eosin, is about 3×10^8 sec.$^{-1}$ [11] so that k_4 would be 6×10^{13} l./mole/sec. As might be expected, this value of k_4 cannot be accounted for on the basis of diffusion-controlled bimolecular encounters (6.6×10^9 encounters/sec./mole/liter in aqueous systems at 25°) but more likely represents the rate constant for energy transfer between dye molecules fixed on the polymer chain to yield dye molecules in the long-lived excited state. The quenching of this long-lived state by reductant (step 6) is twice as efficient as step 7 which leads to the intermediate complex.

Small amounts of PPD retard the rate of photoreduction of free eosin[6] whereas with bound eosin inhibition as well as retardation occurs (Fig. 4). Since there is no appreciable fluorescence quenching at these low PPD concentrations, the step D* + X → D + X is unimportant but reaction occurs as in step 9 to account for the observed inhibition (compare ref. 5). The retardation effect of PPD requires that products formed in step 9 quench the long-lived excited dye molecules, *i.e.*, (10) D′ + products (II) → D + products (II). Assuming steady-state concentrations for D*, D′ and M we derive the following expression for the ratio R_0/R_x of the rates of photoreduction in the absence and in the presence of substance X

$$\frac{R_0}{R_x} = \left[1 + \frac{k_9}{k_8}(\mathrm{X})\right]\left[1 + \frac{k_{10}(\text{Products (II)})}{k_5(k_6 + k_7)(\mathrm{A})}\right]$$

Since no photofading occurs until the inhibition period is ended k_9 must be much larger than k_{10}. Step 9 requires that the concentration of Product II be proportional to the amount of PPD added (X_0). We may express the amount of retardation which occurs after the inhibition period is completed as

$$\frac{R_0}{R_x} = 1 + \frac{k_{10}'(X)_0}{k_5 + (k_6 + k_7)(\mathrm{A})}$$

Thus, as shown in Fig. 4, the retardation is directly proportional to the amount of PPD originally added. From the slope of this line and using the ratios of the rate constants enumerated above we obtain $k'_{10}/k_6 = 1.35 \times 10^6$. If the concentration of Products II is comparable in magnitude to that of X_0 then quenching by this product is much more efficient than quenching by reductant. These results are consistent with the observation that PPD itself does not quench the phosphorescence of bound eosin although it strongly quenches the phosphorescence of free eosin.

The purely inhibiting action of nitrobenzene on the photoreduction of bound eosin is explainable in exactly the same way as that for bound triphenylmethane dyes.[5] In this case, step 10 is not important since no retardation occurs.

It has been known for many years that eosin applied to silver halide photographic emulsions will render the emulsion sensitive to green light.[12] Silver bromide emulsions sensitized with eosin have been studied in our laboratory.[13] The sensitivity of the emulsion is a maximum at the wave length where the bound dye absorbs light maximally. The binding curve for the dye as a function of silver bromide concentration is similar to that of Fig. 1. The emulsion exhibits sensitivities as a function of silver halide concentration and eosin concentration in a manner analogous to the fading curves of Figs. 1 and 3. Small amounts of nitrobenzene suppress the green sensitivity while the blue sensitivity (a property of the silver halide itself) is unchanged. It would appear that in this system, at least, the bound dye is photoreduced and the reduced dye donates electrons to the silver halide to form the latent image. This is an alternative suggestion to those contained in current theories of dye-sensitization in photography which postulate photoelectric phenomena.[14]

(11) Compare, P. Pringsheim, "Fluorescence and Phosphorescence," Interscience Publishers, Inc., New York, N. Y., 1949, p. 316.

(12) J. Waterhouse, *Brit. J. Photo.*, **23**, 233 (1876).

(13) G. Oster, to be published.

(14) For review, see W. West and B. H. Carroll in "The Theory of the Photographic Process," Ed. by C. E. K. Mees, Revised Edition, The Macmillan Co., New York, N. Y., 1954.

BROOKLYN, N. C.

[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH AND DEVELOPMENT CENTER]

Spectroscopic Studies on Dyes. IV. The Fluorescence Spectra of Thioindigo Dyes[1]

BY DELBERT A. ROGERS, J. DAVID MARGERUM AND GEORGE M. WYMAN[1a]

RECEIVED JANUARY 28, 1957

The fluorescence spectra of eight thioindigo dyes in benzene solution were determined, using the 546 mμ Hg-line for excitation. Each dye has a fluorescence band at a wave length somewhat longer (usually by *ca.* 35 mμ) 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 fluorescence.[2] While a large number of articles dealing with fluorescence spectra have appeared in the lit-

(1) Presented before the Division of Physical and Inorganic Chemistry at the 130th Meeting of the American Chemical Society, Atlantic City, New Jersey, September 16–21, 1956. (1a) U. S. Army Res. and Dev. Liaison Group, (D671 DU), Rheingau Allee 2, Frankfurt-am-Main, Germany.

