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Spectroscopic Studies on Dyes. IV. The Fluorescence Spectra of Thioindigo Dyes¹

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The fluorescence spectra of eight thioindigo dyes in benzene solution were determined, using the 546 m μ Hg-line for excitation. Each dye has a fluorescence band at a wave length somewhat longer (usually by *ca.* 35 m μ) than its first absorption maximum. Exposure of the dye solutions to yellow light prior to the measurement results in decreased fluorescence. The intensity of fluorescence was found to be proportional to the concentration of *trans* isomer present. This behavior, which is similar to that observed for stilbene,² indicates that *trans*-thioindigo possesses a tightly-held coplanar structure, while its *cis* isomer is non-coplanar. These conclusions are shown to be consistent with the visible and infrared absorption data. The addition of ethanol quenches the fluorescence of these dyes. The possible implications of this phenomenon with regard to the photochemistry of thioindigo-dyed cellulosic materials are discussed.

Introduction

In their study of the fluorescence spectra of *cis*- and *trans*-stilbene, Lewis and his co-workers have found that only the *trans* isomer exhibits fluores-

cence.² While a large number of articles dealing with fluorescence spectra have appeared in the literature, New Jersey, September 16-21, 1956. (1a) U. S. Army Res. and Dev. Liaison Group, (D671 DU), Rheingau Allee 2, Frankfurt-am-Main, Germany.

(1) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic

(2) G. N. Lewis, T. T. Magel and D. Lipkin, THIS JOURNAL, 62, 2973 (1940).

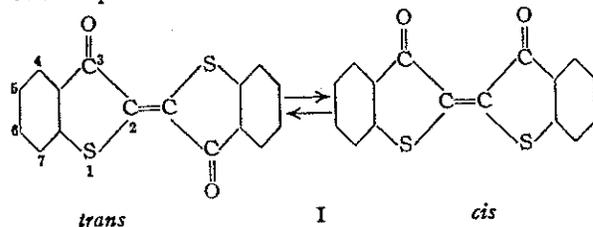
TABLE I
THE DEPENDENCE OF FLUORESCENCE INTENSITY ON THE *cis-trans* ISOMERIZATION OF THIOINDIGO DYES

Dye	Substituents on thioindigo	Concn. mole/l. $\times 10^4$	From absorption measurements			From fluorescence measurements	
			λ_{\max} (m μ) <i>trans</i>	λ_{\max} (m μ) <i>cis</i>	$\frac{[trans]_{yellow}^a}{[trans]_{blue}}$	λ_{\max} (m μ)	$\frac{I_{yellow}^b}{I_{blue}}$
I	None	0.64	546	485	0.35	582	0.38
II	4,4'-Dimethyl-6,6'-dichloro-	1.1	538	483	.37	575	.36
III	4,4'-Dimethyl-5,6,7-trichloro-	0.5	551	493	.37	583	.36
IV	5,5'-Dichloro-4,4',7,7'-tetramethyl	1.9	568	505	.51	602	.52
V	5,5',7,7'-Tetramethyl-	3.4	564	491	.56	600	.62
VI	4,4',5,5',7,7'-Hexachloro-	1.5	564	493	.55	590	.59
VII	6,6'-Diethoxy	6.6	515	458	.25	553	°
VIII	"Vat Scarlet G" (a hemi-thioindigo)	4.1	514	465	.48	581	.46

° Ratio of concentrations of *trans* isomer present after pre-irradiations. ° Ratio of intensities of fluorescence observed after pre-irradiations. ° Fluorescence obscured by mercury emission line.

erature since that time, further mention of the fluorescence of *cis-trans* isomers has been limited to the derivatives^{3a,3b} or the vinylogs^{4a,4b} of stilbene. In harmony with the behavior of stilbene, in each of these instances the solutions containing the largest concentration of *trans* isomers showed greatest fluorescence intensity.

Brode and Wyman have reported the existence of an equilibrium between *cis* and *trans* isomers in



solutions of thioindigo (I) dyes in inert solvents.⁵ They found that the position of the equilibrium was a function of the wave length range of the light to which the solution had been exposed. It was also possible to separate the two isomers by chromatographic adsorption in the dark. These findings made it appear desirable to undertake a study of the fluorescence of thioindigo dyes for the following reasons: (1) to find out whether the behavior of these dyes followed the pattern shown by the aromatic olefins; and (2) to see if an examination of their fluorescence spectra would yield additional information concerning the structure of dyes of this type.

