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Spectroscopic Studies on Dyes. I. The Association of Indigo Dyes in the Solid Phase

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[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH & DEVELOPMENT CENTER]

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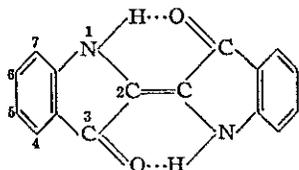
BY JULIUS WEINSTEIN AND GEORGE M. WYMAN

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The visible spectra of indigo and seven of its alkyl- and halogen-substituted derivatives were determined in the solid phase as pellets in potassium bromide and also as aqueous suspensions. The first absorption band of indigo was found to exhibit a strong bathochromic shift when the solid spectrum was compared with that obtained in solution. The introduction of methyl or chlorine substituents in the 4- and 7-positions was found to decrease the magnitude of this shift. No such shift was observed in 5,5',7,7'-tetrabromoindigo. On the basis of these observations it was concluded that, in the solid state, indigo dyes are associated, probably by means of hydrogen-bonding. Bulky substituents in the 4,4'- or 7,7'-positions prevent the close approach of the -CO- and -NH- groups of neighboring molecules and thus interfere with the formation of molecular aggregates. A study of the infrared spectra of these dyes in the -CO- and -NH- stretching regions also supports this explanation. The absorption spectra of cellophane and gelatin films dyed with indigo indicate that under these conditions indigo is also present in the associated form.

Introduction

The problem of the structure and the configuration of indigo has intrigued organic chemists since Baeyer's classic work on the synthesis and constitution of this dye.² This has resulted in a large number of frequently conflicting reports in the literature on the subject.³ There appears to be general agreement that indigo (I) is the *trans* isomer, preferentially stabilized by intramolecular hydrogen-bonding (which is only possible in the *trans* configuration), as had first been suggested by Scholl.⁴ This was recently confirmed by spectrophotometric techniques when it was observed that, in contrast to thioindigo dyes,⁵ indigo dyes in



solutions in organic solvents do not undergo photochemical *trans-cis* isomerization.⁶ In addition, the same authors also found evidence for hydrogen-bonding in indigo in the solid phase from a study of its infrared spectrum.

During a study of the effect of solvents on the spectrum of indigo, Sheppard and Newsome determined the visible spectrum of a solid film of this dye sublimed on glass.⁷ They found that the absorption band occurs at considerably longer wave lengths in the solid phase than in solutions in organic solvents. This bathochromic shift is readily seen from the curves in Fig. 1. Since this unusually large shift in the position of the absorption band suggests the occurrence of structural changes, it was decided to undertake a study of the spectra of indigo and some of its derivatives in the solid phase in the hope of obtaining a better understanding of this phenomenon.⁸

Experimental

(a) Dyes.—4,4'-Dichloro-5,5'-dibromoindigo and 7,7'-dimethylindigo were research samples provided through

(6) W. R. Brode, E. G. Pearson and G. M. Wyman, *THIS JOURNAL*, 76, 1054 (1954).

(7) S. E. Sheppard and P. T. Newsome, *ibid.*, 64, 2937 (1942).

(8) Shortly after the results of the present investigation were first reported it came to our attention that a study of the X-ray diffraction pattern of indigo disclosed that in the solid phase indigo exists in the *trans* configuration with association between neighboring dye molecules, probably by means of hydrogen bonding (*cf.* Helene v. Eller, *Compt. rend.*, 239, 975 (1954)).

(1) Presented before the 127th Meeting of the American Chemical Society, Cincinnati, Ohio, April, 1955.

(2) A. v. Baeyer, *Ber.*, 16, 2204 (1883).

(3) (a) T. Posner, *ibid.*, 59B, 1799 (1926); (b) R. Pummerer and H. Fiesselmann, *Ann.*, 544, 206 (1940); (c) G. Heller, *Ber.*, 77B, 163 (1944); (d) J. v. Alphen, *Rec. Trav. Chim.*, 60, 138 (1941).

(4) *Cf.* W. Madelung and O. Wilhelm, *Ber.*, 57, 237 (1924).

