sistent, however, with the results 1.573 Å., 1.093 Å. (ass.) and 106.7° which were obtained by Herzberg[27] on the assumption of the preliminary moment values and the same C–H distance as is found for methane. Nevertheless, the agreement of our results with the moments of inertia is in fact most satisfactory, as may be seen from the excellent agreement (relative to our limits of error) with the model which follows from the reasonable conditions that (1) the completely reliable value $I_B = 42.234 \times 10^{-40}$ g. cm.^{2} be fitted exactly, (2) the indications from the less reliable value $I_A = 10.81 \times 10^{-40}$ g. cm.[2] [28] and our point be averaged, and (3) that with due regard for its likely error as a function of direction in parameter space our point be otherwise adhered to as closely as possible. This model has C–C = 1.533 Å., C–H = 1.110 Å., and $\angle$C–C–H = 110.4°; it is fixed by the spectroscopic data to the extent that a change in any one of the electron diffraction parameter values would result in changes of the parameter values of the model of at most about half the change in the electron diffraction value, if distances are expressed in hundredths of an ångström and the angle in degrees.[29] We feel, accordingly, that the indications that C–C is not greater than 1.54, that C–H is considerably greater than in methane, and that $\angle$C–C–H is somewhat greater than the tetrahedral value are most probably correct even though the diffraction results alone, because of their large limits of error, would hardly justify this conclusion. It is interesting that values for the C–H distance which have been reported recently for the methyl halides, partly[30] or wholly[31] on the basis of microwave spectra, are also considerably greater than the methane value of 1.094 Å.; the H–C–H angles, however, are reported to be slightly greater than tetrahedral, in disagreement with our finding for ethane. On the other hand, the microwave values for the HCH angle in methyl cyanide[32] and methylacetylene[33] are less than tetrahedral and in methyl isocyanide[32] only a trifle greater than tetrahedral, while in all three molecules the C–H distance is very nearly the same as in methane.

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[27] G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand and Company, Inc., New York, N. Y., 1945, p. 440.

[28] I_A, having been revised downward a full 2% from the preliminary value of 11.03×10^{-40} g. cm.^{2} on the basis of difficult considerations of complicated perturbations in the $\perp$ bands, appears still to be somewhat uncertain,[26] and Smith makes no definite claims for its accuracy. The average of the preliminary and final values, it happens, would correspond to our diffraction results.

[29] The coefficients of variation due to deviations from our diffraction values respectively of C–C, C–H and $\angle$C–C–H are approximately the following: for C–C, +0.5, −0.3 and −0.5; for C–H, −0.2 +0.1 and +0.2; and for $\angle$C–C–H, −0.4, +0.2 and +0.4.

[30] See W. Gordy, *Rev. Modern Phys.*, **20**, 712 (1948).

[31] B. P. Dailey, J. M. Mays and C. H. Townes, *Phys. Rev.*, **76**, 136 (1949).

[32] M. Kessler, H. King, R. Trambarulo and W. Gordy, *ibid.*, **79**, 54 (1950).

[33] R. Trambarulo and W. Gordy, private communication.

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[CONTRIBUTION FROM THE NATIONAL BUREAU OF STANDARDS]

The Relation between the Absorption Spectra and the Chemical Constitution of Dyes XXII. *cis–trans* Isomerism in Thioindigo Dyes[1]

BY GEORGE M. WYMAN AND WALLACE R. BRODE

The ultraviolet and visible absorption spectra of seven purified thioindigo dyes in benzene and in chloroform were determined under several conditions of temperature and illumination. It was concluded that these compounds exist in solution as two forms (*cis* and *trans*) in equilibrium. The position of the equilibrium is a function of the temperature and the illumination. The approximate spectral absorption curves were calculated for the two isomers of each dye, and the relative amount of each isomer present at the several equilibrium conditions was computed. The two isomers of thioindigo and of 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo were separated chromatographically and their absorption spectra were obtained. Definite configurations were assigned to the two isomers of each dye. Correlations between the absorption spectra and the structures of thioindigo dyes are discussed.

Introduction

The determination of the spectral absorption curves of purified samples of seven thioindigo dyes in the ultraviolet and visible regions is a part of the National Bureau of Standards research project on the spectrophotometry of pure dyestuffs. Stearns had reported on the revisible change occurring in the absorption spectra of two thioindigo dyes when the dye solutions were exposed to intense white light.[2] Preliminary measurements indicated the existence of such a phototropic effect in the case of the dyes studied in this work; the absorption spectra were found to be a function of the color of the light to which each dye solution had been exposed prior to the measurement. In addition, it was observed that the absorption spectrum of each dye was also affected by a change in the temperature. It was, therefore, necessary to study the influence of these two variables in order to obtain reproducible spectral absorption curves for this important group of dyestuffs. As a result of this investigation a single explanation has been found for these two related effects.

Experimental

(a) **Purification of Dyes.**—The dyes used for this investigation were commercial products of known structure. All but one were purified by adsorption on silica gel (Davison Chemical Corp., Commercial Grade, 200-mesh) followed by selective elution. The solvents used were: redistilled carbon tetrachloride, benzene and absolute alcohol. After elution the solution was evaporated to dryness, the residue recrystallized from benzene or chloroform and dried at 60–65°. Bis-4,5-benzothioindigo was purified by recrystallization from benzene due to its low solubility at room temperatures. Table I summarizes the conditions of the chromatographic purifications; the dyes are listed in order of increasing adsorption affinity.

