

## Spectroscopic Studies on Dyes. III. The Structure of Indanthrones<sup>1</sup>

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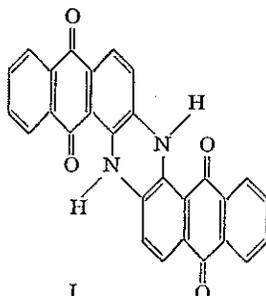
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The infrared spectra of indanthrone, some of its halogenated derivatives and N-methylindanthrone fail to exhibit the expected -NH- stretching absorption band near 3.0  $\mu$ . They show a strong band near 6.3  $\mu$ , which is also shown by the corresponding anthraquinoneazines and which is probably characteristic of a -C=N- stretching vibration. On the basis of these observations a revised structure (III) is proposed for indanthrone. The seemingly anomalous chemical properties of indanthrone, such as its chemical stability, behavior in the vatting reaction, salt-formation with anhydrous strong bases, etc., are also readily explained on the basis of this structure.

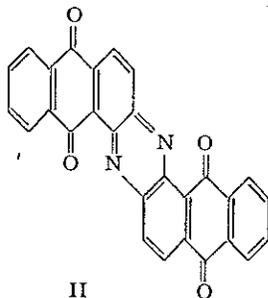
### Introduction

The discovery of indanthrone, a bright blue dye of exceptional light and wash-fastness properties, at the turn of the century<sup>2</sup> ushered in a new era in the development of synthetic dyes. Even now, more than 50 years later, indanthrone derivatives are still among the most sought after of the blue dyes that are available.

The determination of the structure of indanthrone was the subject of a series of papers by Scholl and co-workers shortly after the discovery of this dyestuff.<sup>3</sup> As a result of these studies they assigned structure I to indanthrone, and this



formula has generally been accepted since. Although this structure seemed largely consistent with what was known about the chemical behavior of indanthrone at the time, it was somewhat difficult to reconcile it with the blue color of the dye, since such a deeply colored substance might have been expected to possess a fully conjugated structure. Moreover, the azine (II), which results when indanthrone is oxidized, is a dull yellow in color even though it has a fully conjugated struc-



(1) Presented before the Division of Organic Chemistry at the 119th Meeting of the American Chemical Society, Dallas, Texas, April, 1956.

(2) R. Bohn, German Patent 129,845 (1902).

(3) (a) R. Scholl, *Ber.*, **36**, 3410 (1903); (b) R. Scholl and H. Berblinger, *ibid.*, **36**, 3427 (1903); (c) R. Scholl, H. Berlinger and J. Mansfield, *ibid.*, **40**, 320 (1907); (d) R. Scholl, W. Steinkopf and A. Kabacznik, *ibid.*, **40**, 390 (1907).

ture. Aware of this apparent anomaly, Scholl attributed the deeper color of the dye to the auxochromic effect of the -NH- groups upon the two quinone chromophores.<sup>3a</sup>

It was this inconsistency between the structure and the color of this dye and of the corresponding azine that made it appear desirable to reopen this problem. Therefore, it was proposed to investigate indanthrone and some of its derivatives with the aid of spectrophotometric techniques that have only recently become available and to re-examine the data in the literature in the hope of reconciling these anomalies.

### Experimental

**Dyes.**—Indanthrone and 3,3'-dichloroindanthrone were research samples obtained through the courtesy of Mr. P. Kronowitz of Ciba States Ltd. 3,3'-Dibromoindanthrone and the 1-methylamino-2-bromoanthraquinone which was used in the synthesis of N-methylindanthrone were kindly provided by Dr. O. Stallmann of the du Pont Co. N-Methylindanthrone and N,N'-dimethylindanthrone were prepared according to the procedure of Bradley and Leete.<sup>4</sup> The methylated derivatives were identified by comparing their visible spectra in pyridine solutions with the spectra reported by these investigators.

**Oxidation of Indanthrones.**—The anthraquinoneazines used in this investigation were prepared by the oxidation of the appropriate indanthrone with nitric acid, according to Scholl's procedure.<sup>3c</sup>

**Deuteration of Indanthrone.**—Twenty mg. of indanthrone was added to 20 ml. of a 5% solution of NaOD in D<sub>2</sub>O contained in a 50-ml. erlenmeyer flask. This suspension was heated to 60–65° and sufficient sodium hydrosulfite added to effect reduction of the dye. The flask was then loosely stoppered and the deep blue solution maintained at this temperature for 5 minutes with periodic gentle swirling. The vat was reoxidized by blowing dry air through it for 5 minutes. The precipitate was filtered, washed with a small amount of water and dried at 85°. Combustion of the product, followed by mass-spectrometric analysis of the water formed in the combustion indicated that the replacement of the active hydrogen atoms by deuterium was at least 35% effective under these conditions.

