[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes. XXVII. *cis-trans* Isomerism and Hydrogen Bonding in Indigo Dyes[1]

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The ultraviolet and visible absorption spectra of indigo and of six halogen-substituted indigo dyes were determined in chloroform solution. In contrast with the behavior of thioindigo dyes, no evidence was found for photochemical isomerization. This was believed to be attributable to the preferential stabilization of the *trans* configuration by hydrogen-bonding. The discovery of phototropism in N,N'-diacetylindigo and a comparison of the infrared absorption spectra of indigo and thioindigo provided evidence for this hypothesis. In addition, the effect of halogen substitution on the ultraviolet and visible spectra was considered.

Introduction

The *cis–trans* isomerism of indigo has been the subject of many, sometimes conflicting, reports in the chemical literature.[2–5] Although derivatives of *cis*-indigo have been reported,[3] and the appearance of a fleeting blue color during the oxidation of leucoindigo (below 15°) has been attributed to *cis*-indigo,[4] the existence of this unstable isomer has not been established beyond doubt.

In view of the results of recent work in this Laboratory on the photochemical *cis–trans* isomerization of thioindigo dyes,[6,7] it was believed that a critical comparison of indigo and thioindigo dyes might shed more light on the question. Moreover, it was thought that such information, when obtained, would be helpful toward a fuller understanding of the *cis–trans* isomerism of highly conjugated organic molecules (*e.g.*, dyes) that possess a central double bond. For these reasons the study of the spectra of a number of indigo dyes was undertaken.

Experimental

(a) **Purification of Dyes.**—The dyes used (except N,N'-diacetylindigo) were commercial samples of known structure, purified by alkaline reduction with sodium hydrosulfite and filtration, followed by oxidation of the filtrate with air. The recovered dye was dried at 65–70°, ground to a fine powder and extracted with chloroform in a Soxhlet extractor. The purified dye was recovered by evaporating the chloroform solution to dryness. N,N'-Diacetylindigo was made by the acetylation of indigo, according to Liebermann and Dickhuth.[8]

(b) **Preparation of Solutions.**—A 6–8-mg. sample of each dye was dissolved in 100 ml. of chloroform (U.S.P. grade) by gentle refluxing. Ten ml. of this solution was then diluted to 100 ml. (except in the case of N,N'-diacetylindigo, where because of the low intensity of absorption a more concentrated solution was required) and the absorption spectrum determined.

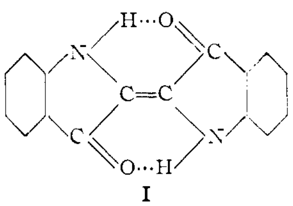
Measurement of the Absorption Spectra in the Ultraviolet and Visible Regions.—The absorption spectra were determined by means of a Cary recording spectrophotometer (model 12) using 2-cm. matched fused quartz absorption cells with the solvent as reference.

(d) **Irradiation of the Solutions.**—The solutions were irradiated with the aid of the shutter-illumination device described in an earlier paper.[9] The sample was subjected to uninterrupted irradiation for several minutes; its spectrum was then measured, while the solution was exposed to intermittent irradiation.

(e) **Determination of the Infrared Absorption Spectra.**—A small amount of the dye was intimately ground with some "Halocarbon Oil No. 13-21."[10] The infrared spectrum of this mull was measured in the 2–7 μ region by means of a Beckman IR2T spectrophotometer equipped with rock salt optics, with "Halocarbon Oil No. 13–21" as reference. The scanning rate was set at "8 seconds/slit width" on the instrument in order to provide good resolution.