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[1] Presented at the 118th Meeting of the American Chemical Society, Chicago, Ill., September, 1950.

[2] E. I. Stearns, *J. Opt. Soc. Am.*, **32**, 282 (1942).

TABLE I

CHROMATOGRAPHIC PURIFICATION OF THIOINDIGO DYES

Thioindigo	Solvents (per cent. by volume) Adsorbed from	Eluted with	Crystallized from
5,5'-Dichloro-4,4',7,7'-tetramethyl-	CCl_4	75% CCl_4 25% C_6H_6	$CHCl_3$
4,4'-Dimethyl-6,6'-dichloro-	CCl_4	50% CCl_4 50% C_6H_6	$CHCl_3$
5,5'-Dichloro-7,7'-dimethyl-	75% CCl_4 25% C_6H_6	33% CCl_4 67% C_6H_6	$CHCl_3$
Thioindigo	75% CCl_4 25% C_6H_6	C_6H_6	$CHCl_3$
6,6'-Diethoxy-	C_6H_6	99% C_6H_6 1% EtOH	C_6H_6
5,5'-Dibromo-6,6'-diethoxy-	C_6H_6	99% C_6H_6 1% EtOH	C_6H_6

(b) **Preparation of Solutions.**—Approximately 0.010 g. of each dye was weighed and dissolved in 600–700 ml. of benzene or chloroform by heating near the boiling point for several hours. The solution was then cooled to 25° and diluted to 1 liter.

(c) **Irradiation of Solutions.**—The dye solution contained in the absorption cell was exposed for 5–10 minutes to colored light using a 100-watt Spencer Microfilm Projector with Corning glass filters. These filters are listed in Table IV along with the manufacturer's numbers and observed transmission cut-off (wave length at which the transmission is less than 1%).

(d) **Measurement of Absorption Spectra.**—The absorption spectra were determined at room temperature (except as noted otherwise) by means of a Cary Recording Quartz Spectrophotometer (Model 12) using matched fused quartz absorption cells and the solvent as the reference standard.

(e) **Chromatographic Separation of *cis* and *trans* Isomers. Thioindigo.**—A solution of about 0.010 g. of thioindigo in 50 cc. of distilled benzene was exposed to yellow light ($\lambda >$ 520 mμ) for 20 minutes. This solution was then poured into a column packed witn silica gel. The dark ring of the adsorbed dye at the top of the column was continuously eluted with distilled benzene until about one liter of benzene had been used. The entire operation was carried out in a darkened room in the presence of a deep red light of low intensity (Corning 243, $\lambda >$ 600 mμ) to which wave length region both isomers are transparent. When elution is complete, a colorless zone can be observed separating a narrow maroon ring at the top of the column and a diffuse blue zone further down the column. The column was then sucked dry and the two colored zones extruded separately. The dye was dissolved in benzene containing 1% absolute alcohol,[3] and kept in darkness until its spectrum was measured.

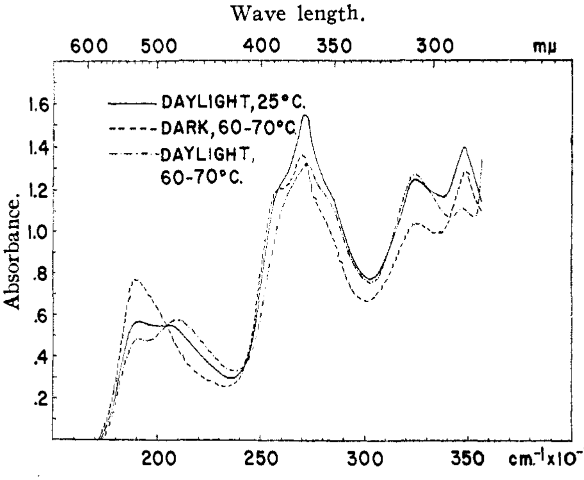

Fig. 1.—Absorption spectra of 5,5'-dibromo-6,6'-diethoxythioindigo in benzene at different temperatures (c = app. 0.02 g./l., d = 2.00 cm.). In all figures absorbance is plotted against frequency in wave numbers.

5,5'-Dichloro-4,4',7,7'-tetramethylthioindigo.—The chromatographic separation of the two isomers of this dye was carried out in a manner similar to that described above for thioindigo, except that the dye was dissolved in carbon tetrachloride and illuminated with red light ($\lambda >$ 575 mμ) and the absorbed dye was eluted with a mixture of 75% carbon tetrachloride and 25% benzene (by volume). At the end of the elution the two forms appeared as a narrow gray band at the top of the column and a diffuse blue zone further down the column, separated by a colorless zone. The dye was dissolved from the adsorbent by means of chloroform and kept in darkness until its spectrum was determined.

Discussion of Results

The spectral absorption curve of each of the seven dyes studied was found to change considerably when the spectra were determined at a temperature just below the boiling point of the solvent instead of room temperature (*cf.* Fig. 1). Still more pronounced changes occurred when the dye solutions were exposed to selective irradiation prior to the measurement. Figures 2–5 show typical spectral absorption curves obtained for two of these dyes in benzene and in chloroform under different conditions of illumination.