Experimental

Preparation of Solutions.—Approximately 10 mg. of each dye was dissolved in ca. 300 ml. of benzene by heating near the boiling point for several hours. The solution was then cooled to room temperature and diluted to a suitable concentration. The concentrations were determined spectrophotometrically, using appropriate data from reference 3a and 3b.

Pre-irradiation of Solutions.—The dye solution contained in a 2-cm. or 5-cm. absorption cell was exposed for five minutes to filtered light from a Bausch and Lomb Microscope Illuminator (Catalog No. 31-35-85-11), using either a blue or a yellow filter. The blue filter used for all of the dyes was Corning No. 5543. Three yellow filters were used:

(3) (a) A. J. Henry, *J. Chem. Soc.*, 1156 (1946); (b) Y. Hirshberg and F. Bergmann, *This Journal*, **72**, 5118 (1950).

(4) (a) A. Sandoval and L. Zechmeister, *ibid.*, **69**, 553 (1947); (b) Y. Hirshberg, E. Bergmann and F. Bergmann, *ibid.*, **72**, 5117 (1950).

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

Corning No. 3385 for dyes VII and VIII; No. 3484 for dye II and Filter No. 3482 for the five other dyes (*cf.* Table I). The cell length was selected to give an absorption measurement in the range of maximum sensitivity of the spectrophotometer.

Measurement of Absorption Spectra.—The absorption spectra of the pre-irradiated dye solutions were determined in the 400–650 m μ region by means of a Cary Recording Spectrophotometer (Model 11), against the solvent as the reference. The solutions resulting from the chromatographic separation described below were measured on a Beckman DU spectrophotometer.

Measurement of Fluorescence Spectra.—The Fluorescence Attachment of the Model 11 Cary Spectrophotometer was used to measure the fluorescence spectra. All measurements were made at a slit width of 0.5 mm., using the 546 m μ Hg-line for excitation. Whenever fluorescence measurements were desired, immediately upon completion of the pre-irradiation in the longer cell, the solution was transferred to a 1-cm. absorption cell and its fluorescence determined. This operation was necessary because, probably due to self-absorption, the amount of *trans* to *cis* conversion was found to be a function of cell length. In no instance was there evidence for a shift in the *cis-trans* equilibrium caused by the exciting light of the Hg-arc of the fluorescence attachment.

Chromatographic Separation of *cis*- and *trans*-Thioindigo.—The chromatographic separation of the two isomers of thioindigo was carried out as described in reference 3a. However, in view of the quenching action of ethanol on the fluorescence of thioindigo, it was necessary to evaporate the solution containing the *cis*-isomer to dryness and dissolve the residue in benzene before measuring its fluorescence spectrum.

Results

The behavior of 4,4'-dimethyl-6,6'-dichlorothioindigo, which is shown in Fig. 1, is characteristic of all the dyes studied in this investigation. Each dye has a band of fluorescent emission in the visible region at a wave length somewhat longer than its first absorption band. Thioindigo dyes enriched with respect to the *cis* isomers (by pre-irradiation with yellow light) show fluorescence at the same wave lengths but with diminished intensity. There was also no evidence for any new fluorescence bands that may be attributable to the *cis*-isomers when the 436 or 366 m μ Hg-lines were used for the excitation, even for dyes VII and VIII, the *cis* isomers of which absorb strongly near 450 m μ (*cf.* Table I). Consequently this suggests that only the *trans* isomers exhibit fluorescence.

Further confirmation of this conclusion was obtained from a comparison of the fluorescence intensity with the relative concentration of the *trans* isomer as shown in Table I. The last column in this table shows the ratio of the fluorescence in-

nol does not favor the formation of the *cis* isomer, but on the contrary stabilizes *trans*-thioindigo.

