combination ratios. It is apparent from comparison of the quantity of the combination product from reaction II of Table II to the sum of the chloropropene yields that combination dominates over disproportionation. The quite significant yield of 1,2-$C_3H_6Cl_2$ is also evidence that Cl atom transfer is important in these disproportionation reactions. Such results have been previously observed for chloroethyl radicals.[22] A novel feature is the 5:1 dominance of *cis*- over *trans*-1-chloropropene. This chloropropene isomer arises from the removal of a hydrogen from the chlorinated end of CH_3CHCH_2Cl during disproportionation. In view of the widely accepted loose nature of the activated complex for disproportionation reactions, it is surprising that small stereochemical effects are important. It should be noted that the *cis*-halopropenes are perhaps slightly more stable than the *trans* isomers.[31]

Acknowledgment. The author wishes to thank Mr. Norman Craig for preparing a sample of the 1,3-dichloro-2-methylpropane. This work was supported by the Research Grants Branch, National Center for Air Pollution Control, Bureau of Disease Prevention and Environmental Control under Contract AP-00391.

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cis–trans Isomerization and Pulsed Laser Studies of Substituted Indigo Dyes[1]

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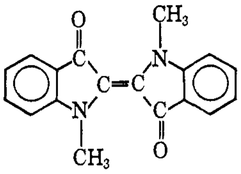
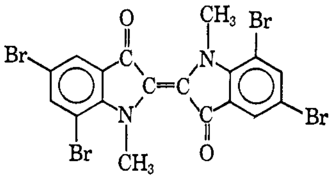
Abstract: The photochromic behavior of N,N′-dimethylindigo and N,N′-dimethyl-5,5′,7,7′-tetrabromoindigo was investigated in the visible region with photostationary and flash photolysis techniques and at 6328 and 6943 Å with laser systems. Calculated spectra of the *cis* isomers, quantum yields (~0.01 in benzene) for the *trans* → *cis* photoconversions, lifetime estimates of intermediates, and kinetic data for the *cis* → *trans* thermal isomerization are presented. The latter process was found to be acid catalyzed and was studied in detail for dimethylindigo in alcohol–water solutions. Laser experiments at high intensities (~10^{26} quanta/(sec cm^2)) give rise to the observation of a short-lived transient state believed to be the triplet intermediate in the photoisomerization process.

Geometrical isomerization of highly substituted ethylenic structures is a basic photochromic mechanism[2] and has been studied for several classes of compounds including polyenes and carotenoids,[3] stilbenes,[4,5] azo compounds,[6,7] conjugated anils[8] and nitriles,[9] and cyanine,[10] thioindigo, and indigo dyes.[11] Although *cis–trans* isomerization of indigo itself has not been observed,[11] alkyl substitution at the nitrogen atom allows photoconversion to occur between the *cis* and *trans* structural isomers.[12,13] We have obtained quantitative spectroscopic evidence for the photoisomerization of N,N′-dimethylindigo (I) and N,N′-dimethyl-5,5′,-7,7′-tetrabromoindigo (II) by conventional flash photolysis and photostationary methods and by unique measurements carried out with a pulsed ruby laser. Additionally, the thermal *cis* → *trans* conversion of I was found to be acid catalyzed, and rate constants for this process in a variety of solvents also are reported.



I



II

The previous qualitative observations on compound I by Weinstein and Wyman[12] differ significantly from the work reported by Pummerer and Marondel.[13] Both groups reported a decrease in optical absorption at 650 mμ when I was irradiated with yellow light (λ >520 mμ), but the former emphasizes that the thermal back reaction (*cis* → *trans*) proceeds rapidly (seconds) in benzene, whereas Pummerer and Marondel report a long-lived (18 hr) photoinduced absorption band at 410 mμ in carbon tetrachloride. Their assignment of this band to the *cis* isomer does not correspond with Weinstein and Wyman's data, nor does it follow the photoisomerization expected by comparison with analogous structures such as N,N′-diacetylindigo[11] and thioindigo.[14] Pummerer and Marondel also reported photo-

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(1) This work was supported in part by the Air Force Office of Scientific Research, Directorate of Chemical Sciences, Contract No. AF 49(638)-1264, and Directorate of Engineering Sciences, Contract No. AF 49(638)-1607.

(2) R. Dessauer and J. P. Paris, *Advan. Photochem.*, **1**, 275 (1963).

(3) L. Zechmeister, "*Cis-Trans* Isomeric Carotenoids, Vitamins A and Arylpolyenes," Academic Press Inc., New York, N. Y., 1962.

(4) See G. S. Hammond, J. Saltiel, A. A. Lamola, N. J. Turro, J. S. Bradshaw, D. O. Cowan, R. C. Counsell, V. Vogt, and C. Dalton, *J. Am. Chem. Soc.*, **86**, 3197 (1964), and references therein.

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(11) W. R. Brode, E. G. Pearson, and G. M. Wyman, *J. Am. Chem. Soc.*, **76**, 1034 (1954).

(12) J. Weinstein and G. M. Wyman, *ibid.*, **78**, 4007 (1956).

(13) R. Pummerer and G. Marondel, *Ann. Chem.*, **602**, 288 (1957).

(14) G. M. Wyman and W. R. Brode, *J. Am. Chem. Soc.*, 73, 1487 (1951).

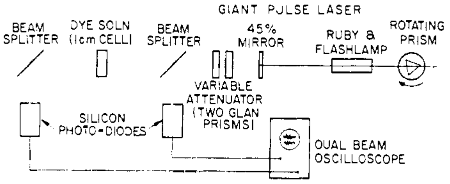

Figure 1. Schematic representation of ruby laser apparatus; giant pulse operation is indicated. Modification for quantum yield determination involves fixed optical alignment of the rotating prism and incorporation of a second dual-beam oscilloscope equipped with an operational amplifier.

induced absorption in the 430–440-mμ region for N,N′-diethylindigo in halogenated solvents and for compound II in both chloroform and benzene.[13] Our results are consistent with Weinstein and Wyman's work on compound I and Wyman and Zenhausern's recent work with II[15] but disagree in several respects with the studies on I and II reported by Pummerer and Marondel.