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

TABLE I

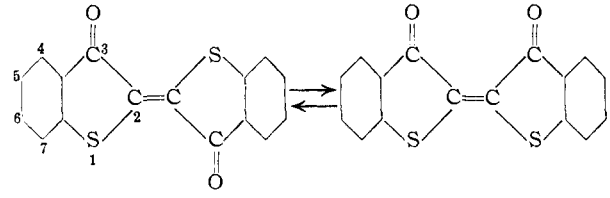
THE DEPENDENCE OF FLUORESCENCE INTENSITY ON THE *cis–trans* ISOMERIZATION OF THIOINDIGO DYES

Dye	Substituents on thioindigo	Concn. mole/l. × 10^5	From absorption measurements λmax (mμ) *trans*	*cis*	$\frac{[trans]_{yellow}}{[trans]_{blue}}$[a]	From fluorescence measurements λmax (mμ)	$\frac{I_{yellow}}{I_{blue}}$[b]
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	[c]
VIII	"Vat Scarlet G" (a hemi-thioindigo)	4.1	514	465	.48	581	.46

[a] Ratio of concentrations of *trans* isomer present after pre-irradiations. [b] Ratio of intensities of fluorescence observed after pre-irradiations. [c] 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



trans I *cis*

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: 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 mμ 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 mμ 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 mμ Hg-lines were used for the excitation, even for dyes VII and VIII, the *cis* isomers of which absorb strongly near 450 mμ (*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-

(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).

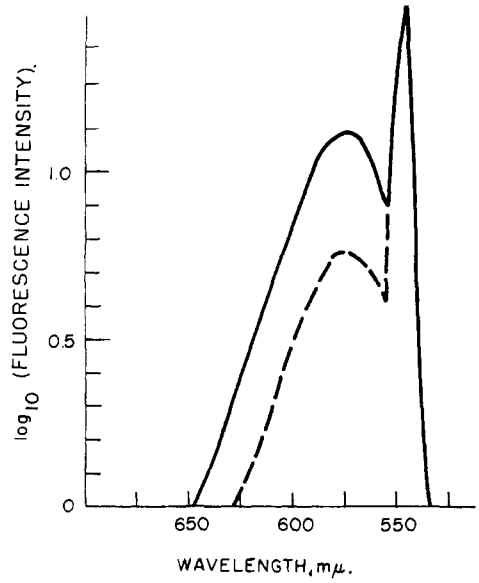


Fig. 1.—Fluorescence spectrum of 4,4′-dimethyl-6,6′-dichlorothioindigo in benzene: (————) pre-irradiated with blue light; (- - - -) pre-irradiated with yellow light. Concentration: 2.8 mg./l.; exciting light, 546 mμ.

tensity of each dye solution that had been preirradiated with yellow light (*i.e.*, enriched with respect to *cis*) to that of the same solution pre-irradiated with blue light (*i.e.*, essentially all-*trans*). Correspondingly, the fourth column in the table gives the ratio of the concentrations of the *trans* isomer present under these two sets of conditions, determined independently from absorption measurements. The good agreement between these two figures shown for each dye indicates that the fluorescence intensity is directly proportional to the concentration of *trans* isomer. It is then evident from these data that the *cis* isomers can possess little or no fluorescence in this region of the spectrum.

In order to obtain direct proof of this conclusion it was decided to measure the fluorescence of a solution of *cis*-thioindigo. Accordingly, the chromatographic separation of the isomers was carried out and the fluorescence and absorption spectra of the resulting solutions were measured, as shown in Fig. 2. While the solution contained mostly *cis*-thioindigo, the absorption at 550–570 mμ showed that there was also an appreciable amount (*ca.* 10%) of *trans* isomer present. (It is believed that the *trans* compound formed during the additional operations required for the removal of the ethanol.) However, a comparison of the fluorescence spectra obtained on this solution before and after irradiation with blue light (thus representing the two extremes with respect to the concentration of each isomer) disclosed that the fluorescence intensity was again proportional to the concentration of the *trans* form (*cf.* Fig. 2.) On the basis of all this evidence it is possible to conclude that only the *trans* isomers of thioindigo dyes exhibit fluorescence.