**Measurements in the Infrared Region.**—The samples (as mulls or as pellets in KBr) were measured by means of a Beckman IR-3 spectrophotometer, utilizing NaCl or LiF optics, as required. The pellets used were 13 mm. in diameter and a pellet of pure KBr was used as the reference. In addition, where the entire infrared spectrum was desired, the pellets were also measured on a Baird Associates double-beam spectrophotometer equipped with a NaCl prism.

**Measurements in the Visible Region.**—The Cary spectrophotometer (Model 11) was used for measurements in this region. Spectra were measured on solutions (against the solvent as reference) and on KBr pellets.<sup>5</sup>

### Discussion

The salient feature of the infrared spectra of the indanthrones that were studied in this work is the

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

(5) G. M. Wyman, *J. Opt. Soc. Am.*, **45**, 965 (1955).

absence of any absorption band in the N-H stretching region (near 3.0  $\mu$ ). This wholly unexpected result was carefully verified by making several measurements using different techniques of sample preparation (e.g., mulls in Nujol or in a polytrifluoro-chloroethylene oil and as KBr pellets) and by observing that other compounds containing N-H groups adjacent in space to carbonyl groups, (e.g., 1-aminoanthraquinone and indigo) exhibited the typical N-H stretching band under the same conditions of measurement (cf. Tables I and II). Although absorption bands that are due to the stretching of O-H linkages have been known to become almost indistinguishable as a result of hydrogen-bonding,<sup>6</sup> such weakening and broadening has never been reported for N-H bands.<sup>7</sup> To the contrary, indigo exhibits a distinct N-H stretching band at 3.05  $\mu$ <sup>8</sup> in the solid phase, even though the N-H group is involved in both intra- and intermolecular hydrogen-bonding.<sup>9</sup> Moreover, the partial replacement of the two active hydrogen atoms of indanthrone by deuterium (which would be expected to shift any N-H bands from the 3  $\mu$  region, where they may have been obscured, to wave lengths longer than 4  $\mu$ ) also failed to give rise to any new absorption bands. Consequently, the absence of the N-H stretching frequency presents a strong argument against the presence of the N-H groups in the indanthrone molecule.

TABLE I  
INFRARED ABSORPTION BANDS IN THE N-H STRETCHING REGION (IN  $\mu$ )

|                            | In KBr     | As Nujol mull | As KCl-F mull |
|----------------------------|------------|---------------|---------------|
| Indanthrone                | ..         | ..            | ..            |
| N-Methylindanthrone        | ..         | ..            | ..            |
| 3,3'-Dichloroindanthrone   | ..         | ..            | ..            |
| 1-Aminoanthraquinone       | 2.92, 3.02 | 2.92, 3.02    | 2.92, 3.02    |
| Indigo                     | 3.06       | 3.06          | 3.06          |
| 5,5',7,7'-Tetrabromoindigo | 2.97       | 2.97          | 2.97          |

Another conspicuous feature of the infrared spectra of most of these compounds is the strong broad band near 6.3  $\mu$ . In indanthrone this band is almost as strong as the carbonyl band (cf. Fig. 1), and it is also present in the spectra of the azines studied. Although this is the wave length range where aromatic ring vibrations are likely to occur, it is believed that these would not give rise to such an intense band as that shown by indanthrone. Instead, this strong band is very probably the C=N stretching frequency which would be expected to obscure the weaker aromatic ring vibrations that

(6) (a) D. Hadzi, Abstracts of the XIVth International Congress of Pure and Applied Chemistry, Zurich, 1955, No. 23, p. 14; (b) K. Nakamoto, M. Margoshes and R. E. Rundle, THIS JOURNAL, 77, 6480 (1955).

(7) Cromwell, *et al.*, could not detect the N-H stretching frequency in the infrared spectra of some  $\beta$ -amino- $\alpha,\beta$ -unsaturated ketones. However, they attributed this to a shift of the N-H bands to slightly longer wave lengths (near 3.4  $\mu$ ) where they would be obscured by the C-H stretching frequencies (N. H. Cromwell, *et al.*, THIS JOURNAL, 71, 3337 (1949)).