Experimental Section

A. **Materials.** N,N′-Dimethylindigo (I) was obtained in pure form (mp 195.5–196.5°) from D. Ross, RCA Laboratories, Princeton, N. J., and was used without further purification. N,N′-Dimethyltetrabromoindigo (II) was obtained from G. M. Wyman, Army Research Office, Durham, N. C. It was synthesized from Algosol Blue 04B by the method of Pummerer and Meininger.[16] The elemental analysis[15] of II for C, H, and N was in good agreement with the empirical formula, and the compound was used as received. All solvents were analytical reagent grade and were not subjected to further purification. Dye solutions were carefully filtered with the use of 0.2-μ Millipore filters.

B. **Photostationary and Normal Absorption Spectra.** Spectra of mixtures of the *cis* and *trans* isomers of I and II were recorded during irradiation of samples consisting initially of the pure *trans* compound. This is conveniently accomplished by using the near-ir light source (200-W tungsten filament lamp) and detector of a Cary 14 spectrophotometer while scanning in the visible region. In this mode of operation the light beam passes through the sample before entering the monochromator and is sufficiently intense for an appreciable amount of photoconversion to occur in a short time. Corning filters (CS 3-72) and 5-cm quartz cells containing benzene were placed between the light source and optical cells in both the sample and reference compartments in order to absorb infrared and ultraviolet radiation from the lamp. Photostationary state spectra were recorded with this system after about 25 min for I and 1 min for II; *i.e.*, repeated spectral scanning showed no further change. Subsequent scans were also made in the visible region with the system in normal operation to check for sample decomposition. All of the solutions were found to be stable in this regard; *i.e.*, they exhibited photochromic reversibility.

Visible and ultraviolet absorption spectra were obtained with the same instrument operated in the normal manner. No changes in the spectra were observed upon repeated scanning, as expected, since the light intensity incident upon the sample is too weak in this mode of operation for photoisomerization to compete with the thermal *cis* → *trans* relaxation process.

C. **Flash Photolysis Apparatus.** This system consists of a linear 3-in. xenon flashlamp (PEK XE1-3, using 360 joules discharged in 3 msec) and a 7-cm sample cell placed in a polished aluminum elliptical cavity. Corning glass filters (3 × 4.75 in.) were placed between the flashlamp and absorption cell to isolate specific spectral regions of the lamp output. A CS 3-69 filter was used to cut off light below 410 mμ, and an infrared absorbing filter (CS 1-69) was used to reduce thermal gradients in the sample cell, which otherwise can produce significant distortions of the analyzing beam.

Kinetic data on flashed samples were obtained at selected wavelengths with the use of an auxiliary beam (42-W tungsten–iodine–quartz Sylvania lamp, filtered and attenuated with CS 3-72 and ND 1.0 filters) monitored through a Bausch and Lomb grating monochromator with an RCA 7326 photomultiplier, and recorded with either a Tektronix 555 oscilloscope or a Sanborn 7701 recorder.

D. **Laser Experiments.** A Hughes Model 35 helium–neon gas laser equipped with a camera shutter was used for photobleaching studies with monochromatic light (6328 Å) of intermediate intensity (~10^{18} quanta/(sec cm^2)). The laser beam was filtered with both a CS 3-67 glass filter to remove the blue light from the excitation source, and a 5-cm path length silica cell filled with benzene to remove infrared radiation. The laser beam (1-mm diameter) passed through a 1-cm path length sample cell (22-mm diameter) and was attenuated with an ND 3.0 filter, diffused with a frosted glass plate, and recorded with the photomultiplier and recorder cited above. The beam intensity (1.7 mW) was measured at the sample position with a Spectra-Physics 401B power meter.

Two types of optical transmission measurements were carried out with a pulsed ruby laser (6943 Å). In the first type, a rotating prism Q-switched laser was used; the output in this case consists of a a single light pulse (giant pulse) of short duration (35 nsec) and high power density (~10^{26} quanta /(sec cm^2)).[17] A diagram of the apparatus is shown in Figure 1. The light intensity incident upon the dye solution is varied over five orders of magnitude by means of a pair of Glan prisms; the first prism is rotated to give the desired attenuation, while the second prism remains fixed so that the polarization incident upon the dye cell is always in the same plane (horizontal). The light is sampled with a pair of silicon photodiodes before entering and after leaving the dye cell. The resulting signals are integrated and displayed on a dual-beam oscilloscope giving a measure of the total integrated per cent transmission. Correction for reflection losses and losses due to scattering in the solvent is accomplished by using a pair of optically matched cells (one containing the solvent, the other containing the dye solution) and measuring the transmission of each one at every power level.

A modification of this procedure was used to measure quantum yields of photoisomerization. For this purpose the laser was operated in an alternate manner which produces a closely spaced series of pulses several orders of magnitude lower in power and lasting for approximately 250 μsec (see Figure 9a). The signal from each of the photodiodes was divided and connected to a Tektronix Type O operational amplifier and to a Type L preamplifier; this arrangement requires the use of two dual-beam oscilloscopes but allows simultaneous observations of the temporal and integrated response of both photodetectors. Hence, the per cent transmission can be measured at any time during the 250-μsec laser output by comparison of corresponding pulses on the time-resolved display from each detector. In addition, the integrated outputs can be used to determine the total number of quanta absorbed when appropriate calibrations have been carried out. Combination of the extinction coefficients of the isomers with these data then gives quantum yields for the photoconversions. The laser output power was determined with a calibrated Korad biplanar photodiode which intercepted a small portion of the light scattered from a magnesium oxide block; laser output energies were similar (~0.3 joule) in both modes of operation. In the above pulsed experiments, the beam diameter was limited by an aperture to 5-mm diameter.

E. **Emission and Excitation Spectra.** Total emission (fluorescence and phosphorescence) and emission excitation spectra from benzene solutions of I and II at 25° were investigated qualitatively with an Aminco-Keirs spectrofluorimeter. The instrument was used without modification except for incorporation of an RCA 7102 photomultiplier (S-1 surface) operated at −80° for detection of visible and near-infrared radiation. Excitation spectra were recorded in both the visible and ultraviolet regions; emission was monitored at the first maxima, 705 mμ for I and 723 mμ for II.

