave length taken as unity. [b] Solvents and dyes arranged roughly in order of decreasing tendency to phototropism. [c] For explanation of symbols, *cf.* Table I. [d] Qualitative evidence for decrease in absorption, immediately after exposure to uninterrupted irradiation.

(2′-hydroxyphenylazo)-2-naphthol, which is probably stabilized by two hydrogen bonds, resists isomerization in all solvents under these conditions.

II. Temperature Effect

Experimental. Apparatus.—In order to measure the absorption spectra of solutions at temperatures other than room temperature, a heating (or cooling) jacket was constructed. The jacket was suspended from a bakelite replica of the cover of the cell compartment of the spectrophotometer at such an angle and distance that, when the bakelite cover was placed in position, the measuring beam would pass along the axis of the heating jacket. Dimensions of the heating jacket were so designed as to accommodate the ordinary 2-cm. and 5-cm. path length absorption cells. Twin air outlets were incorporated at both ends, in order to permit dry air to be blown on the cell windows during measurements at low temperatures and were not used in the present work.

Measurement of the Spectra.—The solutions were prepared according to the technique described in the earlier paper.[1] A 2.00-cm. quartz absorption cell (volume 10 ml.) was filled with the solution at room temperature and, in order to allow for thermal expansion, a 0.5-ml. portion was withdrawn by means of a hypodermic syringe. The cell was subsequently placed inside the jacket which was heated by circulating hot water (72°) from a thermostated reservoir. The temperature of the solution in the cell was determined with the aid of a thermocouple. When temperature equilibrium was attained (usually at 65°) the entire assembly was placed in position in the spectrophotometer and the absorption spectrum of the hot solution determined against the cold solvent as reference.

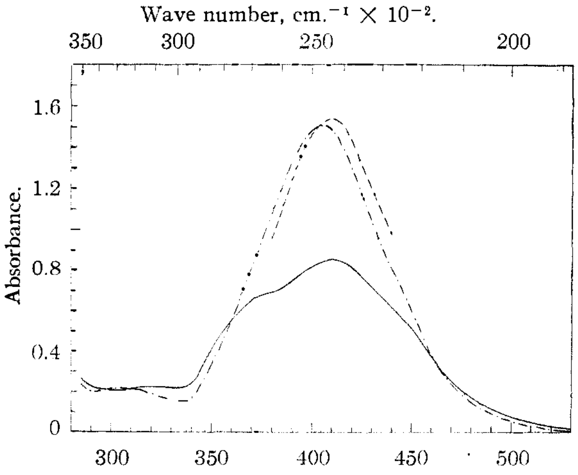

Fig. 3.—Absorption spectra of 4-dimethylaminoazobenzene in benzene: - - - -, after storage in darkness, at 25°; —, in laboratory illumination, at 25°; ·-·-·-·, in laboratory illumination, at 65°. Concentration, 0.0063 g./l.; cell length, 2.00 cm.

Discussion of Results

The absorption curves of the strongly phototropic dye, 4-dimethylaminoazobenzene in benzene solution at different temperatures, are shown in Fig. 3. It is apparent that, upon heating the solution, the spectrum changes considerably from the "daylight" curve which represents an equilibrium between the *cis* and *trans* forms at room temperature in ordinary laboratory light. The absorption spectrum of the hot solution shows a sharp band similar in shape and intensity to the spectrum of the *trans* form, except that it is displaced toward shorter wave lengths by about 5 mμ. Other, strongly phototropic, aminoazobenzene derivatives exhibit similar behavior.

The spectra of azo dyes which are weakly phototropic (*cf.* reference 1) undergo only relatively minor changes upon heating: the shape of the absorption curve changes relatively little; there is, however, an even smaller, but still appreciable, displacement of the position of the absorption band toward shorter wave lengths, as shown for dye VI (*cf.* Table I) in Fig. 4. The effect of heat upon the absorption spectra of a number of typical azo dyes is summarized in Table III.

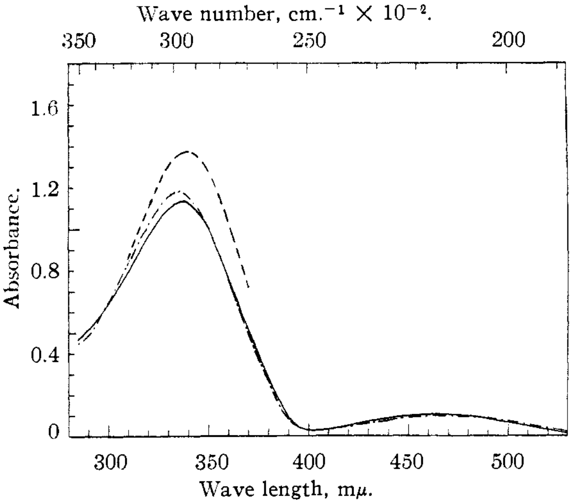

Fig. 4.—Absorption spectra of 4-hydroxy-2,2′,4′,6,6′-pentamethylazobenzene in benzene: - - - -, after storage in darkness, at 25°; —, in laboratory illumination, at 25°; ·-·-·-·, in laboratory illumination, at 65°. Concentration, 0.0110 g./l.; cell length, 2.00 cm.

The results indicate that, upon heating, the equilibrium that exists between the *cis* and *trans* isomers of dyes of this type at room temperature is shifted toward the more stable, *trans* modification, wherever possible. This is similar to the behavior of azobenzene and its derivatives.[9] Thus the spectra of those dyes, the benzene solutions of which contain considerable amounts of

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(9) G. S. Hartley, *J. Chem. Soc.*, 633 (1938).