(8) W. R. Brode, E. C. Pearson and G. M. Wyman, *ibid.*, 76, 1034 (1954).

(9) (a) Helene v. Eller, *Compt. rend.*, 239, 975 (1954); (b) J. Weinstein and G. M. Wyman, THIS JOURNAL, 78, 2387 (1956).

TABLE II  
PRINCIPAL INFRARED ABSORPTION BANDS OF THE DYES (IN  $\mu$ )<sup>a</sup>

| Indanthrone        | N-Methylindanthrone | N,N'-Dimethylindanthrone | 3,3'-Dibromoindanthrone | 3,3'-Dichloroindanthrone |
|--------------------|---------------------|--------------------------|-------------------------|--------------------------|
| 3.38w <sup>b</sup> | 3.38w               | 3.40w                    | 3.36w                   | 3.42w                    |
| 5.87w              | 6.03s               | 6.02s                    | 6.06s                   | 6.05s                    |
| 6.06s              | 6.10w               | 6.09w                    | 6.13w                   | 6.13w                    |
| 6.15w              | (6.22)              | 6.22w                    | 6.28m                   | 6.29s                    |
| 6.30s              | 6.29m               | 6.36m                    | 6.37m                   | (6.33)                   |
| 6.70s              | 6.47w               | 6.76s                    | 6.78sb                  | (6.38)                   |
| 7.08w              | 6.63m               | 6.86m                    | 7.45m                   | 6.70s                    |
| 7.40m              | 6.79w               | 7.03m                    | 7.58w                   | (6.82)                   |
| 7.52m              | 6.96w               | 7.26s                    | 7.96sb                  | 7.45s                    |
| 7.83sb             | 7.04w               | 7.50m                    | 8.50m                   | (7.52)                   |
| 8.46m              | 7.27m               | 7.62m                    | 9.50s                   | 7.87sb                   |
| 8.62m              | 7.50m               | 7.93sb                   | 9.76s                   | 8.50w                    |
| 9.25w              | (7.72)              | 8.02w                    | 10.76m                  | 8.98w                    |
| 9.60m              | 7.86s               | 8.38w                    | 11.26w                  | 9.48s                    |
| 9.84s              | 8.41w               | 8.58w                    | 11.47w                  | 9.71s                    |
| 11.20w             | 9.51m               | 8.72w                    | 12.05m                  | 10.44m                   |
| 11.57m             | 9.75w               | 9.87m                    | 12.67w                  | 11.96w                   |
| 11.97s             | 9.92w               | 11.42m                   | 13.28s                  | 12.46w                   |
| 12.21w             | 11.30w              | 12.28w                   | 14.06s                  | 13.31m                   |
| 12.59w             | 11.52w              | 13.34w                   |                         | 14.07s                   |
| 13.33s             | 13.33w              | 14.07m                   |                         | 14.40w                   |
| 13.90s             | 14.08s              |                          |                         | 14.95w                   |
| 14.56mb            |                     |                          |                         |                          |

<sup>a</sup> As pellets in KBr, measured on the Baird Spectrophotometer; <sup>b</sup> w, weak; m, medium; s, strong; b, broad; parentheses indicate points of inflection.