Results

Extinction coefficients at absorption maxima and wavelengths of maximum emission are summarized in Table I. Excitation spectra (not shown) closely resemble the absorption spectra of I and II. Photostationary-state spectra and their resolution into spectra of isomers of I and II are shown in Figures 2 and 3. The saturable absorption observed by irradiation of I with monochromatic light (6328 Å) is illustrated in Figure 4. Pertinent data for an estimation of the quantum yield

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[15] G. M. Wyman and A. F. Zenhausern, private communication.

[16] R. Pummerer and F. Meininger, *Ann. Chem.*, **590,** 173 (1954).

[17] C. R. Giuliano and L. D. Hess, *Appl. Phys. Letters*, **9,** 196 (1966).

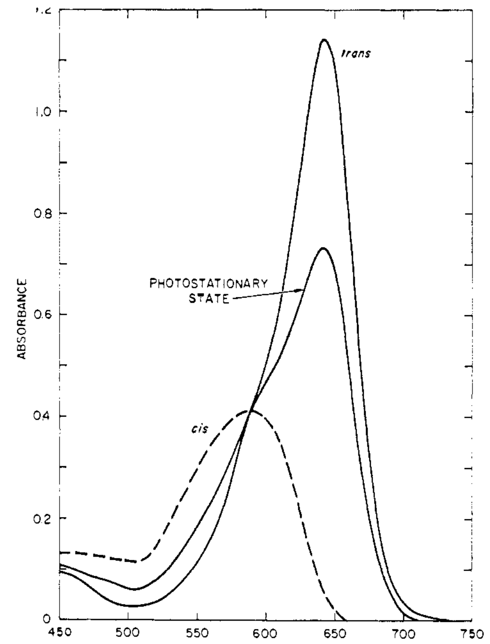

Figure 2. Spectra of N,N′-dimethylindigo (5.0 × 10^{-5} M, 1-cm cell) in benzene using a Cary 14 spectrophotometer; *trans*, normal scan; photostationary state, scan with near-ir source; *cis*, calculated for 100% conversion.

by this measurement are given in Table II which shows the values averaged over three runs. The isomerization yield estimation (0.08) assumes that the following factors can be ignored during the first 30–40 msec of exposure: diffusion of dye molecules in and out of the laser beam (1-mm diameter), absorption by the *cis* isomer, and thermal *cis* → *trans* conversion. If any of these processes is significant, the estimate would be too low.

Table I. Spectral Characteristics of N,N′-Dimethylindigo Dyes in Benzene[a]

Compound	*trans* Absorption λ_{max}	$\epsilon \times 10^{-4}$	*trans* Emission λ_{max}	*cis*[b] Absorption λ_{max}	$\epsilon \times 10^{-4}$
I	644	2.31	705	588	0.83
	430	0.23			
	350[c]	0.75			
	306	2.25			
II	663	2.30	723	590	0.92
	437	0.25			
	318	2.42			

[a] Measured with dilute solutions, 6 × 10^{-5} M or less; wavelengths given in mμ and ε in l./(mole cm). [b] Calculated from photostationary-state spectra. [c] Shoulder.

Table II. Quantum Yield of I in Benzene from Initial Photoisomerization Rates at 6328 Å

Incident photon flux	6.9 × 10^{17} photons/(cm^2 sec)
Initial fraction absorbed	0.82
Initial rate of photon absorption	5.7 × 10^{17} photons/(ml sec)
Initial *trans* concentration	3.6 × 10^{-5} M
Initial rate of isomerization	4.5 × 10^{16} molecules/(ml sec)
Approximate quantum yield	0.08

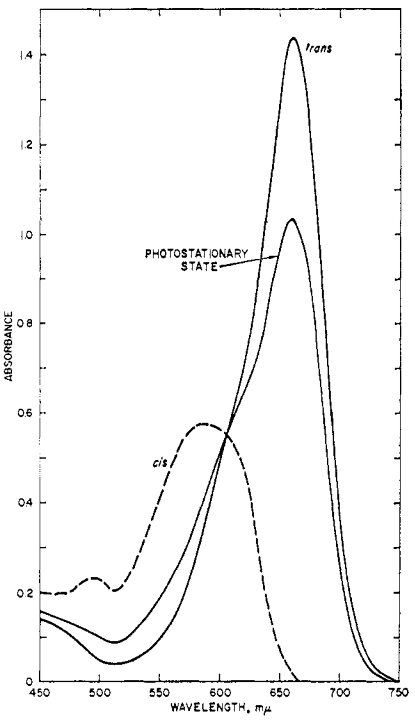

Figure 3. Spectra of N,N′-dimethyl-5,5′,7,7′-tetrabromoindigo (6.2 × 10^{-5} M, 1-cm cell) in benzene using a Cary 14 spectrophotometer: *trans*, normal scan; photostationary state, scan with ir source; *cis*, calculated for 100% conversion.

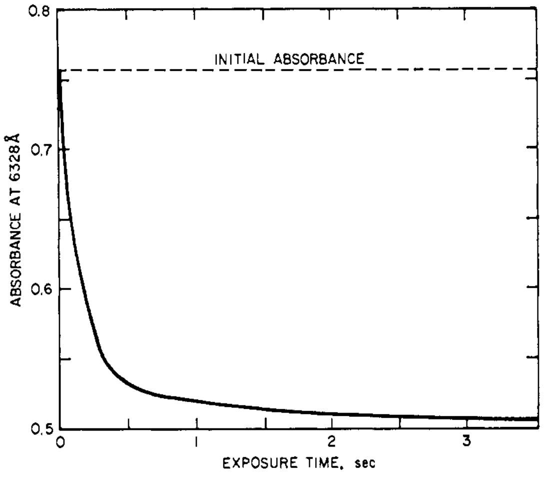

Figure 4. Absorbance of N,N′-dimethylindigo (3.6 × 10^{-5} M in benzene, 1-cm cell) as a function of time when exposed to a cw helium–neon laser with an output of 1.7 mW at 6328 Å.

