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The Structure of Indanthrone

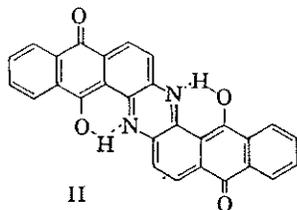
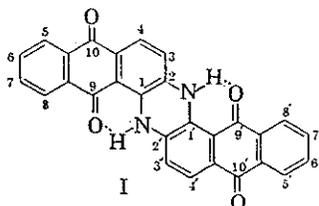
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Studies of spectra of indanthrone and related compounds in the ultraviolet, visible and infrared regions of the spectrum have led to the conclusion that indanthrone in the solid state and in inert solvents exists primarily in a keto form. This conclusion is based on the following evidence: (1) The presence of an N-H stretching band in the infrared spectrum of indanthrone and N-methylindanthrone at 3.16μ ; (2) indanthrone, N-methylindanthrone and N,N'-dimethylindanthrone all have approximately the same integrated absorbancy index for the carbonyl stretching absorption band at about 6.0μ ; (3) nearly identical spectra are observed for indanthrone and its N-methyl substituted derivatives in both the ultraviolet and visible regions of the spectrum.

Introduction

The structure of indanthrone, N,N'-dihydro-1,2:2',1'-anthraquinoneazine (I), has been a subject of controversy for many years. In a recent



paper Wyman¹ has proposed an enol structure II based substantially on the interpretation of infrared spectra. The argument presented is based on a failure to observe an N-H stretching band in the 3μ region. This argument, however, is weakened considerably by the fact that an hydroxyl stretching band expected to be shown in the same region by the enol structure was also not observed. A second feature of the argument is the assignment of the 6.3μ band for indanthrone to C=N, but this also appears doubtful.

Recently, Durie and Shannon² have questioned Wyman's interpretation of the spectra for the same reasons. They, however, were also unable to observe either an O-H or an N-H band in the 3μ region. Moreover, their argument in favor of the keto structure is unfortunately based on an interpretation of bands in the 6μ region which were incorrectly tabulated by Wyman for N-methylindanthrone and N,N'-dimethylindanthrone.

(1) G. M. Wyman, *THIS JOURNAL*, **78**, 4599 (1956).

(2) R. A. Durie and J. S. Shannon, *Aus. J. Chem.* **11**, 189 (1958). This paper was called to our attention by one of the reviewer's after the manuscript had been submitted for publication.

Since the keto structure I and the enol structure II involve a change in the electronic configurations of the molecule, the visible and ultraviolet regions of the spectrum might yield more decisive information. Accordingly, it seemed desirable to re-examine the infrared spectra and to investigate the visible and ultraviolet spectra of indanthrone and its N-methyl derivatives.

Experimental

Indanthrone and 3,3'-dichloroindanthrone were obtained through the courtesy of Mr. P. Kronowitz of Ciba States Ltd. The sample of indanthrone was purified by repeated recrystallization from 1,2,4-trichlorobenzene. N-Methylindanthrone and N,N'-dimethylindanthrone were prepared according to the procedure of Bradley and Leete.³ The methylated derivatives were characterized by analysis for carbon, hydrogen and nitrogen and by comparing their visible spectra in pyridine solutions with the spectra reported by Bradley and Leete. The amino anthraquinones, 6-chloroindanthrone and 3,3'-dibromoindanthrone were kindly provided by Dr. O. Stallman of the du Pont Co. The anthraquinoneazines were prepared by oxidation of the appropriate indanthrone with nitric acid, according to Scholl's procedure.⁴ The infrared spectra of indanthrone and its N-methyl derivatives were obtained in the 3 and 6μ regions by means of a Beckman IR-3 spectrophotometer equipped with LiF and NaCl optics as required. Samples were prepared as mulls in a perfluorocarbon oil and their transmittancy measured against the oil as a reference.

Samples for the quantitative study of the intensity of the carbonyl absorption bands were ground and dispersed in the mull by means of a "wiggie bug" in order to achieve a fine particle size and uniform distribution. Transmittancy values were measured in 1-mm. cells. The integrated absorbancy indices were calculated by the approximation method of Ramsay.⁵ The Napierian logarithm of the reciprocal of the recorded transmittance ratio was divided by the product of concentration in moles per liter and cell thickness in centimeters. This quotient multiplied by the half intensity band width (*i.e.*, effective slit width) in reciprocal centimeters gives the approximate integrated molar absorbancy index.

Spectra of indanthrone, its N-methyl derivatives and the amino anthraquinones in the visible region were obtained in 1,2,4-trichlorobenzene as a solvent. The spectra in the ultraviolet region were obtained on dyed cellophane films. Spectra in the ultraviolet were also measured in dimethylformamide as a solvent, but intense general absorption by the solvent at wave lengths shorter than $270 m\mu$ obscures the shorter wave length portions of the spectra. All measure-

(3) W. Bradley and E. Leete, *J. Chem. Soc.*, 2147 (1951).