Discussion of Results

The existence of two hydrogen-bonded rings (as shown in I) in the indigo molecule was first tentatively suggested by Scholl[11] to account for its exceptional stability and the absence of a second geometrical isomer. This concept was consistent with the results of an X-ray diffraction study indicating that indigo possesses a symmetrical structure characteristic of a *trans* configuration.[12] However, when chemical evidence showed that indigo could form derivatives of both the *cis* and *trans* isomers, depending on the nature of the reagent,[2,4] a number of other possible structures were advanced by different research workers to explain this behavior.[4,5] The hydrogen-bonded formula was revived when Dokunikhin and Levin attributed the difference in the color of indigo and of thioindigo to the existence of a chelate ring in the former.[13] They observed that the ultraviolet absorption spectra of the sulfuric acid esters of the corresponding leuco-forms (II and III), neither of which could possess a hy-



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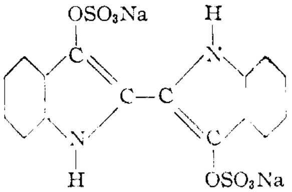

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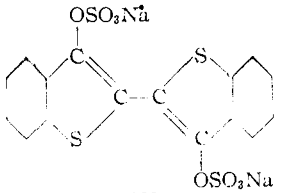

III

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[1] Presented before the 124th Meeting of the American Chemical Society, Chicago, Ill., September, 1953.

[2] T. Posner, *Ber.*, **59B**, 1799 (1926).

[3] R. Pummerer and H. Fiesselmann, *Ann.*, **544**, 206 (1940).

[4] G. Heller, *Ber.*, **77B**, 163 (1944).

[5] J. V. Alphen, *Rec. trav. chim.*, **60**, 138 (1941).

[6] G. M. Wyman and W. R. Brode, THIS JOURNAL, **73**, 1487 (1951).

[7] W. R. Brode and G. M. Wyman, *J. Research Natl. Bur. Standards*, **47**, 170 (1951).

[8] C. Liebermann and F. Dickhuth, *Ber.*, **24**, 4131 (1891).

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

[10] Consists of low molecular weight polymers of chlorotrifluoroethylene; provided through the courtesy of Halocarbon Products Corp., North Bergen, N. J.

[11] *Cf.* W. Madelung and O. Wilhelmi, *Ber.*, **57**, 237 (1929).

[12] A. Reis and W. Schneider, *Z. Krist.*, **68**, 543 (1926).

[13] N. Dokunikhin and E. Levin, *Compt. rend. acad. sci., U.S.S.R.*, **35**, 110 (1942).

drogen-bonded structure, where essentially identical.

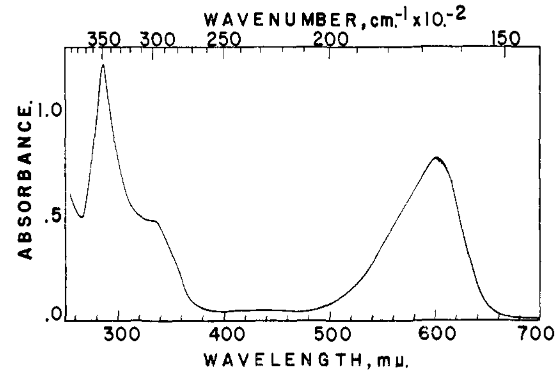


Fig. 1.—Absorption spectrum of indigo in chloroform (*c* 8.1 mg./l., *d* 2.00 cm.).

The ultraviolet and visible spectrum of indigo in chloroform is shown in Fig. 1. The curve is in good agreement with data in the literature.[14] It is also similar in shape to the absorption curve of *trans*-thioindigo[1] except that it is displaced toward longer wave lengths, and the ratio of the frequencies of the two absorption peaks for indigo is unusually large (*cf.* Table I). The substituted indigo dyes studied resemble indigo closely in their absorption curves; their principal spectral data are listed in Table I.

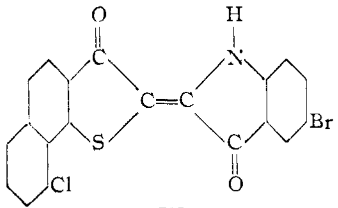
TABLE I

ABSORPTION SPECTRA DATA OF INDIGO DYES

Substituents	λ_1[a]	ϵ_1[b]	λ_2	ϵ_2	ν_2/ν_1[c]
None	604	12,300	285	19,800	2.12
5,5′-Dibromo	611	[d]	289	[d]	2.04
5,5′,7,7′-Tetrabromo	615	20,300	301	32,100	2.04
4,5,5′,7,7′-Pentabromo	620	24,200	306	40,100	2.03
4,4′-Dichloro	605	24,300	290	36,400	2.08
4,4′-Dichloro-5,5′-dibromo	611	18,400	297	28,400	2.06
5,5′-Difluoro[e]	618	[d]	290	[d]	2.12
N,N′-Diacetyl	599	6,890	278	21,400	2.01[f]

