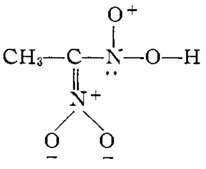
are not appreciably stronger acids than the acid



forms of the mononitroparaffins because one of the dinitroparaffin resonance forms shows an increased electron density on nitrogen. This would tend to counterbalance the electronegative effect of the second nitro group. At any rate the considerable variation in K_{app} values for nitroparaffins is almost entirely due to differences in the acid strengths of the nitro forms.

CHARLOTTESVILLE, VIRGINIA

[CONTRIBUTION FROM THE QUARTERMASTER RESEARCH & DEVELOPMENT CENTER]

Spectroscopic Studies on Dyes. II. The Structure of N,N'-Dimethylindigo[1]

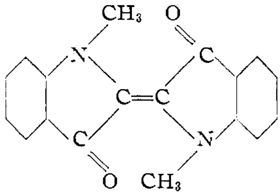
BY JULIUS WEINSTEIN AND GEORGE M. WYMAN

RECEIVED FEBRUARY 8, 1956

In contrast with other indigo dyes, N,N'-dimethylindigo is a low-melting green compound which is very soluble in organic solvents and has little affinity for cellulosic fibers. The wave length of the visible absorption band of this dye is strongly dependent on the nature of the solvent; hydroxylic solvents, in particular, cause a strong bathochromic shift. The absorption band shifts to still longer wave lengths in the solid phase. Rapid *trans* to *cis* isomerization occurs when a solution of this dye is irradiated with yellow or red light; reversal of the reaction in the dark is almost instantaneous. The compound also forms hydrogen-bonded complexes with phenol and ethanol. These observations suggest that, probably due to the steric effect of the methyl groups, the central double bond of this compound has considerably more single-bond character than in other indigo or thioindigo dyes.

Introduction

When in 1912 Ettinger and Friedlaender first described N,N'-dimethylindigo (I),[2] they observed that this dye possessed some rather unexpected properties. They found the contrast between N,N'-dimethylindigo and indigo to be particularly striking; the principal differences noted by these investigators are tabulated in Table I. It is clear from this tabulation that the extent of these differences far exceeds that which might normally be expected to result from the replacement of two hydrogen atoms by methyl groups.



I

TABLE I

PHYSICAL PROPERTIES OF N,N'-DIMETHYLINDIGO

	N, N'-Dimethylindigo	Indigo
M.p., °C.	182°	>300°
Solubility in common organic solvents	Very soluble	Almost completely insoluble
λ_{max} (in xylene), mμ	644.5	591
Color	Green	Blue
Behavior toward hot aq. bases	Rapid dec.	No reaction
Behavior toward aq. mineral acids	Forms soluble salts	No reaction
Affinity of leuco-form for cotton	Almost none	Good

Since recent investigations, using modern physical techniques, have shed much light on the structure of other indigo dyes,[3] a spectroscopic study of this dye was undertaken in the hope of arriving at a better understanding of its unusual properties. Moreover, it was believed that the results of such a study would constitute an important addition to the over-all picture of the structure, configuration and behavior of dyes containing a central double bond (*e.g.*, indigo,[3] thioindigo[4] and azo dyes).[5]

Experimental

(A) Preparation of N,N'-Dimethylindigo.—The dye was prepared from N-methylanthranilic acid (Eastman Kodak Co.; reagent grade) by the procedure (1) of Ettinger and Friedlaender.[2] The dye was obtained in essentially pure form, m.p. 181–182° (reported[2] 182°).

(B) Measurement of the Spectra.—Spectra in the visible and ultraviolet regions were determined by means of a Cary Model 11 Spectrophotometer. For measurements on solutions the solvent was used as the reference, utilizing matched fused quartz absorption cells. The spectra were also determined in the solid phase by the KBr-pellet technique.[6] In addition, measurements were made in the visible region on a solution of this dye in benzene, using an American Optical Co. (AO) Rapid-Scanning Spectrophotometer. A Beckman IR-3 Spectrophotometer equipped with NaCl or LiF optics, as appropriate, was used for measurements in the infrared region. Infrared spectra were determined in solutions in CCl_4 (against the solvent as reference), on a mull in Nujol (against Nujol), and on a pellet mixed with KBr (against KBr).