Transmission of ruby laser giant pulses at a series of power levels by benzene solutions of I and II is shown in Figures 5 and 6. For comparison, Figure 7 illustrates the optical bleaching behavior frequently observed for dye solutions subjected to high light intensities.[18]

Examples of optical transmission data of low-power multiple pulses from the ruby laser apparatus are shown in Figure 8. Comparison of peak heights in Figure 8a between the upper and lower traces in conjunction with calibrated electrical and optical attenuators enables calculation of the optical density of the dye solution,

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(18) C. R. Giuliano and L. D. Hess, *IEEE J. Quantum Electron.*, 3, 358 (1967), and references therein.

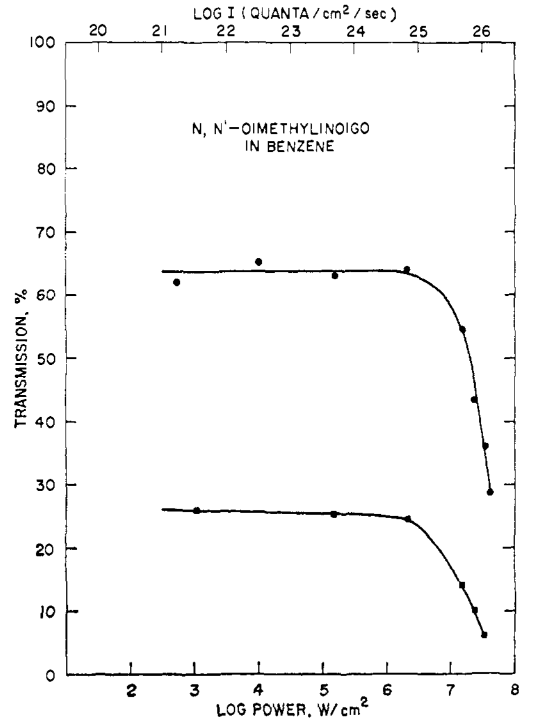

Figure 5. Per cent transmission at 6943 Å of I in benzene as a function of laser giant pulse peak intensity; concentrations, 1.6×10^{-4} and 4.8×10^{-4} *M*, 1-cm cell.

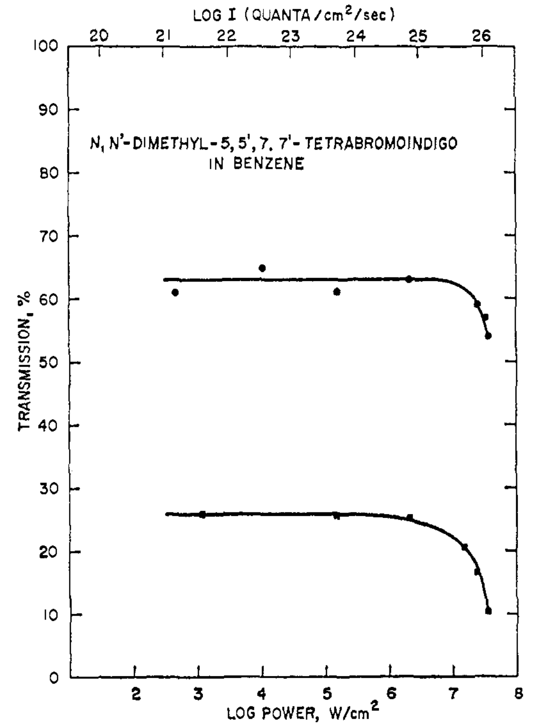

Figure 6. Per cent transmission at 6943 Å of II in benzene as a function of laser giant pulse peak intensity; concentrations, 2.5×10^{-5} and 7.0×10^{-5} *M*, 1-cm cell.

Optical densities computed in this way from the first few pulses agree with values measured with the spectrophotometer. At later times a decrease in optical density with respect to the initial value is observed. The optical density at the end of the train of pulses is proportional to the amount of *trans* isomer remaining, and

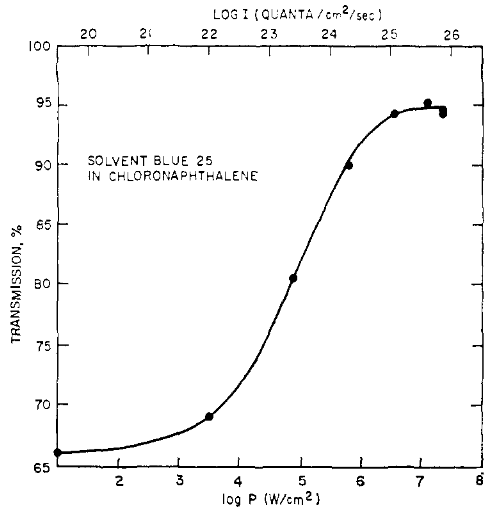

Figure 7. Per cent transmission at 6943 Å of a copper phthalocyanine derivative (Color Index No. 74350) in chloronaphthalene as a function of laser giant pulse peak intensity.

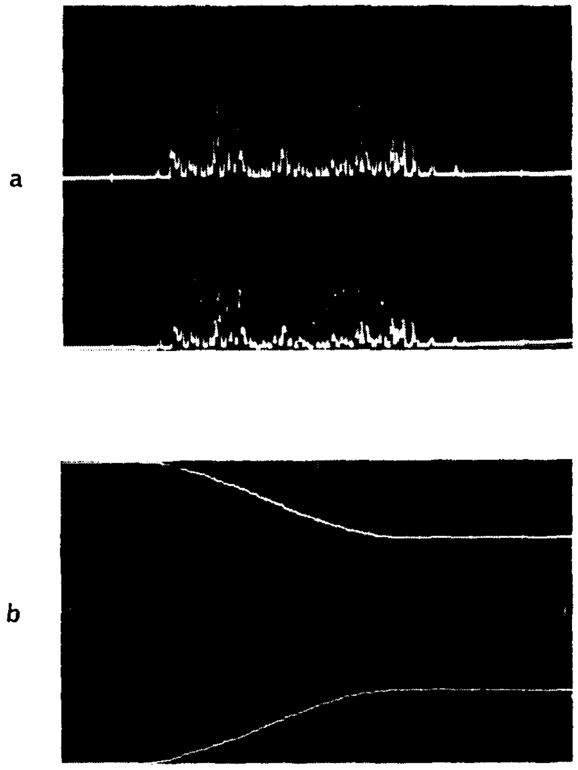

Figure 8. Ruby laser output monitored before and after passing through dye solutions; upper and lower traces in each photograph are proportional to the light incident on and transmitted by the sample; detector signals are time resolved in (a), and integrated in (b); traces in (b) have opposite polarity; time scale 50 μsec/division.