(4) R. Scholl, H. Berblinger and J. Mansfield, *Ber.*, **40**, 320 (1907).

(5) D. A. Ramsay, *THIS JOURNAL*, **74**, 72 (1952).

ments of spectra in the visible and ultraviolet regions were made on a Cary model 11 double beam recording spectrophotometer. Solution spectra were measured against a reference of pure solvent in matched cells. The reference for the spectra of the dyes on cellophane was a piece of the same cellophane film processed in the vatting solutions without the dye.

Results and Discussion

Much of the controversy concerning the structure of indanthrone is centered about the anomalous chemical behavior during the vatting process. Several papers have reviewed the various proposed structures and discussed the supporting arguments.^{4,6-12} The object of this investigation, however, has been primarily to clarify the interpretation of spectroscopic data in relation to the structure of the parent dyestuff in the solid state and in solution in inert solvents. Accordingly, this discussion is limited in detail to the significance of the observed spectral phenomena.

The Infrared Region.—The spectra in the 3 μ region of indanthrone, N-methylindanthrone and N,N'-dimethylindanthrone milled in a perfluorocarbon oil are shown in Fig. 1. It is clearly seen

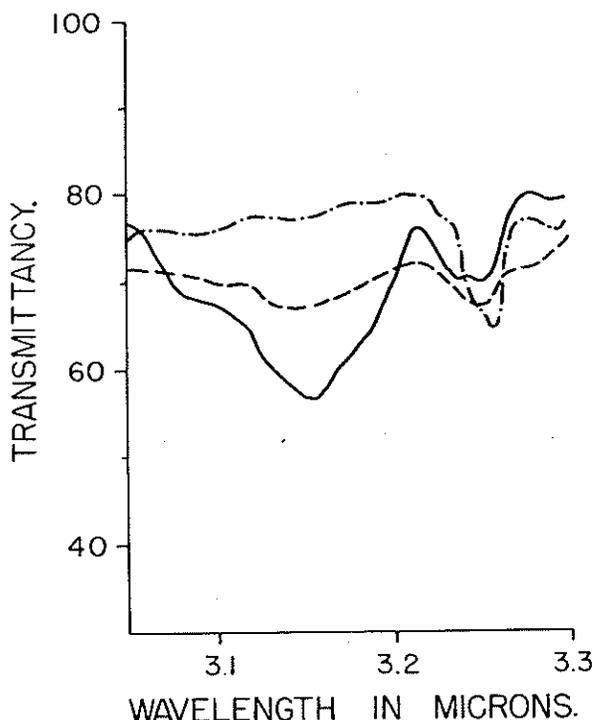


Fig. 1.—The infrared spectra of indanthrone (—), N-methylindanthrone (---) and N,N'-dimethylindanthrone (— · —) in the 3 μ region.

that a broad but distinct band occurs at 3.16 μ in the spectra of indanthrone and N-methylindan-

(6) D. A. Clibbens, *J. Soc. Dyers and Colourists*, **59**, 275 (1943).

(7) H. a. Brassard, *ibid.*, **59**, 127 (1943).

(8) R. Gill and H. I. Stonehill, *ibid.*, **60**, 183 (1944).

(9) D. Appleton and A. Geake, *Trans. Faraday Soc.*, **37**, 60 (1941).

(10) J. Jennen, *Med. Vlaam. Chem. Ver.*, **15**, 29 (1953).

(11) M. S. Whelen in "The Chemistry of Synthetic Dyes and Pigments," H. A. Lubs, Ed., Reinhold Publishing Corp., New York, N. Y., 1955, p. 512ff.

(12) (a) R. Scholl, *Ber.*, **36**, 3410 (1903). (b) R. Scholl and H. Berblinger, *ibid.*, **36**, 3427 (1903). (c) R. Scholl, W. Steinkopf and A. Kabacznik, *ibid.*, **40**, 390 (1907).

throne.¹³ Comparison of the intensities of the N-H bands with the intensities of the adjacent aromatic C-H bands (3.26 μ) shows the intensity of the N-H band in the methyl derivative to be correspondingly less than in the parent dye as expected. The broad shape of the bands indicate a high degree of hydrogen bonding. The proximity of the carbonyl and N-H groups and the possibility for the formation of a six-membered ring strongly suggests that the bonding is intramolecular. This view is further supported by the observation of Weinstein and Wyman¹⁴ that with β -amino- α,β -unsaturated ketones intramolecular hydrogen bonded N-H bands occur at longer wave lengths than the intermolecular hydrogen bonded N-H bands. With these compounds, which like the indantrones are vinylogs of amides and have the same molecular grouping between the carbonyl and N-H groups, intramolecularly bonded bands occur at approximately the same wave length as the band observed in indanthrone.