TABLE III  
PRINCIPAL ABSORPTION BANDS OF THE AZINES<sup>a</sup>

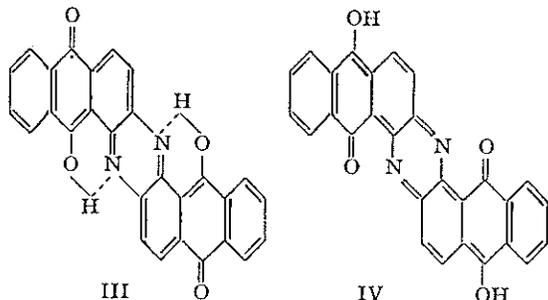
| 1,2:2',1'-Anthraquinoneazine | 3,3'-Dichloro-1,2:2',1'-anthraquinoneazine | 3,3'-Dibromo-1,2:2',1'-anthraquinoneazine |
|------------------------------|--|---|
| 3.40w                        | 3.40w                                      | 3.30w                                     |
| (5.90)                       | (5.90)                                     | 5.98s                                     |
| 5.98s                        | 5.98s                                      | 6.28s                                     |
| 6.03w                        | 6.27m                                      | 6.66s                                     |
| 6.27m                        | 6.61m                                      | (7.56)                                    |
| 6.61m                        | 6.80w                                      | 7.64s                                     |
| 6.85m                        | 7.55m                                      | 7.88s                                     |
| 7.43m                        | 7.65s                                      | 9.00bw                                    |
| 7.52m                        | (7.72)                                     | 9.30w                                     |
| 7.73s                        | 7.92s                                      | 9.50w                                     |
| 7.87m                        | 9.02wb                                     | 9.70w                                     |
| 8.29m                        | 9.44w                                      | 10.62m                                    |
| 8.56w                        | 9.70w                                      | 10.91m                                    |
| 8.70w                        | 10.57m                                     | 11.68m                                    |
| 8.80w                        | 11.63m                                     | 12.13m                                    |
| 9.23w                        | 12.00m                                     | 12.54w                                    |
| 9.92m                        | 12.57m                                     | 13.01w                                    |
| 11.22m                       | 13.02w                                     | 14.03s                                    |
| 11.78s                       | 13.97s                                     |   |
| 12.80w                       | 14.72w                                     |   |
| 13.20w                       | 14.99w                                     |   |
| 14.05s                       |  |   |
| 14.99w                       |  |   |

<sup>a</sup> For conditions of measurement and symbols used, see Table II.

undoubtedly also occur in this region. The behavior of this band in the N-methylated indanthrones is also consistent with this assignment: in N-methylindanthrone (which can possess only one C=N group) this band is but half as strong as

it is in indanthrone, and in *N,N'*-dimethylindanthrone it has been replaced by two relatively weak bands, probably the ring vibrations, as shown in Fig. 1.<sup>10</sup>

Consequently, the infrared measurements suggest that indanthrone exists in one of the two possible dienol structures (III and IV) instead of the hitherto accepted keto structure I. Since intramolecular hydrogen-bonding is only possible in



III, this probably has considerably lower potential energy and is therefore the preferred structure. The arrangement of the atoms is the same in this formula as it is in I, with the exception of the position of the two active hydrogen atoms and the different distribution of the electron-cloud.

A fourth possibility would involve a resonance structure that is intermediate between I and III. Although such a structure is less likely, because it would require that each hydrogen atom should be equally bonded to an oxygen and a nitrogen atom, it cannot be ruled out altogether. Such "symmetrical" hydrogen bonds (where the hydrogen atom is held equally by the two atoms which it bridges) have been reported to occur in a few instances, but only between two like atoms.<sup>11</sup> Results of recent bond-distance measurements (largely by neutron diffraction techniques) suggest that bonding of this type may occur even when hydrogen acts as a bridge between unlike atoms.<sup>12</sup> However, even if resonance of this type were possible, the absence of the N-H stretching frequency suggests that it is structure III that makes the major contribution to the resonance hybrid.

It is of interest to note that Scholl himself had given serious consideration to structure III for indanthrone but found it necessary to eliminate it, along with the other dienol structure IV, because he failed to observe salt formation with alcoholic bases.<sup>13</sup> Recently it has been shown, however, that both indanthrone and *N*-methylindanthrone exhibit a color change indicative of salt formation, when a drop of methanolic potassium hydroxide is

(10) Since anthraquinone and a number of its derivatives are known to exhibit a strong band near  $6.3 \mu$ , it was suggested by one of the referees that the apparent decrease in the intensity of the  $6.3 \mu$  band on methylation (relative to the carbonyl band) may merely be due to increased carbonyl absorption resulting from an increase in the number of carbonyl groups in the molecule. (On the basis of the proposed structures, indanthrone (III) has two carbonyl groups and *N*-methylindanthrone (VI), three.)

(11) (a) E. F. Westrum, Jr., and K. S. Pitzer, *J. Chem. Phys.*, **15**, 526 (1947); (b) E. F. Westrum, Jr., and K. S. Pitzer, *THIS JOURNAL*, **71**, 1940 (1949); (c) H. M. E. Cardwell, J. D. Dunitz and L. E. Orgel, *J. Chem. Soc.*, 3740 (1953).

(12) Cf. reference 6b, p. 6486.

(13) Reference 3a, p. 3420.