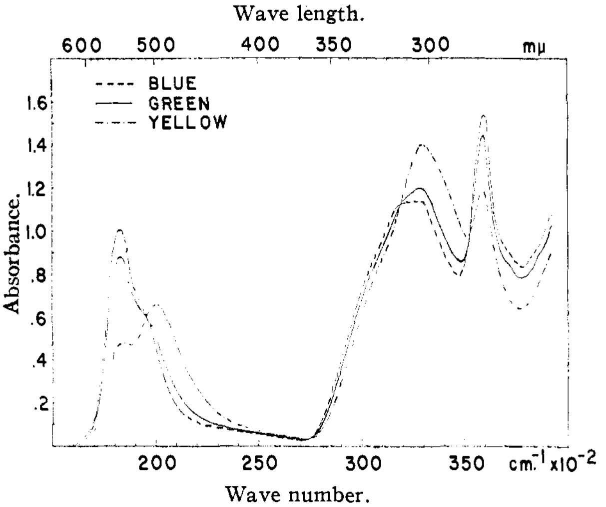

Fig. 2.—Absorption spectra of thioindigo in chloroform, exposed to: (a) blue light ($\lambda <$ 495 mμ); (b) green light ($\lambda >$ 350 mμ); (c) yellow light ($\lambda >$ 520 mμ) (c = 0.0101 g./l.; d = 2.00 cm.).

The various spectral absorption curves for each dye have the following features in common:

(1) The absorption curve in each solvent (at room temperature) is a function of the wave length range of the light to which the solution had been exposed prior to the measurement. The absorption curve obtained after exposing the dye to light of a given wave length range can always be reproduced by irradiating the solution with light of the same wave lengths prior to the second measurement.

(2) Greatest change in the normal (daylight) absorption spectrum is brought about by irradiating the solution with light of a wave length range

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[3] It had previously been shown that small amounts of alcohol did not change the absorption spectrum of thioindigo dissolved in benzene.

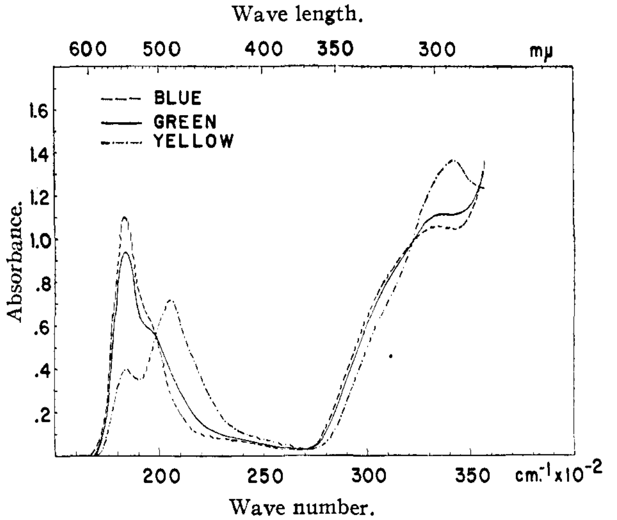


Fig. 3.—Absorption spectra of thioindigo in benzene, exposed to colored light of different wave lengths as in Fig. 2 (c = 0.0104 g./l.; d = 2.00 cm.).

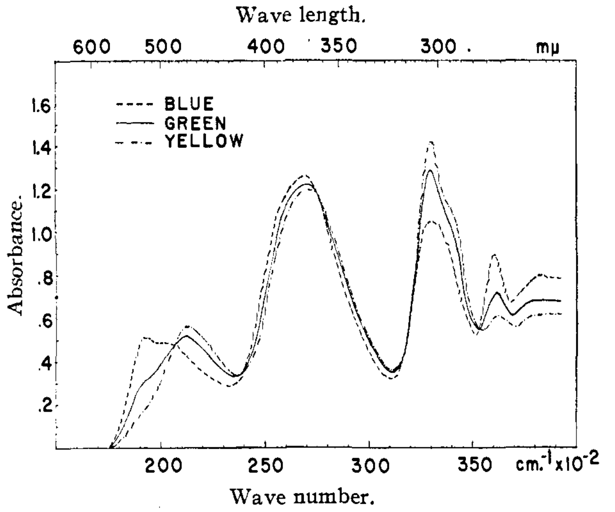


Fig. 4.—Absorption spectra of 6,6′-diethoxythioindigo in chloroform, exposed to (a) blue light (λ < 495 mμ); (b) green light (λ > 350 mμ); (c) yellow light (λ > 487 mμ) (c = 0.0107 g./l.; d = 2.00 cm.).