(C) Photochemical ***trans→cis*** **Isomerization.**—The photochemical isomerization of this dye was studied using both the Cary and AO instruments. Exploratory experi-

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[1] Presented before the Pittsburgh Conference of Analytical Chemistry and Applied Spectroscopy, March, 1956, Pittsburgh, Pennsylvania.

[2] L. Ettinger and P. Friedlaender, *Ber.*, **45**, 2074 (1912).

(3) (a) W. R. Brode, E. G. Pearson and G. M. Wyman, THIS JOURNAL, **76**, 1034 (1954); (b) J. Weinstein and G. M. Wyman, *ibid.*, **78**, 2387 (1956); (c) H. v. Eller, *Compt. rend.*, **239**, 975 (1954); (d) E. A. Gribova, *Compt. rend. Acad. Sci. USSR*, **102**, 279 (1955).

(4) (a) G. M. Wyman and W. R. Brode, THIS JOURNAL, **73**, 1487 (1951); (b) W. R. Brode and G. M. Wyman, *J. Research Natl. Bur. Standards*, **47**, 170 (1951); (c) W. R. Brode and G. M. Wyman, THIS JOURNAL, **73**, 4267 (1951).

(5) (a) W. R. Brode, J. H. Gould and G. M. Wyman, *ibid.*, **74**, 4641 (1952); (b) **75**, 1856 (1953); (c) W. R. Brode, I. L. Seldin, P. E. Sporri and G. M. Wyman, *ibid.*, **77**, 2762 (1955).

(6) G. M. Wyman, *J. Opt. Soc. Amer.*, **45**, 965 (1955).

TABLE II

ABSORPTION BANDS OF N,N'-DIMETHYLINDIGO

Wave length mμ

Medium	N,N'-Dimethylindigo						Indigo	N,N'-Diacetylindigo
Isoöctane	(242)[b]	246	251	282	307	625	Insol.	560
Carbon tetrachloride			[c]	284	307	638	600[a]	560
Chloroform		[c]	254	(290)	304	653	604	559
Acetone					[c]	640	596[a]	552
Benzene				[c]	306	643	595[a]	559
Abs. ethanol		250		293	342	648	607	563
95% ethanol		250		293	346	655	611	562
30% ethanol		248		294	358	676	Insol.	551
Concd. HCl	(228)	(239)			362[d]	695	Insol.	Insol.
KBr			[c]	297		680	662	558

[a] From reference 9. [b] Inflection points are indicated in parentheses. [c] Medium too opaque to permit measurement. [d] Inflection point at 587.

ments showed that with this compound the reverse reaction occurs rapidly in the dark even at room temperature. Therefore, for measurements with the Cary Spectrophotometer, it was necessary to make use of the shutter-illumination device described by Gould and Brode.[7] In these measurements the solution was first exposed to uninterrupted filtered irradiation for several minutes, after which its spectrum was measured while the sample was exposed to intermittent radiation, as described in reference 7.[8] It was noted that even by this technique considerable reversal occurred during the measurement.

In the AO instrument the sample is irradiated by the full intensity of the light beam emitted by the source, and thus the absorption curve obtained is characteristic of the photostationary state that exists with respect to the light impinging on the sample. Irradiation of the solution with filtered light was effected by inserting a suitable filter between the light source and the sample. Since this instrument scans the visible spectrum 60 times per second, the absorption curve that was obtained immediately upon removal of the filter is believed to be characteristic of the solution exposed to such filtered radiation.