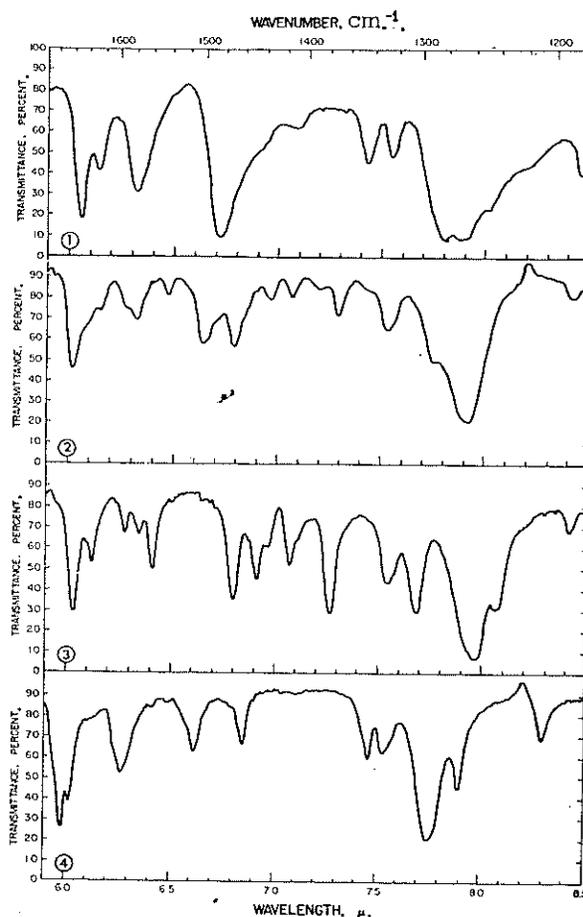
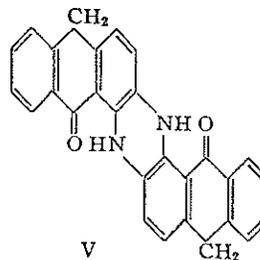


Fig. 1.—The infrared spectra of: (1) indanthrone; (2) *N*-methylindanthrone; (3) *N,N'*-dimethylindanthrone; (4) anthraquinoneazine in KBr (range:  $5.9$ – $8.5 \mu$ ); Beckman IR-3 instrument, NaCl optics.

added to a dilute solution of the dye in pyridine.<sup>14</sup>

The characterization of this dye as a derivative of *N,N'*-dihydrophenazine has always been somewhat difficult to accept in view of the well-known chemical instability of such compounds: the parent compound is stable only under reducing conditions and is readily oxidized by air to the much more stable phenazine.<sup>15</sup> The introduction of carbonyl groups conjugated with the N-H groups would be expected to bring about some stabilization of the *N,N'*-dihydrophenazine structure, since such compounds are vinylogs of amides and would be stabilized by amide-type resonance. However, *N,N'*-dihydroanthranoneazine (V) (which is also a vinylogous amide and which is structurally similar to

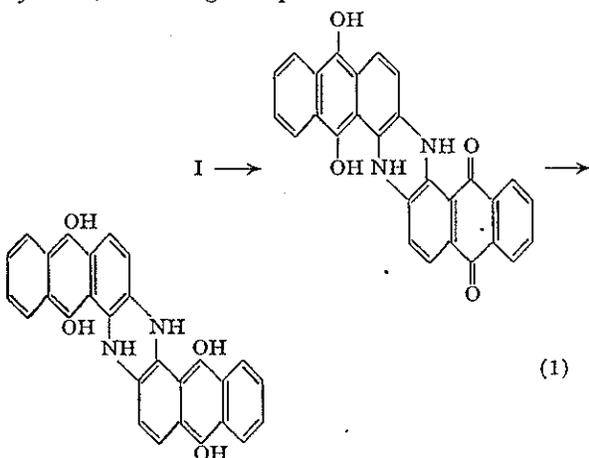


(14) W. Bradley and E. Leete, *J. Chem. Soc.*, 2129 (1951).

(15) "Beilstein," Second Supplement, Vol. 23, 1954, p. 225.

Scholl's indanthrone structure) is converted to the corresponding azine when it is heated to *ca.* 340°. In sharp contrast to this behavior indanthrone is exceedingly stable; in this case, it is the azine which is reduced to the dye when the former is heated to *ca.* 400°.<sup>16</sup> In order to reconcile this exceptional stability of indanthrone with the known instability of other *N,N'*-dihydroazines, Scholl suggested that the four negative carbonyl groups bring about stabilization of the molecule. The proposed fully conjugated dienol structure III is then clearly more consistent with the great stability of indanthrone, as it is also more in accord with the deep color of this compound.