the integration traces (Figure 8b) give the total number of quanta absorbed by this isomer. Hence, the quantum yield for *trans* → *cis* photoisomerization is readily determined. Results for two concentrations of I and II in benzene are summarized in Table III.

Rate data corresponding to the thermal *cis* → *trans* reaction obtained from flash photolysis of II in benzene are plotted in Figure 9. Table IV gives a summary of similar data for I and II in several solvents. The *cis* → *trans* isomerization of both I and II was found to be

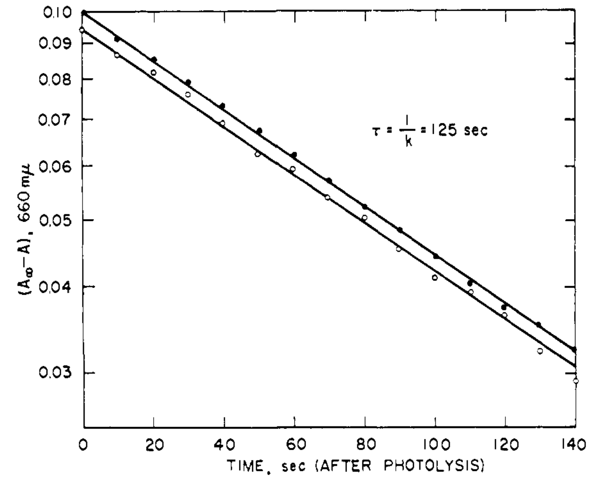

Figure 9. First-order plots of *cis–trans* isomerization of II in benzene (1.7×10^{-6} *M*, 7-cm cell). A_∞ is final absorbance and *A* is time-dependent absorbance. The two plots correspond to different degrees of *trans* → *cis* photoconversion.

acid catalyzed. Because of its low solubility in aqueous solvents where the pH can be accurately controlled, compound II was not investigated quantitatively in this regard. Kinetic data for the acid-catalyzed reaction of I at 25° are plotted in Figure 10 for ethanol–water solutions acidified with hydrochloric acid. The apparent first-order rate constant for this process with several acids is shown in Figure 11.

Table III. Quantum Yield of *trans* → *cis* Isomerization (6943 Å, ruby laser)

Dye	Concn, *M*	No. of quanta absorbed[a]	Absorbance change	Φ
I	4.5×10^{-4}	7.6×10^{17}	0.034	0.004
	1.5×10^{-4}	3.1×10^{17}	0.07	0.02
II	6.3×10^{-5}	5.4×10^{17}	0.35	0.009
	1.9×10^{-5}	1.8×10^{17}	0.12	0.009

[a] Beam cross section = 0.196 cm^2.

Table IV. First-Order Recovery Rate Constants after Flash Photolysis

Compound	Solvent	λ_{max}, mμ	*k*, sec^{-1}	τ, sec
N,N′-Dimethylindigo	Benzene	644	0.033	30
	$CHCl_3$	653	0.053	19
	CCl_4	640	0.32	3.1
	$EtOH–H_2O$ (1:2)	672	1.7	0.59
	$EtOH–H_2O$ (1:2, pH 3)	672	4.5	0.22
N,N′-Dimethyl-5,5′,-7,7′-tetrabromoindigo	Dimethylformamide	660	0.075	13.3
	Benzene	663	0.0080	125

Discussion

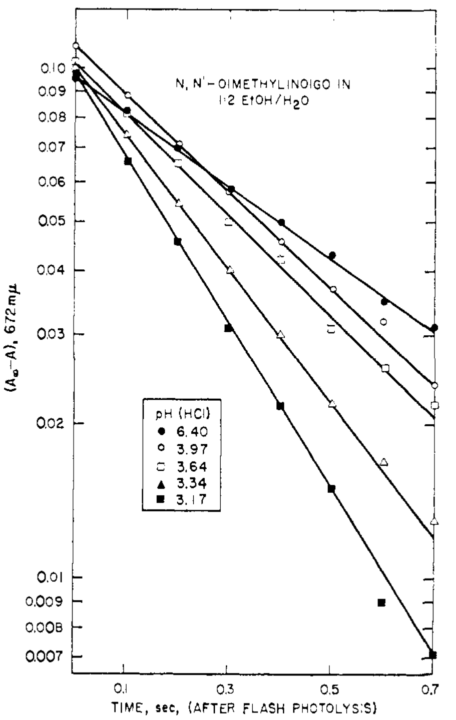

Figure 10. First-order plots of acid-catalyzed *cis–trans* isomerization of I in ethanol–water solutions (A_∞ = 0.642, 7-cm cell).

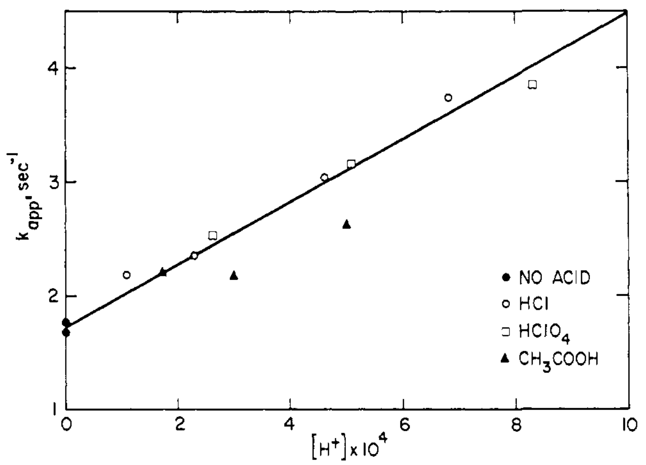

Figure 11. Specific acid catalysis of *cis–trans* isomerization of I in ethanol–water (1:2 by volume) solutions; k_{app} is the apparent first-order kinetic rate constant observed after flash photolysis.