Absorption bands for azomethine (*i.e.*, C=N) groups are usually found in the wave length range 5.9 to 6.1 μ .¹⁵ Conjugation does not appear to change the region of absorption appreciably as shown by a recent study of substituted N-benzylidene anilines.¹⁶ The observed band in the indantrones at 6.3 μ appears, therefore, at too long a wave length to be normally attributed to C=N. Furthermore, when the azomethine group is part of a conjugated cyclic system, it cannot be considered separately due to interaction with other double bonds and, therefore, the application of C=N correlations to conjugated cyclic systems cannot be made safely.¹⁵

The spectra of a number of related compounds were studied in the region 6.0 to 6.4 μ and are summarized in Table I. Three types of compounds are represented; amino-substituted anthraquinones, indantrones and anthraquinoneazines. In addition the spectrum of anthraquinone is included. All the compounds have medium to strong bands in the vicinity of 6.3 μ . Examination of these spectra strongly suggests that these bands are due to ring absorptions.¹⁷ Indanthrone shows a strong broad band with a maximum at 6.33 μ . N-Methylindanthrone shows a similar broad band at 6.33 μ but with a shoulder at 6.28 μ . N,N'-Dimethylindanthrone and 3,3'-dibromoindanthrone each have two clearly discernible bands with maxima near 6.28 and 6.34 μ . Similar broad or double bands are found in the amino-substituted anthraquinones and anthraquinoneazines. Furthermore, anthraquinone itself is found to have also two distinct bands at 6.28 and 6.32 μ . On the basis of these comparisons it is clearly indicated that the 6.33 μ band of indanthrone cannot be reasonably assigned to C=N.

A quantitative study of carbonyl absorption

(13) The presence of these bands has been verified by Professor D. Hadzi of Ljubljana, Yugoslavia, in a recent private communication which was forwarded to us through the courtesy of Dr. Wyman.

(14) J. Weinstein and G. M. Wyman, *J. Org. Chem.*, **23**, 1618 (1958).

(15) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 226ff.

(16) L. E. Clougherty, J. A. Sousa and G. M. Wyman, *J. Org. Chem.*, **22**, 462 (1957).

(17) M. St. C. Flett, *J. Chem. Soc.*, 1444 (1948).

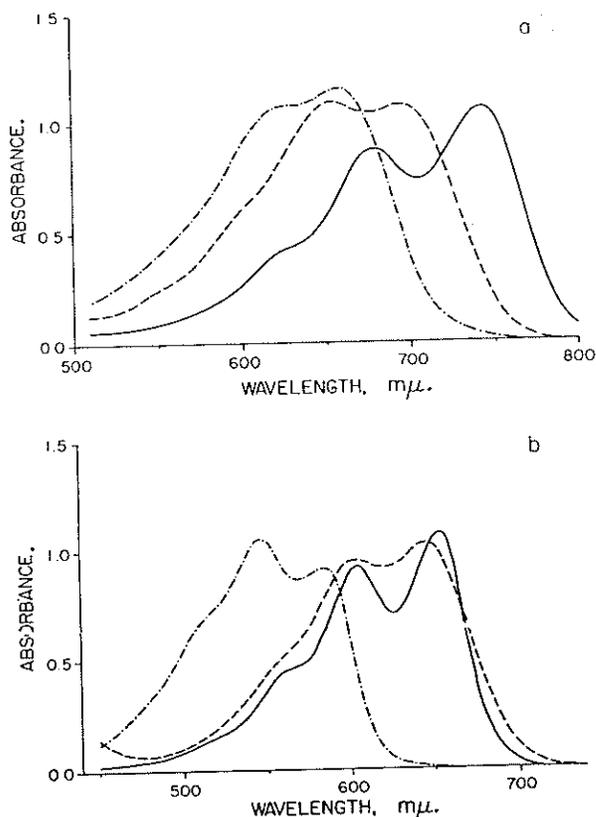


Fig. 3.—Spectra in the visible region of indanthrones and amino-substituted anthraquinones in solution in 1,2,4-trichlorobenzene: (a) indanthrone (—), N-methylindanthrone (---) and N,N'-dimethylindanthrone (-·-·-); and (b) 1,4-bis-methylaminoanthraquinone (—), 1,4-bis-N-phenylaminoanthraquinone (---) and 1,4-diaminoanthraquinone (-·-·-).