(5) (a) G. M. Wyman and W. R. Brode, *THIS JOURNAL*, 73, 1487 (1951); (b) W. R. Brode and G. M. Wyman, *J. Research Natl. Bur. Standards*, 47, 170 (1951).

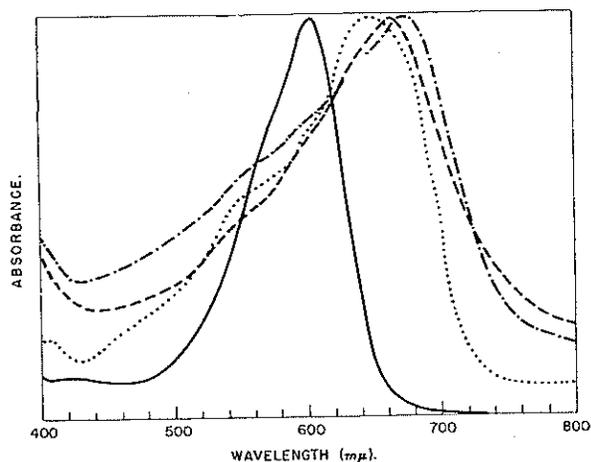


Fig. 1.—The visible spectrum of indigo (.....) as a sublimed film⁷; (—) in chloroform solution; (----) as a pellet in KBr, and (-·-·-) in aqueous suspension.

the courtesy of Dr. D. S. Davies of Imperial Chemical Industries, Ltd., Manchester, England; 5,5'- and 7,7'-difluoroindigos were research samples kindly provided by Prof. Arthur Roe of the University of North Carolina. N,N'-Diacylindigo was prepared as described by Liebermann and Dickhuth.⁹ The other dyes used in this work were commercial samples of known structure.

(b) Preparation of Samples for Measurement.—In the visible region the solid phase spectra were determined by two techniques: (1) as pressed pellets made from an intimate mixture of the dye with KBr¹⁰; and (2) as aqueous dispersions.¹¹ For measurements on solutions in this region and for all the infrared measurements standard techniques of sample preparation were utilized.

(c) Measurement of the Absorption Spectra.—The visible spectra were measured by means of a Cary Model 11 quartz spectrophotometer with the aid of the techniques described in references 5, 10 and 11. The infrared spectra were determined by means of a Beckman IR-3 spectrophotometer, using NaCl or LiF optics, as appropriate. For the measurement of KBr pellets a pellet-holder made of an opaque material was constructed which also acted as a diaphragm, since the pellets were not as wide as the measuring beam of the instrument. A pellet of pure KBr was used as the reference in these measurements.

Discussion of Results

The absorption bands found in the visible spectra of the indigo dyes that comprised this investigation are listed in Table I. The data on the solutions

TABLE I
ABSORPTION BANDS OF INDIGO DYES IN THE VISIBLE REGION

Substituted indigo	Wavelength, mμ ^a		
	In CHCl ₃	In KBr	In aq. suspension
Indigo	604	660	668
5,5'-Difluoro-	618	686	681
7,7'-Difluoro-	619	683	680
7,7'-Dimethyl-	613	(600), 642	(607), 646
4,4'-Dichloro-	605	(590), 640	(600), 643
5,5'-Dibromo-	611	(612), 655	(617), 662
4,4'-Dichloro-5,5'-dibromo-	611	(610), 648	(612), 650
5,5',7,7'-Tetrabromo-	615	614	607
N,N'-diacetyl-	559	558	559

^a Major inflection points are indicated in parentheses.

(9) C. Liebermann and F. Dickhuth, *Ber.*, **24**, 4131 (1891).

(10) G. M. Wyman, *J. Opt. Soc. Am.*, **45**, 965 (1955).

(11) K. Shibata, A. A. Benson and M. Calvin, *Biochim. et Biophys. Acta*, **15**, 461 (1954).

have been taken from reference 6, with the exception of 7,7'-difluoroindigo (which had previously been considered to be too insoluble for measurement) and 7,7'-dimethylindigo. Measurements were made on aqueous suspensions as well, although the potassium bromide technique usually gives clearer spectra, in order to eliminate the possibility of a reaction with potassium bromide or any effect of the pressure which is used in making the pellets.¹² It is evident from the data in Table I that the measurements obtained in the solid phase by the two techniques are in good agreement. In general, although the absorption curves obtained on the solid samples exhibit much broader maxima than those obtained on solutions, the absorption bands are readily located with an uncertainty of but a few millimicrons; this is shown in Figs. 1 and 2.