A. Photoisomerization. The photostationary-state spectra (Figures 2 and 3) obtained upon irradiation of the *trans* isomers of I and II are in agreement with the spectral behavior expected from the established spectroscopic properties of *cis* and *trans* isomers of a variety of compounds.[2–14,19,20] Ratios of optical densities between the *trans* and photostationary spectra are approximately constant on the long-wavelength side (λ >665 mμ) of the absorption maxima, indicating little or no absorption by the *cis* isomer in this region. This experimental evidence coupled with theoretical considerations[20,21] provides a firm basis for determination of the *cis* spectra which are normalized in Figures 2 and 3 for 100% conversion of the *trans* forms of I and II. Similar spectra (not shown) of II in dimethylformamide were obtained from a series of flash photolysis exposures.

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(19) G. M. Wyman, *Chem. Rev.*, **55**, 625 (1955).

(20) H. H. Jaffé and M. Orchin, "Theory and Applications of Ultraviolet Spectroscopy," John Wiley and Sons, Inc., New York, N. Y., 1962.

(21) P. Borrell and H. H. Greenwood, *Proc. Roy. Soc.* (London), **A298**, 453 (1967).

In contrast to the results of Pummerer and Marondel,[13] we found that the maxima of the *cis* absorption spectra are in the 580- to 590-mμ range for both I and II in various solvents. Also, the *cis* decays quickly in the dark; the *cis* of I lasts only a few seconds in carbon tetrachloride. In addition we found larger extinction coefficients for the long wavelength *trans* absorption band than reported by these workers (*e.g.*, the ϵ of II is 40% higher than their value in benzene), and our spectra have a less pronounced shoulder at 590 mμ. Their *trans* spectra resemble our photostationary-state spectra in both respects.

Noting here that the *cis* → *trans* thermal relaxation (isomerization) of I and II in benzene proceeds with a characteristic lifetime of 30 and 125 sec, respectively, we defer further discussion of the kinetic data for this reaction until a later section. The extent of saturable absorption shown in Figure 4 is, of course, dependent on this relaxation time and on the relative extinction coefficients and quantum yields for photoisomerization of the *cis* and *trans* forms of compound I. In addition to demonstrating the extent of bleaching attainable under specific experimental conditions, this experiment provides an estimate of the quantum yield for the *trans* → *cis* photoconversion (Table II). The experiments conducted with the pulsed ruby laser yielded more accurate results (Table III) which establish the inefficiency of this process for both I and II. The variation of $\Phi_{t \rightarrow c}$ with concentration is not understood at present and requires further investigation, as does the discrepancy between the quantum yields obtained from the two types of experiments. The latter may be due to a wavelength effect as well as the qualitative nature of the experiments at 6328 Å. However, we place major emphasis on the fact that the quantum efficiencies are quite low.

The positions of the emission maxima observed with I and II indicate that these arise from fluorescence of the *trans* isomers; frequency differences between absorption and emission maxima for I and II ($\sim$1300 cm^{-1}) are similar to those observed for a series of thioindigos which were found to fluoresce only from the *trans* forms.[22] A qualitative comparison of the emission intensities observed from I and II with compounds having similar absorption characteristics and known emission yields places the fluorescence efficiency at about 0.01. This value and the natural radiative lifetimes (36 nsec for I and II) computed from the absorption spectra indicate that the actual lifetime of the first excited singlet state is $\sim$0.4 nsec under our experimental conditions (dilute solutions at 25°). Consideration of the low quantum efficiencies of isomerization and emission and stability toward photodecomposition points to very rapid relaxation of excited electronic levels to the ground state. This is borne out further by the results presented in Figures 5 and 6. That is, the ground-state recovery rate apparently competes effectively with the rate of excitation until the incident intensity exceeds $\sim 10^{25}$ quanta/(sec cm^2).[23]

The simplest and most obvious interpretation of these curves is that in the linear (flat) portion the rate of excitation to the first excited singlet state is not sufficiently large to overcome the rate of relaxation back to the ground state. That is, the absorbance does not change over the flat portion because essentially all the molecules are in the ground state. As the rate of excitation increases further (at higher intensities), we are able to sufficiently populate an excited state to effect a change in the per cent transmission. For molecules I and II the extinction coefficient at 6943 Å for the excited state is greater than that for the ground state, and thus the per cent transmission decreases.

If, as suggested above, constant absorbance is maintained over the linear portion of the curves in Figures 5 and 6 by rapid relaxation back to the ground state, a limiting value for this relaxation time can be estimated from a knowledge of the intensity at which the absorbance begins to increase and from the molecular absorption cross section, σ, at the excitation wavelength. The absorption cross section is defined by the expression $I/I_0 = e^{-\sigma N l}$, where N is the number density (molecules/cm^3). Thus σ (cm^2) = $3.8 \times 10^{-21}\epsilon$ (l./(mole cm)). At a critical light intensity I_c, the excitation rate coefficient σI_c, is comparable with the over-all relaxation rate, $1/\tau$. Choosing values for I_c from Figures 5 and 6 of 1×10^{25} and 2×10^{25} quanta /(sec cm^2) and using absorption cross sections of 5×10^{-18} and 3×10^{-17} cm^2, the corresponding maximum recovery times are 2×10^{-8} and 2×10^{-9} sec for I and II, respectively.