Another puzzling aspect of the chemistry of indanthrone which has been subject to much speculation is its behavior during the vatting process. Upon reduction with sodium hydrosulfite solution in alkaline medium at *ca.* 60°, indanthrone yields a deep blue solution which, on prolonged heating with an excess of reducing agent, is converted to a brown vat. Scholl attributed this behavior to a stepwise reduction of the two anthraquinone ring-systems, according to equation 1.<sup>3b</sup>



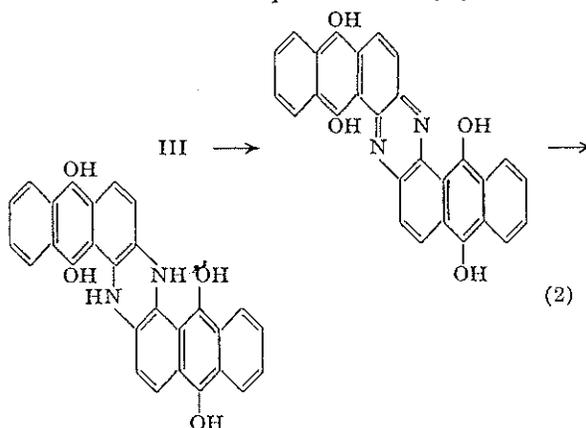
This seems unlikely, however, in view of the observed one-step reduction of *N*-methylindanthrone and of *N,N'*-dimethylindanthrone to a brown vat.<sup>14</sup> Moreover, it has been reported that "without exception in all other vat dyes containing several anthraquinone residues, all keto groups are reduced in forming the leuco compounds,"<sup>17</sup> and equation 1 fails to explain why indanthrone should be an exception to this generalization.

In attempting to account for the anomalous behavior of indanthrone in this reaction, quadrupolar structures have been postulated for this dye<sup>17,18</sup> and for its leuco form,<sup>19</sup> and the latter has also been represented as a double semiquinone.<sup>20</sup> Since all of the suggested structures contain *N-H* groups, they are therefore not consistent with the infrared spectra; in addition they also fail to account for the anomalous blue vat of indanthrone in a satisfactory manner.

Reduction of indanthrone to the blue vat is read-

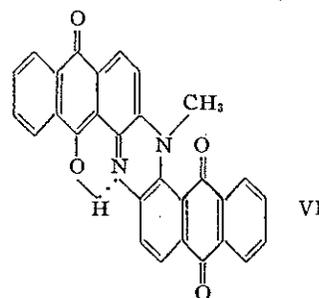
- (16) Reference 3a, p. 3421.  
 (17) H. à. Brassard, *J. Soc. Dyers Colorists*, **59**, 127 (1943).  
 (18) R. Kuhn, *Naturwissenschaften*, **20**, 618 (1932).  
 (19) R. Gill and H. T. Stonehill, *J. Soc. Dyers Colorists*, **60**, 183 (1944).  
 (20) D. A. Clibbens, *ibid.*, **59**, 275 (1943).

ily explained, however, on the basis of the proposed structure III, since this structure contains only one pair of conjugated carbonyl groups. The blue vat is then probably a sodium salt of the fully reduced leuco form of anthraquinoneazine (II), which is

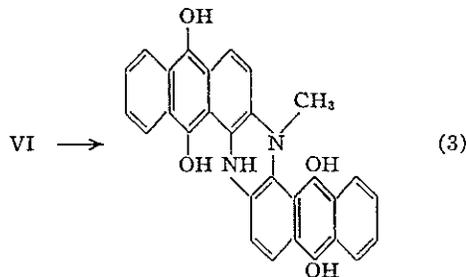


formed according to equation 2 and which may be further reduced under more vigorous conditions to the *N,N'*-dihydroazine derivative.