[a] Wave length of absorption peak, mμ. [b] Molar absorbance. [c] Ratio of the frequencies of the two absorption peaks. [d] Not sufficiently soluble. [e] Research sample provided through the courtesy of Prof. Arthur Roe. This sample was not purified. [f] This ratio probably should be somewhat lower, since the exact location of the ultraviolet absorption band is uncertain because of the presence of another band at slightly shorter wave lengths.

In contrast with the behavior of thioindigo dyes, solutions of indigo and of the several ring substituted indigo dyes in chloroform were found to be unaffected by irradiation. Not even under the conditions devised to study successfully the phototropism of the highly fugitive azo dyes,[15] was there any evidence for a reversible change in the spectra. The mixed indigo–thioindigo dye Solvat Grey BL Base (IV), which can form only one hydrogen-bonded ring in the *trans* configuration, was also found to be unaffected by irradiation under these conditions. When a thioindigo dye is dissolved in sulfuric acid, the solute, which is probably the conjugate acid of the dye itself, may form chelate rings by hydrogen bonding. Since such solutions are also non-phototropic, and also show this abnormally high frequency ratio,[16] it was thought probable that these features are indicative of hydrogen bond formation.



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Further evidence in support of this assumption was obtained from a study of the behavior of N,N′-diacetylindigo. This compound, which with its purple color and ready solubility resembles thioindigo rather than indigo dyes, does not possess any hydrogen atoms that could participate in the formation of chelate rings. Although a solution of this compound in chloroform failed to exhibit phototropism, its spectrum showed extensive changes (reminiscent of the behavior of thioindigo), when its solution in benzene was exposed to light of different wave length ranges, as shown in Fig. 2.[17] Irradiation with light of wave lengths longer than 520 mμ gave rise to a new absorption band at about 430 mμ, accompanied by a decrease in absorption at longer wave lengths, suggesting *trans* → *cis* isomerization. The wave length of the new absorption band almost coincides with the position of the absorption band of the oxalyl derivatives of *cis*-indigo (436 mμ) (V),[18] which is structurally very similar to *cis*-N,N′-diacetylindigo (VI) and, for this reason, would be expected to have a similar spectrum.

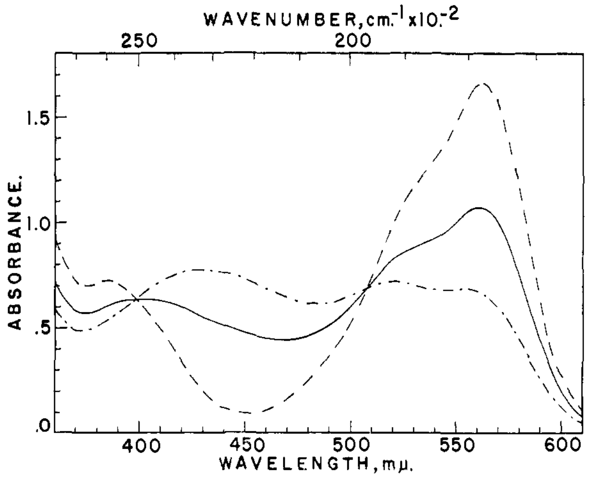

Fig. 2.—Absorption spectra of N,N′-diacetylindigo in benzene, exposed to: blue light (λ < 495 mμ), (- - - -); green light (λ > 350 mμ), (——)· yellow light (-.-.-.), (λ > 520 mμ) (*c* 40.2 mg./l.; *d* 2.00 cm.).

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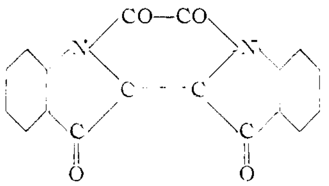
(14) G. Scheibe, *et al.*, *Ann.*, **544**, 240 (1940).