The increase in absorption at very high intensities ($\sim 10^{25}$ quanta/(sec cm^2)) indicates an appreciable population of an excited state which is more highly absorbing at 6943 Å than the ground state. Assuming that the intense visible ($S_0 \rightarrow S_1$) and ultraviolet ($S_0 \rightarrow S_2$) bands belong to the same electronic manifold,[24] an even–odd–odd parity sequence is suggested for the first three singlet states which give rise to absorption maxima at λ and $\sim\lambda/2$ (see Table I). This would cause transitions between S_1 and S_2 to be symmetry forbidden and significantly lower in strength than the $S_0 \rightarrow S_1$ transition. However, $T_1 \rightarrow T_2$ transitions could be intense in accordance with the observed behavior. In addition, because of a relatively longer lifetime, the triplet state (T_1) would be expected to reach a higher population than the first excited singlet state (S_1).

Detailed calculations[18] have shown that in spite of an inefficient intersystem crossing process an appreciable fraction of molecules can be converted to the triplet state by an intense light pulse of $\sim$50-nsec duration. More specifically for compound I, taking $(k_{S_1 \rightarrow T_1}/k_{S_1 \rightarrow S_0}) \sim 0.1$ and $(k_{S_1 \rightarrow T_1}/k_{T_1 \rightarrow S_0}) \sim 10$, we find that 62% of the molecules occupy the triplet state at the peak of a pulse whose intensity is 10^{26} quanta/(sec cm^2) (for comparison only 6% of the molecules would occupy the excited singlet state); $k_{S_1 \rightarrow T_1}$, $k_{S_1 \rightarrow S_0}$, and $k_{T_1 \rightarrow S_0}$ refer to intersystem crossing, singlet–singlet, and triplet–singlet decay processes and for this example were given the values 2×10^8, 2.5×10^9, and 2×10^7 sec^{-1}, respectively. In this example, the triplet-state yield is only moderately low, but the analysis shows that, even though the intersystem crossing rate is generally quite small compared to the excited singlet-to-ground

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[22] D. A. Rogers, J. D. Margerum, and G. M. Wyman, *J. Am. Chem. Soc.*, **79**, 2464 (1957).

[23] It should be noted that although the light intensities used in these experiments are extremely high, the incident energies are not particularly large. However, the number of quanta and molecules in the beam is comparable at $P \sim 10^6$ W/cm^2.

[24] Solvent-induced spectral shifts[12] and bromine substitution indicate that these two bands are correlated and are π,π^* in character; the weak bands at 440 and 350 mμ have not been studied in detail but are thought to arise from n,π^* transitions.

state relaxation rate, the triplet state can become significantly populated during the time of a ruby laser giant pulse because of the many singlet–singlet excitation–relaxation cycles which can take place before triplet–singlet relaxation occurs. The limits which can be placed on the lifetime, τ_T, of the isomerization intermediate (triplet state) from the results of the ruby laser experiments are $\Delta t > \tau_T > (1/\sigma I_c)$, where Δt is the half-width of the pulses shown in Figure 8a, and the other quantities are as defined previously. Hence, the limits of τ_T are $5 \times 10^{-7} > \tau_T > 2 \times 10^{-8}$ for compound I and $5 \times 10^{-7} > \tau_T > 2 \times 10^{-9}$ for compound II.

Thus we favor the mechanism in which, at intensities lower than a critical intensity ($\sim 10^{25}$ quanta/(sec cm^2)), the ground state is essentially completely populated; at intensities higher than this critical value, a significant fraction of the ground-state population is converted to the triplet state which has a larger absorption cross section than the ground state.[25] If we assume that all the molecules are converted to the triplet state at the maximum intensity, absorption coefficients for this state would be approximately twice that of the ground state, $\epsilon_{T_1 \rightarrow T_2}(6943\ \text{Å}) \sim 3 \times 10^3$ and 1.7×10^4 l./(mole cm) for I and II, respectively. If one assumes, by analogy with other systems, that the triplet state is the isomerization intermediate, then this is the first direct observation of the intermediate involved in *trans* → *cis* photoisomerization of olefinic compounds. The techniques of electron spin resonance, triplet–triplet absorption following flash photolysis, and emission spectroscopy have been attempted unsuccessfully by Hammond, *et al.*, for direct observation of the triplet states involved in the isomerization of stilbene and its derivatives.[26] The intensities available from laser systems are significantly greater than from other light sources and when incorporated with conventional methods may make detailed spectroscopic information on these short-lived intermediates[27] accessible. The present high intensity laser experiments serve to demonstrate this particular possibility and along with previous work[18] point out the special type of information which may be obtained from intense pulses of visible radiation.

B. Thermal Isomerization. The rate of spontaneous *cis* → *trans* reaction of I and II follows first-order kinetics as summarized in Table IV and shown in Figure 9 for II subjected to different extents of photoisomerization. Both compounds exhibit a pronounced increase in rate with the addition of acid. Similar observations have been reported for azobenzene derivatives,[28,29] stilbene,[30] and cinnamic acids.[31,32] Quantitative studies of the acid catalysis of II were not carried out because of its low solubility in aqueous systems. However, a trace amount of hydrochloric acid in benzene was sufficient to suppress an appreciable photoconversion of the *trans* form of either I or II with the apparatus employed to obtain the photostationary-state spectra (Figures 2 and 3). A quantitative study of the acid-catalyzed *cis* → *trans* reaction of I was carried out with ethanol–water solutions at controlled pH levels. The evidence for acid catalysis shown in Figures 10 and 11 forms the basis for the following mechanism in which it is assumed that equilibrium always exists between protonated and unprotonated forms. After formation of the *cis* form by photolysis, $I_t + h\nu \rightarrow I_c$, it isomerizes in the following manner.

$$\begin{tikzcd}
I_c + H^+ \arrow[r, shift left] \arrow[d, "k"] & I_cH^+ \arrow[l, shift left] \arrow[d, "k'"] \\
I_t + H^+ \arrow[r, shift left] & I_tH^+ \arrow[l, shift left]
\end{tikzcd}$$