By analogy to indanthrone, *N*-methylindanthrone is best represented by formula VI. Just as *N*-methylindanthrone cannot be oxidized to an azine because of the presence of the methyl group, it can also not be reduced to a tetrahydroazine by



some reaction analogous to the first step in equation 2. Instead, the reduction of *N*-methylindanthrone has to take place by the simultaneous reduction of the three carbonyl groups and the *C=N* group, according to equation 3. The reduction of *N,N'*-dimethylindanthrone would be expected to occur by the simultaneous reduction of all four carbonyl



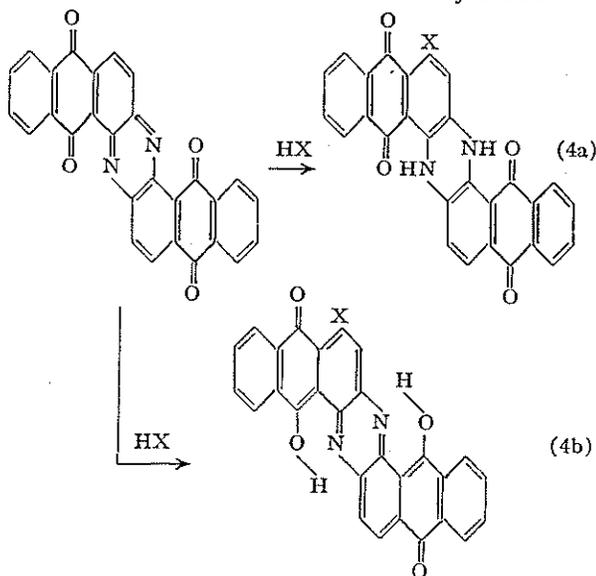
groups, in accordance with the usual behavior of vat dyes containing several anthraquinone ring systems. It is of interest to note that the visible absorption curves of the brown vat of indanthrone and of the leuco forms of the two *N*-methylindanthrones are very similar,<sup>21</sup> consistent with the assignment of

(21) Cf. Fig. 2, in reference 14.

the doubly reduced  $N,N'$ -dihydroanthraquinone-azine-type structure to all of these leuco compounds.

In view of this important role of the behavior of  $N$ -methylindantrones in elucidating the structure of the parent compound, it was considered desirable to make certain that the structures of these compounds were correct as represented. Since  $N,N'$ -dimethylindanthrone was prepared by the methylation of indanthrone,<sup>14</sup> it was possible that the methyl group might have become linked to the oxygen atom. Even in the  $N$ -methylindanthrone, which was made from an intermediate containing the  $N$ -methyl group, a rearrangement might have taken place. An examination of the infrared spectra (cf. Fig. 1) readily shows the appearance of a weak band near  $7.26 \mu$  in the  $N$ -methyl compound, which is absent in the parent dye and which becomes quite strong in the dimethyl derivative. This band is in the wave length region where the symmetrical deformation mode of the methyl group is expected to occur in compounds where the methyl group is attached to carbon<sup>22a</sup> or nitrogen<sup>22b</sup> but not in methyl-aryl ethers.<sup>23</sup> Furthermore, at least  $N$ -methylindanthrone exhibits no bands in the  $7.9$ – $8.2 \mu$  region where such ethers would be expected to absorb.<sup>24</sup> Unfortunately polycyclic quinones have strong absorption bands in this region,<sup>25</sup> and for this reason the bands near  $8.0 \mu$  in the spectrum of  $N,N'$ -dimethylindanthrone cannot be assigned with any degree of certainty. Thus it is apparent from these considerations that the infrared spectra of the two compounds are consistent with the  $N$ -methyl structures that had previously been assigned to them on the basis of the chemical evidence.<sup>4</sup>

The reactions involving the addition of mineral acids or amines to anthraquinoneazine to yield substituted indantrones according to equation 4a were also considered to be anomalous by Schöll.<sup>3a</sup>



(22) (a) L. J. Bellamy, "The Infrared Spectra of Complex Molecules," John Wiley and Sons, Inc., New York, N. Y., 1954, p. 20; (b) p. 221.

(23) Cf. R. B. Barnes, U. Liddell and V. Z. Williams, *Ind. Eng. Chem., Anal. Ed.*, **15**, 687 (1943).

(24) Reference 22, p. 100.

(25) D. Hadzi and N. Sheppard, *Proc. Roy. Soc. (London)*, **A216**, 247 (1953).

Although such a reaction involving the reduction of carbon-nitrogen double bonds is common to quinone imides,<sup>26</sup> and it has, on at least one occasion, also been reported to occur with azines,<sup>27</sup> it is not a usual reaction of this latter class of compounds. On the other hand, such a reaction is known to be common to quinones, resulting in the formation of the appropriate substituted hydroquinone.<sup>28</sup> Consequently this behavior of anthraquinoneazine is also more consistent with the proposed dienol structure for indanthrone, since then the reaction does not require the reduction of carbon-nitrogen double bonds, as shown in equation 4b.