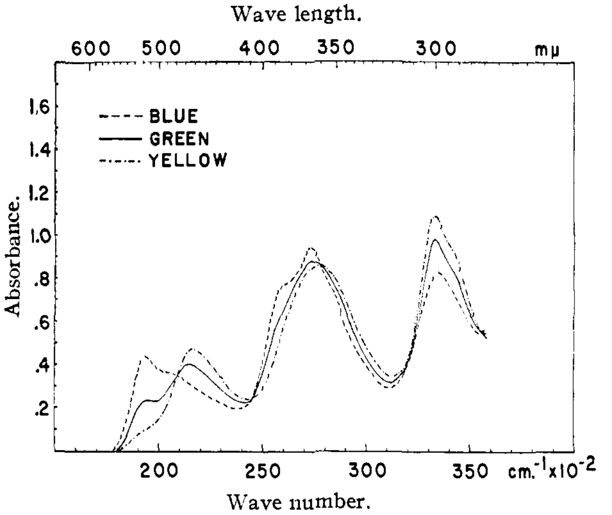


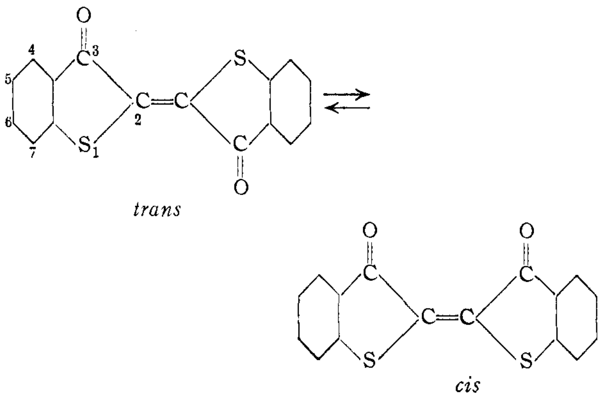
Fig. 5.—Absorption spectra of 6,6′-diethoxythioindigo in benzene, exposed to colored light of different wave lengths as in Fig. 4 (c = 0.0080 g./l.; d = 2.00 cm.).

corresponding to the first (long-wave) absorption band of each dye. This change consists of a decrease in the intensity of the first absorption band and the appearance of a new absorption band at a slightly shorter wave length.

(3) Upon irradiation with light of short wave lengths (λ<495 mμ) the positions of the principal absorption bands of the normal (daylight) spectrum are retained but the intensity and sharpness of the bands are increased.

(4) For each dye there are several isosbestic points, that is, wave lengths at which the absorption curves cross and, consequently, the absorption is independent of the irradiation to which the solution had been exposed. Such isosbestic points are convenient for the rapid quantitative spectrophotometric analysis of such dyestuffs.

These observations indicate that in solution each dye exists as two forms (probably *cis* and *trans*) in equilibrium which may be represented by the equation



The position of the equilibrium is a function of the temperature and the illumination. Heat, in the presence of light, or light of a wave-length range corresponding to the first (long-wave) absorption band of the dye, shifts this equilibrium toward the right (*cis*).[4] Heating in the absence of light, or illumination with blue or ultraviolet light shifts the equilibrium toward the left (*trans*).

At a specific wave length the total absorbance will be the sum of the absorbances due to the *cis* and *trans* forms

$$A_{(\text{total})} = A_{(cis)} + A_{(trans)} \qquad (1)$$

At a specific equilibrium between the two forms the equation will be

$$A' = A'_{(cis)} + A'_{(trans)} \qquad (2)$$

and at a shifted equilibrium condition

$$A'' = A''_{(cis)} + A''_{(trans)} \qquad (3)$$

From the absorption law[5]

$$\frac{A'_{(cis)}}{A''_{(cis)}} = \frac{C'_{(cis)}}{C''_{(cis)}} = R'{}''_{(cis)} \qquad (4)$$

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(4) For reasons which will be discussed later, the form which has its first (long-wave) absorption band at a longer wave length was designated as the *trans* isomer.

(5) W. R. Brode, *J. Opt. Soc. Am.*, **39**, 1023 (1949).

and, similarly

$$\frac{A'_{(trans)}}{A''_{(trans)}} = \frac{c'_{(trans)}}{c''_{(trans)}} = R'/''_{(trans)} \qquad (5)$$

($R'/''_{(cis)}$ and $R'/''_{(trans)}$ are independent of the wave length). Then equation (2) can be rewritten as

$$A' = R'/''_{(cis)}\, A''_{(cis)} + R'/''_{(trans)}\, A''_{(trans)} \qquad (6)$$

In the case of each of these dyes the absorption at the long wave length end of the spectrum appears to be almost entirely due to the *trans* form; hence it is possible to evaluate $R'/''_{(trans)}$ for any pair of conditions of illumination with fair accuracy. It is also frequently possible to estimate $A''_{(cis)}$ from the curve of the dye solution enriched with respect to the *cis* form at a wave length just to the short side of the main observed absorption peak in the visible region. From these estimated values of $R'/''_{(trans)}$ and $A''_{(cis)}$ it is possible to calculate the approximate spectral absorption curves for each isomer of each dye over the entire wave length range by means of equations (3) and (6). The accuracy of these calculated curves is the greater, the higher the concentration of the *cis* form in the solution enriched with respect to that isomer. Figures 6–9 show the principal types of absorption curves calculated in this manner for the dyes studied and Tables II and III list the absorption spectral data calculated for each dye in chloroform and benzene, respectively. It was also possible to calculate from these data the approximate amounts of each isomer present at equilibrium under each set of conditions of illumination (*cf.* Table IV).

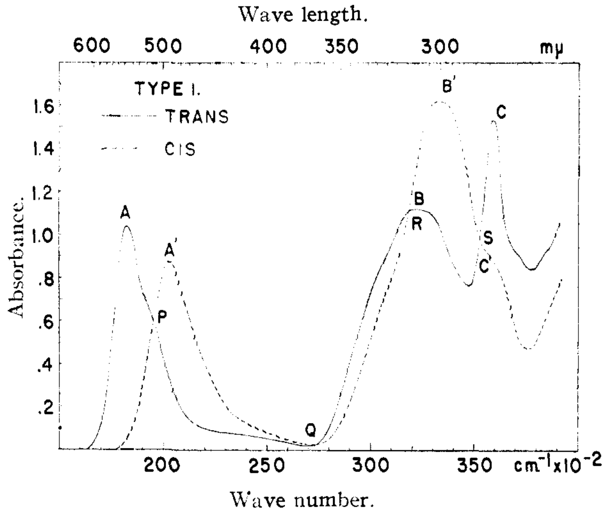

Fig. 6.—Calculated absorption spectra of the two isomers of thioindigo in chloroform (c = 0.0100 g./l.; d = 2.00 cm.).