Solvent	Fraction of <i>trans</i> -thioindigo present ^a	
	Benzene	90% benzene-10% ethanol ^b
Blue light	1.00	1.00
Yellow light	0.38	0.72

^a Calculated from absorbancies at 562 $m\mu$, where the *cis*-thioindigo does not absorb appreciably. ^b In 10% ethanol the *trans* absorption band is shifted slightly (*ca.* 2 $m\mu$) to longer wave length.

Discussion of Results

While at the present time our understanding of the relation between fluorescence spectra and chemical structure is not as thorough as it is with respect to electronic or vibrational spectra, nonetheless, it has been possible to arrive at certain correlations in this respect.⁶ A molecule which has been raised to an electronically excited state by the absorption of a quantum of light of appropriate frequency, can lose this excess energy and return to the ground state by one of three processes: internal conversion, external conversion or fluorescent emission. *Internal conversion* occurs when the energy of electronic excitation is converted to some other form of energy (*e.g.*, heat) by the absorbing molecule. While it is believed that most radiationless transitions occur in this manner, the exact nature of this process is not fully understood at the present time. *External conversion* is said to occur when the excited molecule through collisions transfers its excess energy to one or more other molecules, *e.g.*, solvent molecules. *Fluorescent emission* occurs only when the excited molecule cannot readily lose its energy by either of these processes. The probability for *internal conversion* depends principally on the structure of the molecule, while the ease of external conversion is a function of the solvent and the temperature. Consequently, whether or not a given molecule will exhibit fluorescence under certain conditions will be determined by both structural and environmental factors. By studying the fluorescence of different compounds under comparable conditions, it is possible to cancel out the environmental variables and thus to correlate fluorescence with chemical structure.

The failure of *cis*-stilbene to exhibit fluorescence (in contrast with its *trans*-isomer) was attributed by Lewis, Magel and Lipkin to its non-coplanar structure, which results from the steric interference of the *ortho*-hydrogen atoms of the two benzene rings.² According to their views the coplanar *trans*-stilbene molecule is prevented from *internal conversion* of its electronic energy because of its rigidly-held compact structure. In the non-coplanar *cis* isomer, on the other hand, which is not constrained by nearly as much resonance energy, the energy of electronic excitation is relatively readily

(6) The following references contain up-to-date discussions on this subject: (a) P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949; (b) T. Foerster, "Fluoreszenz Organischer Verbindungen," Vanden-Loek and Ruprecht, Goettingen, 1951; (c) W. West, "Fluorescence and Phosphorescence" (Chapter VI) in "Technique in Organic Chemistry," A. Weissberger, Editor, Vol. IX, Interscience Publishers, Inc., New York, N. Y., 1956.

converted to vibrational energy and/or dissipated as heat. Studies of the fluorescence of 4,4'-stilbenedicarboximidine,^{3a} 9,9'-diphenanthrylethylene and 1,4-diphenylbutadiene^{4a,4b} have indicated that this behavior was characteristic of aromatic olefins and have thus provided further support for this interpretation.

It is clear from the results of the present investigation that thioindigo derivatives also follow the pattern set by the aromatic olefins. This immediately suggests a compact, coplanar structure for the *trans* compounds and a less constrained non-coplanar configuration for the *cis* isomers. Recent X-ray diffraction studies on crystalline thioindigo indicated that in the solid phase the dye exists in a tightly-held, coplanar *trans* configuration.⁷ The unusually short distance (2.82 Å.) between the sulfur and oxygen atoms of adjacent rings was considered to indicate the existence of secondary bonds (probably stemming from electrostatic attraction) between these atoms, thus resulting in further stabilization of the *trans* structure.

A scale drawing of the structure of the two thioindigo isomers is shown in Fig. 4. The *trans* isomer

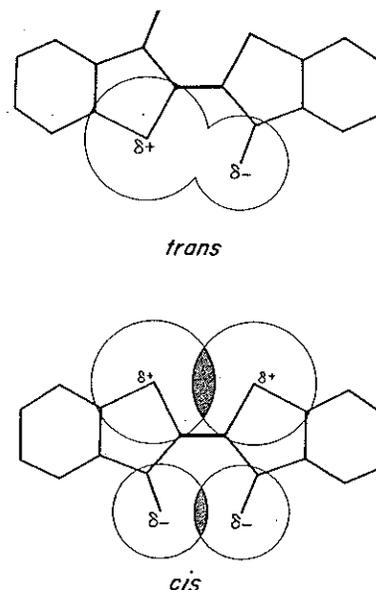


Fig. 4.—Diagram of the spatial arrangement of atoms in *cis*- and *trans*-thioindigo.