Results

(A) Visible and Ultraviolet Spectra.—The absorption bands observed for N,N'-dimethylindigo in a variety of solvents and in the solid phase are listed in Table II. The visible absorption bands of indigo and of N,N'-diacetylindigo are also included for comparison purposes. These data confirm the unexpected strong bathochromic shift which has been reported to occur upon the introduction of the two N-methyl groups in the indigo molecule. It is also apparent from these data that the wave length of the first absorption band of N,N'-dimethylindigo is even more dependent on the nature of the solvent than is that of indigo, even though the latter has long been known to be very susceptible in this respect and has, for this reason, been studied extensively.[9] In addition, the dimethyl derivative also exhibits a bathochromic shift when the spectrum obtained in the solid phase is compared with that in a non-polar solvent. A similar shift also occurs with indigo, and has been attributed to the formation of molecular aggregates by means of intermolecular hydrogen-bonding[3b], an explanation that would be clearly inapplicable to N,N'-dimethylindigo.

(B) *cis–trans* Isomerization.—Irradiation of a benzene solution of N,N'-dimethylindigo with yellow light (*i.e.*, of a wave length range corresponding to its absorption band in the visible region) brings about a decrease in the intensity of the absorption maximum accompanied by an increase in the absorption intensity at somewhat shorter wave lengths (*cf.* Fig. 1 and 2). By analogy with the known behavior of other conjugated compounds possessing a central double bond,[10] this was attributed to *trans*→*cis* isomerization. However, in sharp contrast with the relatively slow rates observed for the thermal isomerization reactions of N,N'-diacetylindigo and of the related thioindigo dyes, the spectrum of an irradiated solution of N,N'-dimethylindigo reverts to the original spectrum upon standing in darkness at room temperature for about 30 seconds, this is shown in Fig. 1. Thus, even by utilizing the rotating shutter, with the Cary instrument it is impossible to obtain the spectrum of a solution that is appreciably enriched with respect to the unstable *cis* isomer. Fortunately, because of the different arrangement of the optics in the AO spectrophotometer, it was possible to obtain such data by means of this instrument. Figure 2 shows the spectra of solutions of this dye enriched with respect to each isomer. These curves were originally obtained by photographing the absorption curves that appeared on the cathode ray screen. Curve T is characteristic of a solution containing almost entirely the *trans* isomer, while curve C was obtained on a solution enriched with respect to the *cis* form; curve *E* represents an equilibrium mixture with respect to the light emitted by the light source of the AO instrument. The isomerization reaction (T or C →E) requires only two seconds when a light source of this intensity is utilized.

(C) Complex Formation with Hydroxy Compounds.—The addition of N,N'-dimethylindigo to a solution of phenol in carbon tetrachloride was observed to cause a decrease in the intensity of the –OH stretching band of phenol at 2.77 μ and to give rise to a new broad band near 3.0 μ, as shown in Fig. 3. This effect, which is similar to that reported for other carbonyl compounds,[11] is characteristic of hydrogen-bond formation between the hydroxyl group of phenol and the carbonyl oxygen.

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(7) J. H. Gould and W. R. Brode, *J. Opt. Soc. Amer.*, **42**, 380 (1952).

(8) We are indebted to Mr. E. G. Pearson of the National Bureau of Standards for his kindness in carrying out these measurements for us.

(9) S. E. Sheppard and P. T. Newsome, THIS JOURNAL, **64**, 2937 (1942).

(10) G. M. Wyman, *Chem. Revs.*, **55**, 625 (1955).

(11) S. I. Mizushima, M. Tsuboi, T. Shimanouchi and Y. Tsuda, *Spectrochim. Acta*, **7**, 100 (1955).