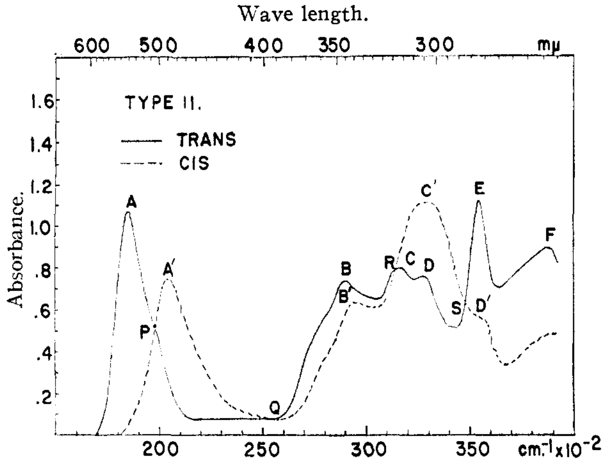

Fig. 7.—Calculated absorption spectra of the two isomers of 4,4'-dimethyl-6,6'-dichlorothioindigo in chloroform (c = 0.0100 g./l.; d = 2.00 cm.).

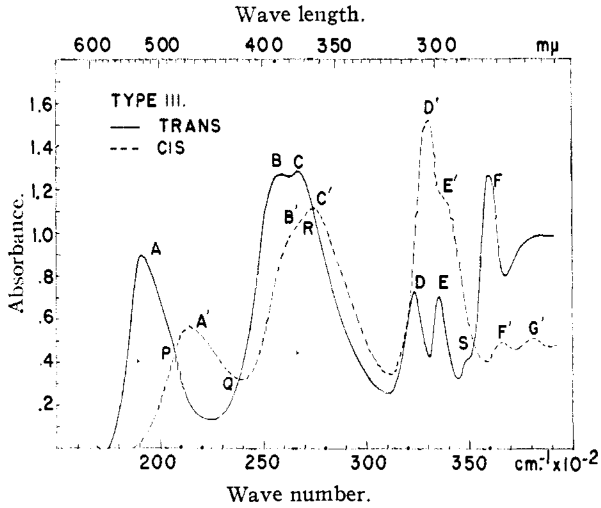

Fig. 8.—Calculated absorption spectra of the two isomers of 6,6'-diethoxythioindigo in chloroform (c = 0.0100 g./l.; d = 2.00 cm.).

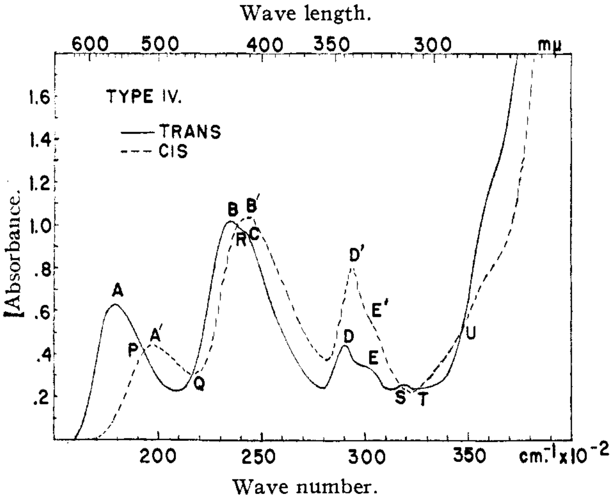

Fig. 9.—Calculated absorption spectra of the two isomers of bis-4,5-benzothioindigo in chloroform (c = 0.0100 g./l.; d = 2.00 cm.).

On the basis of this much information concerning the equilibrium between *cis* and *trans* isomers of these dyes it was possible to effect the chromatographic separation of the two isomers of thioindigo and 5,5'-dichloro-4,4',7,7'-tetramethylthioindigo. Since there was probably some rearrangement in the configuration during the working up of the solutions, the obtained curves (Figs. 10–11) are considered to represent the absorption curves for the almost pure *cis* and *trans* forms of the two

TABLE II

ABSORPTION SPECTRA DATA OF THIOINDIGO DYES

(Solvent: chloroform (U. S. P.)—solvent cut-off at 255 mμ (39200 cm.$^{-1}$)

Dye, thioindigo	Curve type	Calculated absorption maxima (in cm.$^{-1}$ × 10^{-2})[a] *trans* Form							*cis* Form							Isosbestic points (in cm.$^{-1}$ × 10^{-2})			
		A	B	C	D	E	F	G	A′	B′	C′	D′	E′	F′	G′	P	Q	R	S
Thioindigo	I	183	323	359					204	333	(353)					196	272	318	353
5,5′-Dichloro-7,7′-dimethyl-	I	176	305	342					197	319	(337)					189	264	305	337
5,5′-Dichloro-4,4′-7,7′-tetramethyl-	I	174	304	339	385				194	316	(335)					187	254	304	334
4,4′-Dimethyl-6,6′-dichloro-	II	185	290	317	327	354	387		204	295	328	(355)				198	256	314	347
6,6′-Diethoxy-	III	192	259	267	323	335	360	(385)	214	(266)	275	330	(338)	366	381	207	239	275	352
5,5′-Dibromo-6,6′-diethoxy-	III	190	260	268	314	325	348		210	(270)	275	321	351	368		203	239	273	341
Bis-4,5-benzo-	IV	179	235	(241)	290	(300)	318		197	243		294	(302)			193	217	238	317
																T = 326		U = 347	

[a] Major inflection points are listed in parentheses.