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

(16) W. R. Brode and G. M. Wyman, *ibid.*, **73**, 4267 (1951).

(17) In order to make certain that the failure of indigo dyes to show phototropism was not limited to their chloroform solutions, indigo and Solvat Grey BL Base were also studied in benzene. No change was observed in the spectrum of either dye under these conditions.

(18) Unpublished data of the authors. Prepared as described in reference (4).



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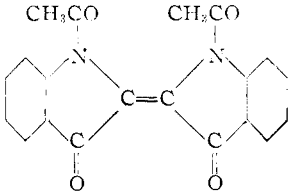

VI

The presence of a chelate structure in indigo was fully verified by a comparison of its infrared spectrum (in the 2–7 μ region) with that of thioindigo. The results of the infrared measurements on the two dyes in the solid state are given in Table II.

TABLE II

INFRARED ABSORPTION BANDS IN μ OF INDIGO AND THIOINDIGO

Indigo	3.03	6.17	6.77
Thioindigo	6.03	6.27	6.83

The thioindigo absorption band at 6.03 μ is characteristic of a carbonyl group that is conjugated with a carbon–carbon double bond, while the band at 6.27 μ is attributable to the stretching frequency of this carbon–carbon double bond.[19] In sharp contrast, indigo has only a single band of great intensity in this region (at 6.17 μ), typical of carbonyl groups which are hydrogen-bonded, in addition to being conjugated. As had been reported for other compounds containing groupings of this type, the band corresponding to the carbon–carbon double bond stretching frequency is absent.[20,21] Indigo also has a sharp band at 3.03 μ, which is probably due to the presence of an N–H group, displaced slightly to longer wave lengths by participation in the chelate structure.[19] The bands near 6.8 μ are probably due to the aromatic rings.

It is apparent then from this analysis of the infrared spectra that, in contrast with thioindigo, in the solid state indigo exists in the hydrogen-bonded *trans*-configuration (I) exclusively. The absence of photochemical isomerization in chloroform or benzene strongly suggests that this is also the situation in organic solvents.[22] It is possible, however, that during a chemical reaction sufficient energy might be gained by the formation of a product of low potential energy to shake the molecule loose from the stable *trans* configuration and form derivatives of the unstable *cis* form. The formation of the oxalyl derivative of *cis*-indigo (V) (from indigo and oxalyl chloride) seems to fall into this pattern; apparently the formation of this compound containing an additional strainless six-membered ring is sufficient to overcome the unquestionably high energy barrier involved in *trans* → *cis* isomerization. The hydrolysis of such a *cis* derivative would be expected to regenerate the *trans* isomer, as has actually been reported for the oxalyl derivative,[4] if the activation energy of the *cis* → *trans* reaction is close to zero.

The effect of halogens on the ultraviolet and visible spectrum of indigo may be evaluated from the data in Table I. The introduction of halogen atoms has the usual *bathochromic* effect, accompanied by an increase in the intensity of absorption. Bromine causes a greater shift than does chlorine, and this effect of halogens appears to be cumulative in character. The unusually high intensity of absorption observed from 4,4′-dichloroindigo may be due to the position rather than the nature of the substituents, although the reasons for this are not clear. Unfortunately indigo dyes containing substituents in the 6-positions were not available for this study. A comparison of their spectra with their thioindigo analogs, which have been shown to exhibit an anomalous hypsochromic shift,[6,7] might have proved interesting.

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[19] F. A. Miller in Gilman's "Organic Chemistry," Vol. 3, John Wiley and Sons, New York, N. Y., 1953, pp. 144–146.

[20] N. H. Cromwell, *et al.*, THIS JOURNAL, **71**, 3337 (1949).

[21] R. S. Rasmussen, D. D. Tunnicliff and R. R. Brattain, *ibid.*, **71**, 1068 (1949).

[22] This is probably also true of mixed indigo-thioindigo dyes (*e.g.*, Solvat Grey BL Base) the *trans*-forms of which are stabilized by the formation of but one hydrogen bond.