for the K bands.¹⁹ This effect has also been observed in the study of the spectra of aminoanthraquinones and methylated aminoanthraquinones.²⁰ The bands exhibited by ultraviolet absorption are probably associated with anthraquinone ring resonance. If indanthrone were enolized, a complete conjugation between both rings would exist across the nitrogen bridge (see structure II). It has been well established that extended conjugation of this type would result in a marked shift of the bands to longer wave lengths.²¹ No such shift, however, is observed for indanthrone or N-methylindanthrone when compared with N,N'-dimethylindanthrone which must exist in a keto form. It is noteworthy that the spectra of indanthrone and its N-methyl derivatives in concentrated sulfuric acid reported by Bradley and Leete³ show identical absorption bands at about 455 mμ. It is probable that these bands are the same bands observed in the ultraviolet on cellophane but shifted to a longer wave length by the formation of the more strongly electron attracting C=OH⁺ group resulting from oxonium salt formation. In addition, identical absorption bands

(19) A. Gillam and E. S. Stern, "Electronic Absorption Spectroscopy," Edward Arnold Publishers, Ltd., London, 1954, p. 113 ff.

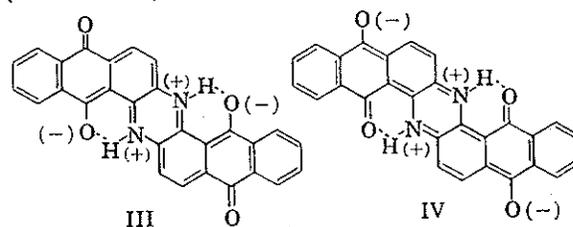
(20) R. H. Peters and H. H. Sumner, *J. Soc. Dyers and Colourists*, **72**, 77 (1956).

(21) D. Graham in ref. 11, p. 666.

having a maximum at 294 mμ have been found for the three compounds in dimethylformamide as a solvent.

Spectra of the indanthrones in the visible region are shown in Fig. 3a. The spectra are seen to be very similar. Moreover, a most striking similarity exists between the spectra of the indanthrones and the spectra of 1,4-diaminoanthraquinone, 1,4-bis-(methylamino)-anthraquinone and 1,4-bis-(N-phenylamino)-anthraquinone shown in Fig. 3b.

Strong amide resonance undoubtedly contributes greatly to the resonance hybrid of the indanthrones.⁶ This amide resonance also contributes in large measure to the transitions to which are due the absorption bands in the visible region.²² Similar amide resonance structures may be drawn for 1,4-diamino-substituted anthraquinones and for indanthrone. The amide resonance forms for aminosubstituted anthraquinones involve only one carbonyl in amide resonance with its vicinal nitrogen at a time. In the corresponding structures for indanthrone, however, the nitrogen atoms are involved in amide resonance forms either separately or simultaneously (structure III), and additional resonance forms involving the 2 and 2' nitrogens and the 10 and 10' carbonyls are also possible (structure IV).



Of the main amide resonance forms possible in indanthrone, those represented by structure III have lower energy due to smaller charge separation and are further stabilized by hydrogen bonding.^{22,23} The vicinal forms, therefore, have a correspondingly greater contribution to the resonance hybrid. This is borne out by the marked similarity of the spectra of the indanthrones and the 1,4-diamino-substituted anthraquinones.

The hypsochromic effect on the visible spectra of the indanthrones observed upon N-methylation is due to a reduced stabilization of the amide resonance in part by a decrease in hydrogen bonding and in part by a steric effect. Consideration of Fisher-Taylor-Hirschfelder models shows that introduction of an N-methyl group forces the nitrogen atom slightly out of the plane of the rings and thereby tends to increase the energy of the amide resonance structures.

The fact that the spectra of all the indanthrones and 1,4-diamino-substituted anthraquinones are markedly similar indicates that visible absorption bands are due to the same chromophore. It is highly significant that all the spectra resemble the spectrum of N,N'-dimethylindanthrone which cannot exist in an enol form. Furthermore, amide-type resonance is not possible for an enol form of indanthrone.

(22) See ref. 20, p. 685.

(23) L. Pauling, "Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, N. Y., 1948, p. 307.

These studies of spectra of indanthrone and related compounds in the ultraviolet, visible and infrared regions of the spectrum have led to the conclusion that indanthrone in the solid state and in inert solvents exists primarily in a keto form. The evidence is summarized: (1) An N-H stretching band is present in the infrared spectrum of indanthrone and N-methylindanthrone at 3.16μ . (2) Indanthrone, N-methylindanthrone and N,N'-dimethylindanthrone all have approximately the same integrated absorbancy index for the carbonyl

stretching absorption band at about 6.0μ . (3) Nearly identical spectra are observed for indanthrone and its N-methyl substituted derivatives in both the ultraviolet and visible regions of the spectrum.

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