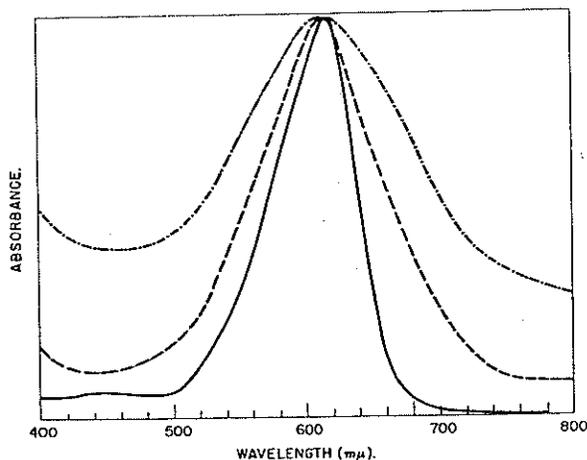
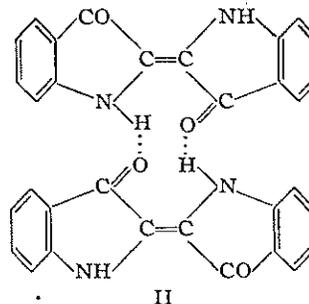


Fig. 2.—The visible spectrum of 5,5',7,7'-tetrabromoindigo (—) in chloroform; (----) as a KBr pellet, and (-·-·-) in aqueous suspension.

It is apparent from Table I that the strong bathochromic shift first noted for indigo in the solid phase⁷ is common to indigo dyes with the exception of those which contain bulky substituents in the 4- and 7-positions. A shift of this magnitude is usually indicative of a considerable extension of the resonating system, suggesting the formation of dimers or higher polymers in the solid phase, held together by intermolecular hydrogen-bonds, as shown in structure (II). In accordance with this picture, bulky substituents in the 4- and 7-positions



II

(12) Such a reaction has recently been reported to occur with thiourea. (Cf. J. E. Stewart, Abstracts of the Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy, Pittsburgh, Pa., 1955, p. 34.)

to-solution shift in the visible spectra) exhibit a broad band in this region at a wave length slightly longer than 3μ (*cf.* Table II). The remaining dyes, containing bulky substituents in the 4,4'- or 7,7'-positions show a sharp band at a wave length somewhat shorter than 3μ . This suggests that in those indigo dyes where the —NH— groups partake in intermolecular hydrogen-bonding, the —NH— stretching frequency occurs at slightly longer wave lengths than that observed in the dyes in which the hydrogen-bonding is mainly intramolecular. A similar difference in the —NH— stretching frequencies has also been observed by Blout in a study of the N,N'-dialkylamides of maleic and fumaric acids where, because of their *cis* configuration, only the former are capable of forming intramolecular hydrogen bonds.¹⁶

In view of the importance of indigo and some of its derivatives as dyestuffs, it is of interest to note

(16) E. R. Blout, private communication.

that cellophane and gelatin films dyed with indigo also exhibited absorption maxima at $662 m\mu$, indicative of the presence of the associated form. Since cellophane and gelatin are structurally similar to cotton and wool, respectively, this strongly suggests that it is the polymeric form that is present in fabrics dyed with indigo. This further deepens the mystery surrounding the nature of the forces that hold dyes of this type to fibers, since it is difficult to envisage a mechanism by which indigo molecules, involved as they are in both intra- and intermolecular hydrogen-bonding, are bound to fibers.

Acknowledgment.—The authors wish to record their appreciation to Dr. E. R. Blout who suggested the study of the —NH— stretching frequencies for evidence of intermolecular hydrogen-bonding and to Mrs. D. A. Rogers for carrying out the study of carbonyl frequencies of the two thioindigo dyes included in this paper.