TABLE III

ABSORPTION SPECTRA DATA OF THIOINDIGO DYES

(Solvent: benzene (C. P. distilled)—solvent cut-off at 280 mμ (35700 cm.$^{-1}$)

Dye, thioindigo	Curve type	Calculated absorption maxima (in cm.$^{-1}$ × 10^{-2})[a] *trans* Form						*cis* Form					Isosbestic points (in cm.$^{-1}$ × 10^{-2})			
		A	B	C	D	E	F	A′	B′	C′	D′	E′	P	Q	R	S
Thioindigo	I	183	330					206	342				199	270	322	354
5,5′-Dichloro-7,7′-dimethyl-	I	177	310	342				200	323	(337)			192	251	307	338
5,5′-Dichloro-4,4′-7,7′-tetramethyl-	I	176	308	340				198	320	(335)			191	259	304	335
4,4′-Dimethyl-6,6′-dichloro-	II	186	290	327		354		207	(304)	337			201	263	309	349
6,6′-Diethoxy-	III	194	258	273	(332)	337		218	(274)	281	334	(343)	209	246	277	355
5,5′-Dibromo-6,6′-diethoxy-	III	190	257	272	(326)		348	214	(273)	280	324		205	241	277	341
Bis-4,4-benzo-	IV	178	234	245	291	303	318	200	247	(254)	295	(306)	193	221	242	315
													T = 331; U = 347			

[a] Major inflection points are listed in parentheses.

TABLE IV

APPROXIMATE AMOUNTS OF THE TWO ISOMERS OF EACH DYE

Dye,[a] thioindigo	Filter	Wave length, mμ	In benzene % *trans*	In benzene % *cis*	In chloroform % *trans*	In chloroform % *cis*
6,6′-Diethoxy- (520 mμ)	None	Daylight	38	62	35	65
	585	<495	61	39	50	50
	397	>350	32	68	30	70
	3230-5.0	>478	41	86	14	86
5,5′-Dibromo-6,6′-diethoxy- (530 mμ)	None	Daylight	57	43	55	45
	585	<495	72	28	65	35
	397	>350	47	53	45	55
	351	>520	15	85	18	82
4,4′-Dimethyl-6,6′-dichloro- (540 mμ)	None	Daylight	78	22	76	24
	585	<495	83	17	83	17
	397	>350	71	29	66	34
	351	>520	24	76	28	72
Thioindigo (545 mμ)	None	Daylight	90	10	86	14
	585	<495	93	7	96	4
	397	>350	74	26	80	20
	351	>520	31	69	43	57
Bis-4,5-benzo- (560 mμ)	None	Daylight	70	30	76	24
	585	<495	78	22	80	20
	397	>350	71	29	72	28
	338	>470	57	43	66	34
	2424	>575	30	70	33	67
5,5′-Dichloro-7,7′-dimethyl- (565 mμ)	None	Daylight	74	26	88	12
	585	<495	86	14	89	11
	397	>350	76	24	81	19
	351	>520	53	47	70	30
	2424	>575	29	71	42	58
5,5′-Dichloro-4,4′,7,7′-tetramethyl- (570 mμ)	None	Daylight	87	13	97	13
	585	<495	94	6	100	0
	397	>350	85	15	91	9
	351	>520	60	40	85	15
	2424	>575	30	70	63	37

[a] Approximate wave length of first (long-wave) absorption maximum is listed in parentheses.

dyes. In each case the less stable form was more strongly adsorbed and remained at the top of the column whereas the stable modification was eluted more readily. The difference in color between the two isomers of thioindigo in benzene solution is particularly striking: the unstable form appears an orange-yellow whereas the stable form is a red-purple.

It is apparent from these data that the main difference in the spectral absorption curves of the *cis* and *trans* forms of thioindigo dyes consists in the location and the intensity of the first (long-wave) absorption band. For the dyes studied this band is always at a considerably shorter wave length (by about 60 mμ) in the case of the unstable form than in that of the corresponding stable isomer, and has a lower intensity. It is because of this large difference in the wave lengths of the first absorption peaks that it is possible to irradiate the solutions with light of such a wave length range that it is only absorbed by the stable form, resulting in solutions greatly enriched in the unstable isomer.

The *trans* configuration was assigned to the more stable form of these thioindigos for the following reasons: (1) The shape of the absorption curve of the stable form of thioindigo is similar to that of the common form of indigo (*cf.* Fig 12) which is known to possess a *trans* configuration,[6] probably because hydrogen bonding tends to fix the molecule in a *trans* configuration.[7] (2) It has been shown for a number of compounds that the *trans* form is obtained in the dark whereas the *cis* form is favored by light.[8,9] (3) Olson and Hudson have claimed

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(6) T. Posner, *Ber.*, **59B**, 1799 (1926).