The quenching of fluorescence that is caused by the addition of a small amount of ethanol to a solution of a thioindigo dye in benzene is readily noticeable even to the naked eye. This interesting effect, which was inadvertently encountered when

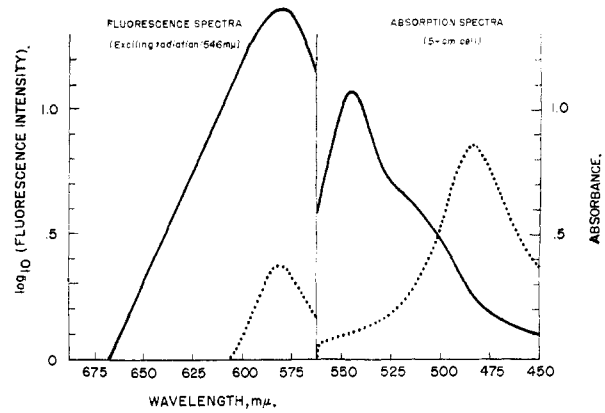


Fig. 2.—(A) Fluorescence spectrum of thioindigo in benzene: (. . . . . .) mainly *cis* form, from chromatographic separation; (————) the same solution, after irradiation with blue light. (B) Absorption spectra of the same two solutions; concentration, 4 mg./l.

the feasibility of using ethanol in the chromatographic separation of the two thioindigo isomers was explored, is shown in Fig. 3.

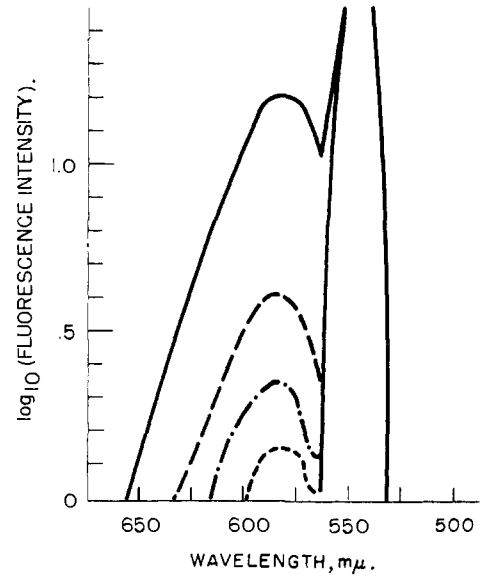


Fig. 3.—Effect of ethanol on the fluorescence spectrum of thioindigo in benzene. Concentration of dye, 2 mg./l.; concentration of ethanol, (————) 0%; (- - - -) 5%; (— · — · —) 10%; (·····) 20% by volume. Exciting light, 546 mμ.

In order to show that the fluorescence quenching by ethanol is not brought about by conversion of the *trans* isomer to the non-fluorescing *cis* form of thioindigo, the following experiment was carried out. Two solutions of equal thioindigo concentration were made up, one in benzene and the other in benzene containing 10% ethanol. The visible absorption spectra of these solutions were recorded after pre-irradiation with blue light and then after pre-irradiation with yellow light. The pre-irradiations were for five minute periods and were made under the same conditions for each solution. The results (*cf.* Table II) show that the presence of etha-

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

TABLE II

EFFECT OF ETHANOL ON *trans–cis* PHOTOISOMERIZATION

Solvent	Fraction of *trans*-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 mμ, where the *cis*-thioindigo does not absorb appreciably. [b] In 10% ethanol the *trans* absorption band is shifted slightly (*ca.* 2 mμ) 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 converted to vibrational energy and/or dissipated as heat. Studies of the fluorescence of 4,4′-stilbenedicarboxamidine,[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

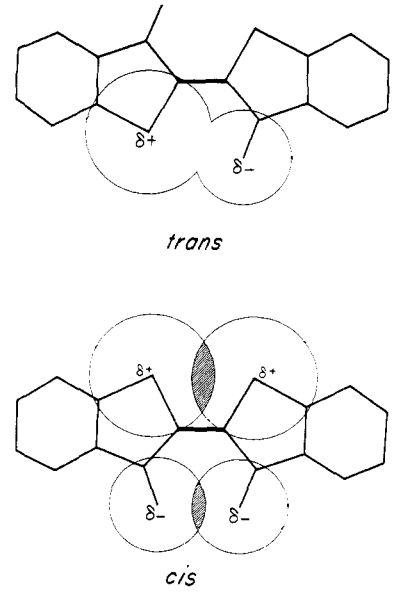


Fig. 4.—Diagram of the spatial arrangement of atoms in *cis*- and *trans*-thioindigo.

was drawn on the basis of Mme. v. Eller's data[7] 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 charge[8] and the sulfur atoms in a resonating system of this type are probably carrying a slight positive charge, the steric

(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.

(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 mμ) than do their *trans* counterparts.[5a,5b] 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 light[9] 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 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.

NATICK, MASS.

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

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

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