On the basis of these considerations it is then possible to assign the principal absorption bands found in the infrared spectra of these compounds to specific atomic groupings. The carbonyl group stretching frequency is found near  $6.0 \mu$  in all of the compounds studied; it is shifted to slightly longer wave lengths in  $N$ -methylindanthrone, in indanthrone and in the halogenated indantrones, probably because of intermolecular hydrogen bonding. The weak bands that sometimes appear only as shoulders on the long wave length side of the carbonyl bands are probably due to the  $-C=C-$  groups. As had already been mentioned, the strong bands near  $6.3 \mu$  are to be attributed to the  $-C=N-$  groups, while the weak bands near  $7.27 \mu$  in the  $N$ -methyl derivatives are ascribed to the  $N-CH_3$  groups. The very intense bands in the  $7.7$ – $8.0 \mu$  region are characteristic of polycyclic quinones. The strong band near  $6.7 \mu$  and any weak bands in the  $6.3$ – $6.4 \mu$  region that are not hidden by the  $-C=N-$  bands are probably due to the aromatic rings, as are most of the strong bands that occur at wave lengths longer than  $11.0 \mu$ .

A study of the visible spectra of these dyes in the solid phase failed to disclose any unequivocal evidence for or against the proposed structures. The spectra of the various indanthrone dyes all show a broad absorption band in the  $600$ – $650 m\mu$  region, as shown in Fig. 2. In addition to this band,  $N$ -methylindanthrone also has a second, weak band near  $730 m\mu$ . The spectrum of indanthrone consists of two broad bands of approximately equal intensity at about  $630 m\mu$  and near  $780 m\mu$ . At first glance these results would seem consistent with structures III and VI for the two dyes. On that basis the long wave length ( $\lambda > 700 m\mu$ ) bands in the spectrum of each of the two dyes could be attributed to the conjugated azine-type structures, while the bands near  $600 m\mu$  could be due to the combination of the two anthraquinone ring systems without the added conjugation. However, by analogy with indigo dyes,<sup>9b</sup> the shift to longer wave lengths may also be attributable to intermolecular hydrogen-bonding which can only occur in indanthrone and in  $N$ -methylindanthrone.

It should also be mentioned that, while the several different solid modifications of indanthrone showed slight differences in their visible spectra, their infrared spectra were found to be identical.

(26) Cf. R. Adams, E. F. Elslager and K. F. Heumann, *This Journal*, **74**, 2608 (1952); also earlier papers in that series.

(27) R. Schöll, *Ber.*, **36**, 3710 (1903).

(28) W. J. Hickinbottom, "Reactions of Organic Compounds," Longmans, Green and Co., London, 1936, p. 184.

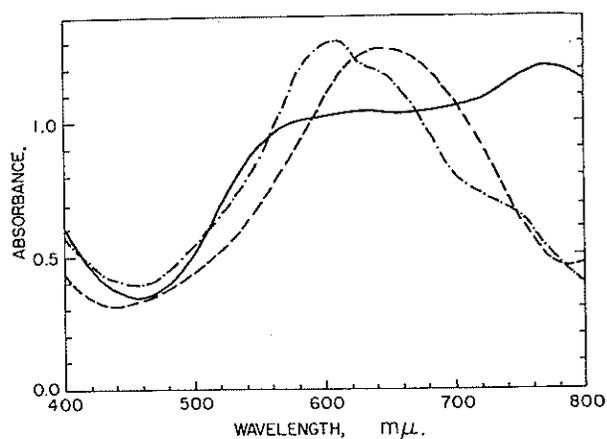


Fig. 2.—The visible spectra of indanthrone (—); N-methylindanthrone (-----); and N,N'-dimethylindanthrone (- - -) in KBr.

This finding confirms the assignment of the various modifications to polymorphism<sup>29</sup> and eliminates

(29) G. Susich, *Anal. Chem.*, **22**, 425 (1950).

the possibility that some of these modifications could have resulted from the existence of indanthrone in different tautomeric forms (e.g., I and III).

Since, in addition to the indantrones, the structures of a large number of vat dyes consist of anthraquinone nuclei that are linked by one or more N-H bridge, the assignment of structure III to indanthrone may have far-reaching implications. If other anthraquinone dyes should also be found to exist in the analogous enol forms, it may be necessary to revise many of our existing views concerning dyes of this type. In that event it may also be possible to gain a better understanding of the forces that bind these dyes to the fibers and thus perhaps arrive at an answer to this problem which is of fundamental importance to dye chemistry.

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