The uncatalyzed reaction is characterized by the rate constant, k, and the acid-catalyzed process by k'. The over-all rate of *cis* → *trans* isomerization is then

$$-d(I_c)/dt = k(I_c) + k'(I_cH^+)$$

Using

$$K = (I_cH^+)/(I_c)(H^+)$$

and

$$(I_c) = (I_t)_\infty - (I_t)$$

we have

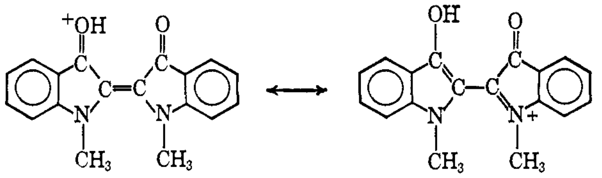
$$d(I_t)/[(I_t)_\infty - (I_t)] = [k + k'K(H^+)]\,dt$$

which, when integrated, yields

$$\ln\,[(I_t)_\infty - (I_t)] = -(k_{\text{app}})t + \text{constant}$$

in accordance with the observed kinetic behavior (Figure 10). Thus, the apparent rate constant, $k_{\text{app}} = k + k'K(H^+)$, varies linearly with hydrogen ion concentration. From the slope and intercept of the plot in Figure 11, $k'K = 2.8 \times 10^3$ l./(mole sec), and $k = 1.7$ sec^{-1}, respectively; hence $k_{\text{app}} = 1.7 + 2.8 \times 10^3(H^+)$.

Since addition of acid to solutions of I_t does not alter its absorption spectrum appreciably, a small value for the ratio, $(I_cH^+)/(I_c)$, is indicated. For example, if there is 1% protonation of I_c at a pH of 3, then $K = 10$ and $k' = 280$ sec^{-1} as compared to $k = 1.7$ sec^{-1}. Although we do not have a completely independent evaluation of k' or K, the protonated form of I_c apparently undergoes isomerization much more rapidly than the unprotonated form. Protonation at the carbonyl oxygen atom is supported by the spectroscopic studies of Weinstein and Wyman.[12] Thus the resonance hybrids, I_cH^+



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[25] Optical absorption by normally transparent liquids subjected to ruby laser giant pulses was reported recently by M. W. Dowley, K. B. Eisenthal, and W. L. Peticolas, *Phys. Rev. Letters*, 18, 531 (1967), and is thought to be a consequence of dielectric breakdown of adventitious macroparticles. The effect could be eliminated by filtration, however. Since all of our solutions were carefully filtered and since the solvents exhibited normal transmission, this effect is not expected to be operative in our experiments.

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would be expected to contribute to the electronic structure of the protonated *cis* isomer, giving the ground state a reduction in bond order at the central double bond compared to the neutral species.

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Far-Infrared Intensity Studies of Iodine Complexes

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Abstract: Measurements have been made of the frequencies and intensities of the "I–I stretching" vibrations for I_2 complexes with pyridine, 3-picoline, 2,6-lutidine, benzene, *p*-dioxane, and diethyl sulfide, and more qualitative measurements on the I_2 complexes with acetonitrile and diethylamine. The measurements were made using polyethylene cells, with a Beckman IR-11 far-infrared spectrometer. For the first three complexes, comparison can be made to the results obtained by Lake and Thompson, using an interferometer. The agreement is good enough to verify the general reliability of these techniques. The results are interpreted in terms of the theory given by Friedrich and Person. For the amine·I_2 complexes, the results are quite reasonable. The results for dioxane·I_2 and for diethyl sulfide·I_2 appear to be anomalous.

A number of spectroscopic studies have been made of charge-transfer complexes with iodine as the acceptor. These studies have been extensively reviewed by Briegleb,[3a] by Andrews and Keefer,[3b] and by Mulliken and Person.[4] Because of instrumental problems, relatively few studies have been made before this year in the far-infrared region where the ν(I–I) vibrational band would be expected.[5] Studies in the far-infrared region have been made for other halogen molecules acting as acceptors, and some ν(X–X) or ν(X–Y) band intensity estimates have been obtained.[6–8] Qualitative studies of the low-frequency infrared spectra of the pyridine·I_2[9–11] and benzene·I_2[9] complexes have been reported and recently, while our manuscript was being prepared, absolute intensity measurements of the I–I and of the N–I stretching vibrations have been presented for iodine complexes with pyridines.[12]

Intensity values for the I–I stretch in I_2 complexes provide a test of the recent theoretical expression[13] for the transition moment and relative change in force constant, $\Delta k/k$. Furthermore, there has been some question about the accuracy of far-infrared intensity work, so that it seems worthwhile to report our results for comparison with those already published.[12]

We have therefore attempted to measure the frequency and intensity of ν(I–I) for D–I_2 complexes with as many different donor molecules as possible. For the most part we have been able to study only *n* donors,[14] and chemical problems (with further reactions) or spectral problems (with interference) have limited even those. However, we have managed to extend our studies to a few systems not included by Lake and Thompson,[12] with some rather puzzling results.

Experimental Section

(a) **Chemicals.** Mallinckrodt analytical reagent grade iodine (resublimed) was used without further purification.

Phillips Petroleum Co. commercial grade *n*-heptane was shaken for 12-hr periods with concentrated sulfuric acid until the acid ceased to turn yellow. It was then washed thoroughly with sodium carbonate solution and water and dried by passing through a 10-ft column packed with silica gel. Final drying was achieved by standing for several days over (Linde) molecular sieves. Purity checks were made by comparison with the known absorption[15] in the 200–250-mμ region.

Dioxane (from Matheson Coleman and Bell) was refluxed with hydrochloric acid for about 8 hr, cooled, and treated with potassium hydroxide (solid) until all the water had been removed.[16] The dioxane was allowed to stand over molecular sieves for a day, and it was then refluxed over sodium in a nitrogen atmosphere for 6 hr and fractionated from sodium, bp 100° (lit.[16] 101°). The ultraviolet absorption spectrum showed only very weak impurity bands. The dioxane was stored in a dark bottle but was used as soon after purification as possible.

The benzene, pyridine, and acetonitrile were Eastman Spectrograde solvents. They were used without further purification as were the 2,6-lutidine and diethylamine (Eastman), and the 3-picoline (Matheson). All the materials were, however, thoroughly dried over molecular sieves immediately prior to use.

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(1) Department of Chemistry, University of Durham, Durham, England.

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