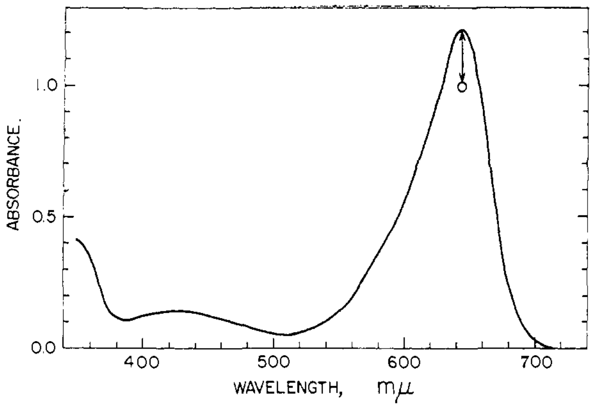
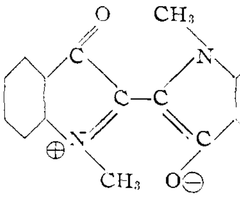


Fig. 1.—Absorption spectrum of N,N'-dimethylindigo in benzene, as obtained on the Cary spectrophotometer: O shows absorption maximum after exposing solution to yellow light (λ >520 mμ) for five minutes; the reverse reaction (←→) is complete in *ca.* 30 seconds at room temperature; cell length, 1.00 cm.; concentration, unspecified.

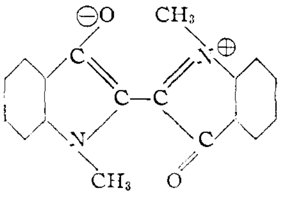
The spectral shifts brought about by the addition of acetone and of N,N'dimethylformamide to phenol have also been included in Fig. 3 for comparison purposes.

Direct evidence for the formation of complexes between N,N'dimethylindigo and organic hydroxy compounds was also obtained from a study of the infrared spectra in the 6 μ region. The addition of phenol or ethanol to a solution of the dye in chloroform causes a shift of the carbonyl-stretching band of the dye to longer wave lengths. The effect of ethanol on N,N'-dimethylindigo is shown in Fig. 4, the transmission curve of thioindigo obtained under similar conditions is also included for the sake of comparison.

The unusually strong bathochromic shift shown when the spectrum of N,N'-dimethylindigo is compared with that of indigo (*cf.* Table I) has been commented upon by Knott.[12] He suggested that, superimposed on the slight shift to longer wave lengths normally caused by methyl groups there is also a stronger bathochromic effect, which is of steric origin. According to this explanation, the introduction of the methyl groups into the indigo molecule causes considerable overcrowding of the *trans*-form. (This would be still more true of the *cis*-form.) In order to accommodate the methyl groups, the molecule has to depart from the coplanar indigo-type structure by twisting about the central double bond. This would tend to cause a shift of the absorption band to longer wave lengths by decreasing the overlap of the π-electron orbitals of the carbon atoms that constitute the central double-bond. Moreover, such a departure from coplanarity would also be expected to lower the potential energy of the dipolar structures IIa and IIb (which are the principal contributing structures in the excited state of molecules of this type), since in these the central bond is single in character.



IIa



IIb

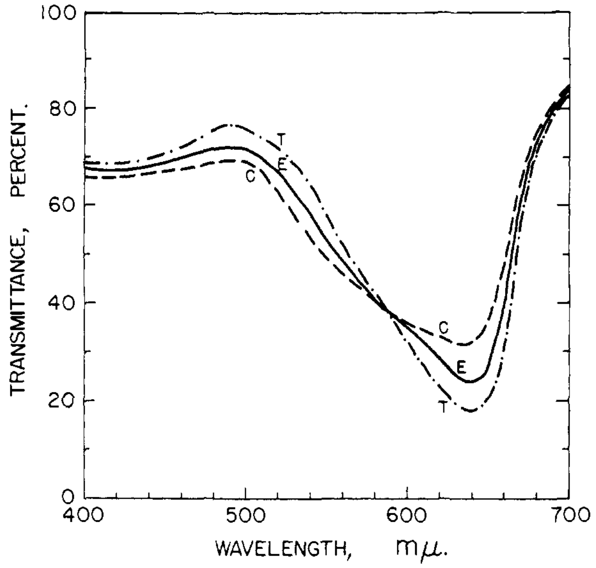


Fig. 2.—The spectral transmission curves of a solution of N,N'-dimethylindigo in benzene which was irradiated with filtered light from the light source of the AO spectrophotometer immediately before the measurement. Curve (–·–·–) was obtained with blue light (λ <495 mμ); (--------) with yellow light (λ >520 mμ); (———) with unfiltered radiation. Upon removal of the filter the solid curve is obtained from either dotted curve in two seconds. Concentration: unspecified; cell length: 1.00 cm.; AO Rapid-Scanning Spectrophotometer.