TABLE III

EFFECT OF HEAT ON ABSORPTION SPECTRA OF AZO DYES IN BENZENE

Dye[a]	λ[b]	λ′[c]	Δλ	$\frac{A_{\text{hot}}}{A_{\text{cold}}}$[d]	Dye	λ	λ′	Δλ	$\frac{A_{\text{hot}}}{A_{\text{cold}}}$
I	377	371	6	1.31	VII	410	408	2	1.01
						450	(448)[e]	2	1.10
II	410	405	5	1.62	VIII	427	421	6	1.01
III	422	419	3	2.18	IX	325	323	2	1.00
IV	353	351	2	1.21	X	475	473	1	1.00
V	347	345	2	1.05	XI[f]	407	403	4	1.16
VI	340	339	1	1.03	XII[g]	440	437	3	1.00

[a] For symbols, *cf.* Table I. [b] Wave length of main absorption band of stable form (in mμ) at 25°. [c] Wave length of main absorption band of stable form (in mμ) at 65°. [d] Ratio of intensity of absorption band of hot solution to that of cold solution, both in laboratory illumination. [e] Inflection point. [f] 4-Dimethylamino-4′-hydroxyazobenzene. [g] 1-Benzeneazo-2-naphthylamine.

cis isomers when made up in ordinary laboratory illumination (*cf.* reference 1), undergo considerable changes upon heating. On the other hand, since solutions of weakly phototropic azo dyes contain almost entirely only the *trans* isomers when made up in the laboratory, the heating of these can cause only a slight shift in the equilibrium and hence but little change in the spectra.

The shift of the absorption maxima of these compounds toward shorter wave lengths as a result of raising the temperature by 40° (relative to the position of the absorption band of the stable form at room temperature) is unusual and difficult to explain. This shift may indicate the existence of some resonating complex between dye and solvent molecules which dissociates at higher temperatures; thus lowering the energy difference between the excited state and the ground state when the solution is at room temperature. It has been observed, however, that 4-dimethylaminoazobenzene showed the same hypsochromic shift in 95% ethanol solution, while azobenzene fails to exhibit it in either solvent, indicating that this shift is probably a characteristic of the dye occurring in a variety of solvents of different polarities. It is then perhaps more plausible to suggest that, when light is absorbed by the dye solution at 65°, the molecule is raised from the ground state to one of the higher vibrational levels of the first excited state, resulting in a shift in the absorption maximum to a slightly shorter wave length. Apparently, only azo compounds containing one or more auxochromic substituents exhibit this hypsochromic shift on heating. Further investigation will be necessary, however, in order to establish the scope and limitations of this effect and to arrive at a more complete understanding of this phenomenon.

WASHINGTON 25, D. C.

[CONTRIBUTION FROM THE DIVISION OF MEDICAL PHYSICS, DONNER LABORATORY, AND THE RADIATION LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Infrared Spectra of Some Long-chain 2-Alkenoic Acids and Their Bearing on the Structure of C_{27}-Phthienoic Acid[1]

BY N. K. FREEMAN

RECEIVED JULY 21, 1952

The infrared spectra of six long-chain 2-alkenoic acids with different types of branching near the double bond are presented and discussed. Several absorption bands are observed which do not appear in the spectra of unconjugated long-chain fatty acids. One of these is the 6.1 μ carbon–carbon double bond stretching vibration band, the intensity of which has evidently been greatly enhanced as a result of conjugation. Other new bands appear in the 10–16 μ region, some of which may prove to be analogous to those in the spectra of alkenes which characterize the arrangement of alkyl groups around the double bond. Such a relationship has not been fully demonstrated with the limited amount of data available. Use of the 7.25 μ band intensity as an index of the number of terminal methyl groups (previously employed in branched alkanoic acids) was found to be valid for this group of alkenoic acids. Comparison of the spectra with that of C_{27}-phthienoic acid provides additional support for previous evidence that this molecule has an α-methyl branch. There is no definite indication regarding the position of a second nearby methyl group, except that the lack of spectral conformity with 2,5-dimethyl-2-heptadecenoic acid rules out this particular structure.

In the course of extensive study of the branched-chain fatty acids of the tubercle bacillus, Cason and collaborators have isolated one of the principal species and shown that it is an α,β-unsaturated acid having twenty-seven carbon atoms and three branching side chains (probably methyl), one of which is on the α-carbon atom.[2,3] This acid has been called C_{27}-phthienoic acid. Infrared spectrometry was employed to aid in establishing these structural features, and certain inferences were based on the results of a broad study of saturated branched-chain fatty acid spectra.[4] In continuing efforts to elucidate the structure of C_{27}-phthienoic acid still further, Cason's group has synthesized several α,β-unsaturated acids with various arrangements of branching methyl groups. The infrared absorption spectra of these acids have been recorded, and are presented here with two purposes in view: (1) to examine the relationships between structure and spectra in this restricted class of compounds; (2) to make direct comparisons with the spectrum of C_{27}-phthienoic acid.

Experimental

Materials.[5]—The first six acids whose spectra are shown in Figs. 2 and 3 are synthetic compounds, whose preparation

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(1) This work was supported in part by the United States Atomic Energy Commission.

(2) J. Cason and G. Sumrell, *J. Biol. Chem.*, **192**, 405 (1951).

(3) J. Cason, N. K. Freeman and G. Sumrell, *ibid.*, **192**, 415 (1951).

(4) N. K. Freeman, THIS JOURNAL, **74**, 2523 (1952).

(5) The author is greatly indebted to Dr. James Cason of the University of California Chemistry Department for furnishing the compounds which form the basis of this paper. Dr. Cason's series of publications on branched-chain fatty acids will contain descriptions of their synthesis and properties. C_{27}-Phthienoic acid is also the subject of previous publications.[2,3]