was drawn on the basis of Mme. v. Eller's data⁷ while the structure of the *cis* isomer was constructed by rotating half of the *trans* molecule 180° about the central axis. The circles were drawn to scale using the van der Waals radii of 1.40 Å. for oxygen and 1.85 Å. for sulfur. It is readily apparent from Fig. 4 that the steric interference of the two carbonyl oxygen atoms and the two sulfur atoms would be expected to cause a departure from coplanarity in the *cis* isomers. Since oxygen atoms of carbonyl groups carry a partial negative charge⁸ and the sulfur atoms in a resonating system of this type are probably carrying a slight positive charge, the steric

(7) Helene v. Eller, *Bull. soc. chim. France*, 1444 (1955).

(8) Cf. L. Pauling, "The Nature of the Chemical Bond," 2nd Edition, Cornell University Press, Ithaca, N. Y., 1943, p. 75.

effect will be further augmented by electrostatic repulsion. Since the hemithioindigoid dye Vat Scarlet G also behaves in a similar manner even though it only possesses one sulfur atom, it appears that the steric hindrance induced by the overlapping and the repulsion of the carbonyl groups alone is sufficient to induce non-coplanarity.

The departure from coplanarity brought about in the *cis*-thioindigo dyes by a combination of steric hindrance and electrostatic repulsion is further substantiated by the visible and infrared spectra of these compounds. In the visible region the *cis* isomers have been reported to show absorption of much shorter wave lengths (by *ca.* 60 m μ) than do their *trans* counterparts.^{8a,8b} This hypsochromic shift has been attributed to the higher potential energy of the *cis* over the *trans* in their excited states, with these excited states pictured as having a central carbon-carbon single bond and charged oxygen and sulfur atoms. Electrostatic repulsion of the two oxygen atoms and of the two sulfur atoms in the excited *cis* form would give it a higher potential energy and would also force non-coplanarity. In the infrared spectrum the observed shift of the carbonyl stretching band from 6.04 to 5.90 μ when a solution of thioindigo in chloroform is irradiated with yellow light⁹ clearly indicates a severe curtailment of the conjugated system in which the carbonyl group participates. Since a departure from coplanarity would, indeed, prevent conjugation between the two halves of the thioindigo molecule, the infrared data are also in harmony with the above conclusions.

The energy difference between the frequencies of

(9) J. Weinstein and G. M. Wyman, *THIS JOURNAL*, **78**, 2387 (1956).

the *trans* absorption maximum and that of the maximum fluorescence intensity is small for the thioindigo dyes I through VII. It varies between 2.1 kcal./mole for dye V and 3.8 kcal./mole for dye VII. These low energy differences indicate that *trans* to *cis* conversion probably cannot accompany fluorescence, but instead is a competitive photochemical process.

The observed effect of the addition of ethanol to a benzene solution of *trans*-thioindigo indicates that not only is the quantum yield of fluorescence decreased, but that the efficiency of the *trans* to *cis* photoisomerization is also diminished. This suggests that a third, competing photochemical reaction is involved. Perhaps this is due to the formation of a loosely held complex between the alcohol and the dye, or, alternatively, some other mechanism by which energy can be transferred from the dye to an ethanol molecule. While the carbonyl stretching frequency of thioindigo in chloroform is only slightly affected by the addition of ethanol,¹⁰ the possibility of complex formation cannot be definitely ruled out. It is interesting to note in this connection that thioindigo dyes do not exhibit fluorescence when dyed on cellophane or on cellulosic fibers. Since these polysaccharides are chemically similar to ethanol, this suggests an analogy between the mechanism by which the fluorescence of these dyes is quenched by ethanol and their reported "tendering" effect on cotton.¹¹

Acknowledgment.—The authors are indebted to Mr. John Sousa for his assistance with the experimental work.

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(10) J. Weinstein and G. M. Wyman, *ibid.*, **78**, 4009 (1956).

(11) A. Landolt, *J. Soc. Dyers Colourists*, **65**, 659 (1949).