The high speed of the thermal *cis–trans*[13] isomerization reaction of N,N'-dimethylindigo which was observed in the present investigation suggests that the activation energy of this reaction is considerably lower for N,N'-dimethylindigo than it is for other indigoid dyes that exhibit *cis-trans* isomerism. Since an increase in the single-bond character of the central double-bond would be expected to lower the activation energy, this finding provides further supporting evidence for Knott's explanation.

The observed very pronounced effect of the medium on the position of the absorption band (*cf.* Table II) indicates that structures IIa and IIb make an important contribution to the ground state of the molecule, since such dipolar structures would tend to form complexes with polar solvents and thus lower their potential energy. In the solid state the same purpose would be served by the formation of dipole-aggregates, which is indicated by the strong bathochromic shift. As a further refinement of this general picture one might also consider the possibility that in a polar medium the shift toward the dipolar structures IIa and IIb is still further increased, in a manner similar to In-

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[12] E. B. Knott, *J. Soc. Dyers Colourists*, **67**, 305 (1951).

[13] Although the terms "*cis*" and "*trans*" are not strictly correct when applied to non-coplanar molecules, they are used here for convenience to denote configurations that are nearly *cis* and nearly *trans*, respectively.

gold's "electromeric shift,"[14] resulting in an additional lowering of the potential energy and a concomitant displacement of the absorption band to longer wave lengths.

The presence of very active carbonyl groups in this molecule (which would be expected to result from increased contributions from structures IIa and IIb) is further substantiated by the reported salt-formation with aqueous mineral acids[2] and by a study of the infrared spectra of solutions of this dye in the presence of organic hydroxy compounds. The data in Fig. 3 show that a given concentration of N,N′-dimethylindigo is more effective in shifting the –OH band of phenol to longer wave lengths than is an equivalent amount of acetone, though not as effective as is N,N′-dimethylformamide. This suggests that the carbonyl groups in this dye do, indeed, possess strong donor activity, even though they are not as active as that in N,N′-dimethylformamide.[15]