(7) N. Dokunikhin and E. Levin, *Compt. rend. Acad. Sci. U. S. S. R.*, **35**, 110 (1942).

(8) A. Smakula, *Z. physik. Chem.*, **B25**, 90 (1934).

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

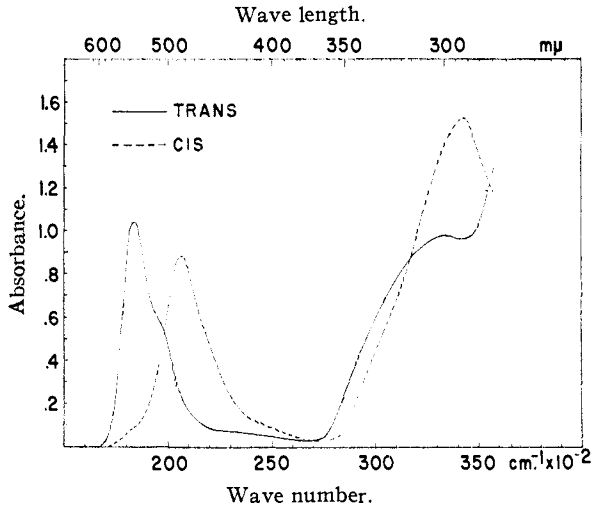


Fig. 10.—Absorption spectra of the two chromatographically separated isomers of thioindigo in benzene containing 2% ethanol (c = 0.0100 g./l.; d = 2.00 cm.).

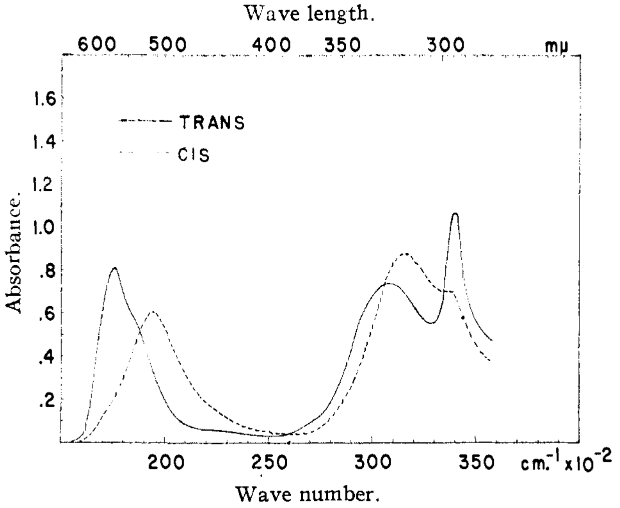
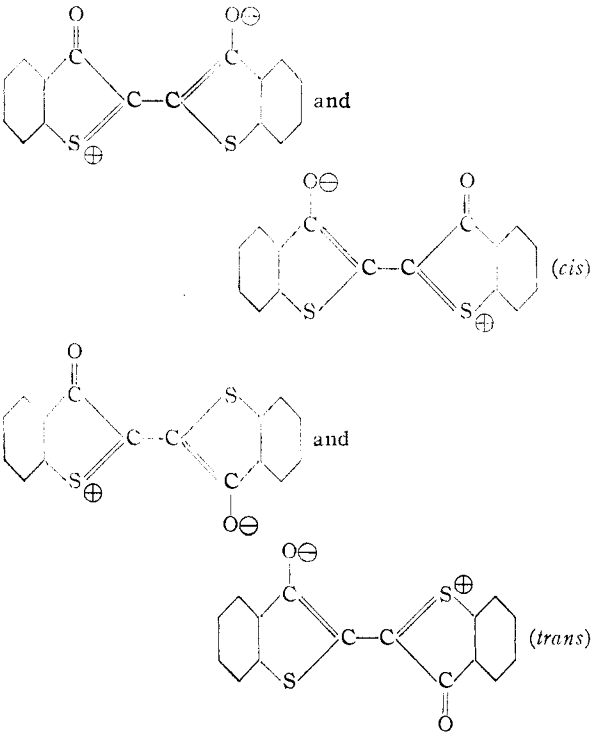


Fig. 11.—Absorption spectra of the two chromatographically separated isomers of 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo in chloroform (c = 0.0100 g./l.; d = 2.00 cm.).

on the basis of quantum-mechanical considerations that the absorption of light should favor the *cis* form in the case of some unsaturated acids.[10] This should be particularly true when the incident light is of such wave length as to be absorbed only by the *trans* isomer. (4) In the chromatographic separation of the two isomers of thioindigo and of 5,5′-dichloro-4,4′,7,7′-tetramethylthioindigo the one which is first eluted from the adsorbent would be expected to be the less polar *trans* form: conversely, the isomer with greater affinity toward the adsorbent would be expected to be the more polar *cis* form.

It can be concluded from these results that the first excited state of structures of the thioindigo type can best be represented by writing a single bond between the central carbon atoms as a consequence of resonance among the structures



(each of which can be written in four Kekule forms) with some rotation around the central bond.