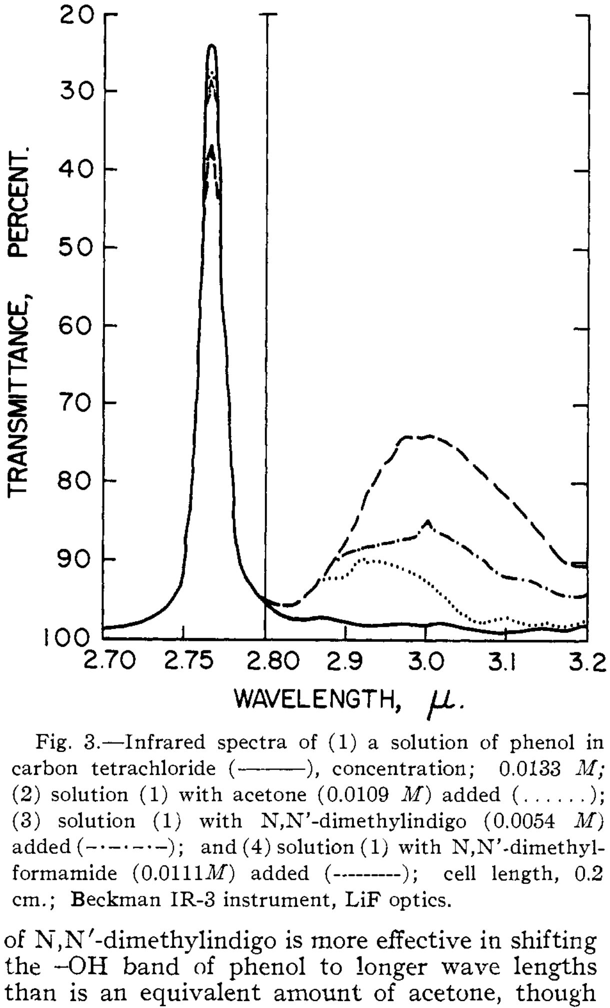

Fig. 3.—Infrared spectra of (1) a solution of phenol in carbon tetrachloride (———), concentration; 0.0133 *M*; (2) solution (1) with acetone (0.0109 *M*) added (......); (3) solution (1) with N,N'-dimethylindigo (0.0054 *M*) added (–·–·–); and (4) solution (1) with N,N'-dimethylformamide (0.0111*M*) added (--------); cell length, 0.2 cm.; Beckman IR-3 instrument, LiF optics.

The addition of ethanol to a chloroform solution of N,N′-dimethylindigo gives rise to a shift in the position of the carbonyl absorption band of the dye to a slightly longer wave length, as shown in Fig. 4. This shift, which first becomes noticeable when the concentration of ethanol reaches 10% (by volume) and which is quite pronounced at a concentration of 25%, indicates the formation of a hydrogen-bonded complex between the dye and ethanol. In contrast with this behavior, the position of the carbonyl band of thioindigo (which was selected as the reference because it is not only similar in structure, but also sufficiently soluble for this comparison) is unaffected by the addition of as much as 25% (by volume) of ethanol. A similar shift in the wave length of the carbonyl band (from 6.06 to 6.09 μ) also takes place when ethanol is added to a solution of N,N′-dimethylindigo in carbon tetrachloride, a solvent in which thioindigo is not sufficiently soluble to permit a direct comparison. Accordingly it is possible to conclude that the carbonyl groups in N,N′-dimethylindigo are more active donor centers than those that are present in the thioindigo molecule; this conclusion is also consistent with the proposed structure for the dimethyl compound.

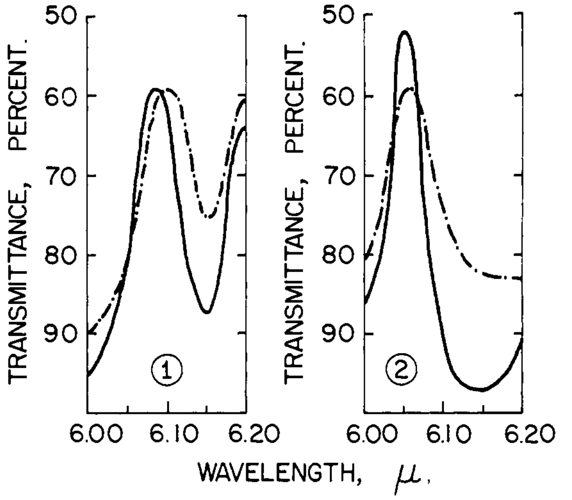

Fig. 4.—Infrared spectra of (1) N,N'-dimethylindigo and (2) thioindigo in the carbonyl region; (———) in chloroform solutions, and (–·–·–) in chloroform containing 25% (by volume) of ethanol; concentrations unspecified; cell length, 0.2 cm. Beckman IR-3 instrument, NaCl optics.

As a result of the observed complex formation of N,N′-dimethylindigo with ethanol it was considered desirable to reëxamine the lack of affinity of this dye for cellulosic fibers reported by Ettinger and Friedlaender.[2] Their observations were fully verified, however, when it was found that cotton could not be dyed with this compound either by the conventional vatting process or by direct application from a solution in benzene. In view of the presence of carbonyl groups of strong donor activity in this molecule this suggests that dyes of this type are not held to the fiber by ordinary hydrogen-bonding between the carbonyl groups of the dye and the hydroxyl groups of the cellulose.[16]

NATICK, MASS.

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[14] C. K. Ingold, *Chem. Revs.*, **15**, 225 (1934).

[15] *Cf.* reference 11.

[16] A similar deduction had been arrived at from a study of the association of indigo dyes in the solid phase (*cf.* reference 3b).