In the ground state the *cis* isomer of each of these thioindigo dyes appears to have the slightly higher potential energy than the corresponding *trans* isomer, probably due to the electrostatic repulsion of the two carbonyl group dipoles when in *cis* position with respect to each other. This intramolecular repulsion would be expected to be further enhanced in the excited state because of the increased negative charges on the carbonyl oxygen atoms; additional electrostatic repulsion would also be developed due to the partial positive charge on each sulfur atom. Thus, it appears that the potential energy of the *cis* isomer in the excited state would be considerably higher than that of the corresponding, electrically more symmetrical, *trans*

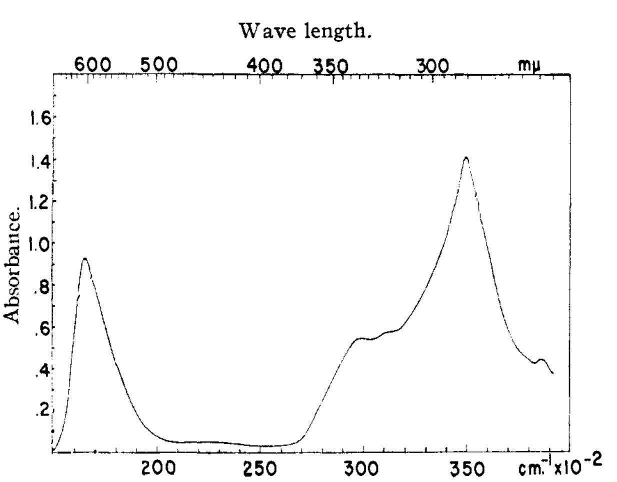


Fig. 12.—Absorption spectrum of indigo in chloroform (concentration unspecified).

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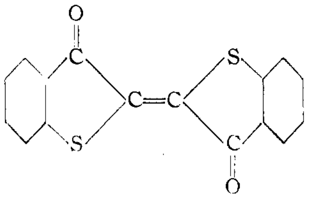
(10) A. R. Olson and F. L. Hudson, THIS JOURNAL, **55**, 1410 (1933).

isomer. This may explain why the first absorption band of the *cis* isomers of these dyes is always at a higher frequency than that of the corresponding *trans* forms.

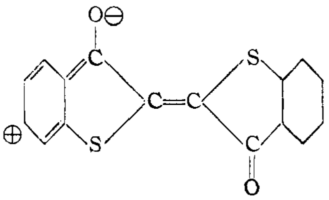
The potential energy difference between the *cis* and *trans* forms in the excited state is greater by $h\Delta\nu$ than this same difference in the ground state (where h is Planck's constant and $\Delta\nu$ is the difference in the frequencies of the absorption bands of the two isomers). Since $\Delta\nu$ is approximately 2000 cm.$^{-1}$ in the case of each of these dyes, $h\Delta\nu$ can be calculated to be about 6000 calories per mole.

It is then also possible to advance the following explanation for the apparently anomalous hypsochromic shift caused by the introduction of substituents in the 6-positions of thioindigo[11] (*cf.* Table II–IV). Thioindigo can best be represented as a resonance hybrid of the following structures in the ground state



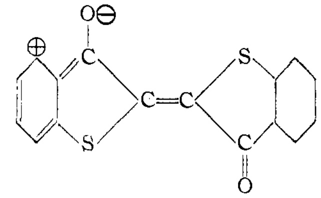
1

(4 Kekulé forms)



2

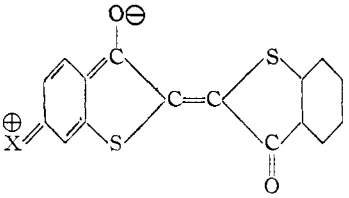
(2 equivalent structures, each of which can be written in 2 Kekulé forms)



3

(2 equivalent structures, each of which can be written in 2 Kekulé forms)

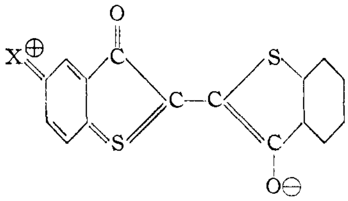
(Structures of types (2) and (3) would be expected to contribute but slightly because of their relatively high potential energies due to a separation of charges.) The introduction of an electron releasing substituent in the 6-position will lower the potential energy of the resonance hybrid by increasing the contribution from structures of type (2) above, *e.g.*



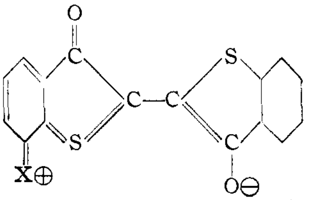
(2 Kekulé forms)

These same substituents would not be expected to affect the energy of the excited state (*v.i.*) because the 6-positions are not conjugated with the electron deficient sulfur atoms. Since the energy of the ground state is thus lowered and the energy of the excited state is left unaffected, the energy difference between the two states is increased and the first absorption band would be expected to shift to a shorter wave length.[12]

Conversely, substituents in the 5- and 7-positions would not be expected to affect the energy of the ground state because they are not conjugated with the carbonyl groups but would be expected to lower the energy of the excited state by some contribution from structures of the type



and



(2 Kekulé forms)

since sulfur is capable of expanding its valence shell to ten electrons and act as a transmitter of resonance, similar to a vinyl group. Since, in this instance, the energy of the excited state is lowered whereas the energy of the ground state remains unaffected, the difference in the two energy levels is decreased and the first absorption band would be expected to shift to a longer wave length.

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[11] J. Formanek, *Z. angew. Chem.*, **41**, 1137 (1928).

[12] A similar theoretical explanation has been advanced for the hypsochromic shifts observed in some biphenyl derivatives (G. F. Woods, A. L. Van Artsdale and F. T. Reed, THIS JOURNAL, **72**, 3221 (1950)).