THE INDIAN ASSOCIATION FOR THE CULTIVATION OF SCIENCE

CONSTITUTIONAL PROBLEMS CONCERNING VAT DYES

By

Director, Department of Chemical Technology, University of Bombay

Based on the lectures delivered as the Cooch-Behar Professor for 1948.

CALCUTTA 1953
CONSTITUTIONAL PROBLEMS CONCERNING VAT DYES

It is clear from the number, variety and complexity of the synthetic dyes that their chemistry presents innumerable problems for investigation. This is particularly true of the anthraquinone vat dyes derived from complex carbocyclic and heterocyclic ring systems. The first dye of this class, indanthrone, was discovered by Bohn in 1901, and extensive work on its constitution was carried out by Bohn, Scholl and others; but the preparation of indanthrone by the alkali fusion of β-aminoanthraquinone involves complicated reactions in which indanthrone is accompanied by several bye-products, and as recently as 1951 Bradley in a series of papers (J. Chem. Soc., 1951, 2129 et sequa) has made an important contribution to the chemistry of the formation of indanthrone, flavanthrone and related dyes.

Chromatographic analysis of vat dyes

The problem of the separation of mixtures of vat dyes has received little attention. Because of the insolubility or sparing solubility of vat dyes in organic solvents at room temperature, column chromatography cannot be conveniently employed; Bradley and Sutcliffe (J. Chem. Soc., 1952, 2120) used trichlorobenzene (250 c.c. for dissolving 0·25 g. of the dye) at 160 to 170° for the isolation of an isoviolanthrone derivative in the pure state.

Conflicting statements have been made on the separability of alkaline vats on alumina (Vickerstaff, The Physical Chemistry of Dyeing, Oliver and Boyd, London, 1950; Fox, Vat Dyestuffs and Dyeing, Chapman and Hall, London, 1946; Bilik, Novosti Tekniki, 1936, No. 42-43, 42). Vat dyes reduced by aqueous caustic soda and hydrosulphite have been chromatographed on columns of bleached sawdust or disintegrated cotton; the chromatogram was then developed in the colours of the oxidized dyes by means of potassium ferricyanide solution. The rate of flow through paper was found to be too slow (Vickerstaff, loc. cit.). Rao and Shah have found that it is only a mixture of dyes of widely different substantivity to cellulose (e.g. α-benzamidoanthraquinone and dibenzanthrone) that can be separated by this method. A generally applicable method for the separation of vat dyes is to vat the mixture of dyes with aqueous tetraethylenepentamine, \( \text{NH}_2(\text{CH}_2\text{CH}_2\text{NH})_3\text{CH}_2\text{CH}_2\text{NH}_2 \), and hydrosulphite, carry out the adsorption on a column of cellulose powder and develop the chromatogram with aqueous tetraethylenepentamine containing a little hydrosulphite (Belen’kii, Zvodskaya Lab., 1948, 14,

* Based on lectures delivered as the Cooch-Behar Professor at the Indian Association for the Cultivation of Science, Calcutta, on the 5th, 6th and 7th March 1953. The author wishes to thank the Council of the Association for the honour of this appointment. Grateful acknowledgment is also made to the Council of Scientific and Industrial Research under whose auspices the work reviewed in the lectures was carried out.
408, has mentioned that tetraethylenepentamine is a useful solvent for dyes). One part of the organic solvent and four parts of water are employed for both adsorption and development. A clear and remarkably stable vat is obtained when a vat dye is made into a paste with tetraethylenepentamine and treated with aqueous hydrosulphite at room temperature (23 to 30°). Employing these conditions the following mixtures have been separated; the dyes in each mixture are mentioned in the order of increasing adsorbability, the last dye being at the top of the column: (1) Caledon Gold Orange G and dibenzanthrone; (2) Caledon Yellow 3G and Caledon Brilliant Purple 4R; (3) Caledon Yellow 3G, Caledon Jade Green, Caledon Red BNS and dibenzanthrone. One difficulty in this method is that the rate of flow of solvent is very slow; and further, since the leuco compounds of vat dyes have great affinity for cellulose, the movement of the zones in the chromatographic column is extremely slow and elution is practically impossible. Primarily it is the difference in the affinity of the leuco derivatives of the vat dyes for cellulose that enables their chromatographic separation. Elution can therefore be effected by cutting down the affinity of the leuco compounds for cellulose; but a careful balance has to be struck so that the leuco compounds of the vat dyes in the mixture retain sufficient affinity to effect a separation on the cellulose column. Cellosolve is useful as a stripping agent for vat dyes, and the addition of cellosolve to the eluant assists in lowering dye-cellulose affinity and increasing the rate of elution. With increase in the affinity of the leuco derivative of the dye, increase in the amount of cellosolve is necessary to effect complete elution. Thus leuco Caledon Yellow 3G can be eluted with aqueous tetraethylenepentamine containing only 2% on volume of cellosolve, whereas the highly substantive leucodibenzanthrone is not completely eluted even when the eluant contains 50% on volume of cellosolve. Larger percentages of cellosolve cannot be used since turbidity appears. As a general method, 10% of cellosolve can be used and the concentration of cellosolve increased when necessary.

The adsorption sequence of the leuco derivatives of the following compounds was found to be in the given order of increasing adsorbability: 1-aminoanthraquinone and 2-benzamidoanthraquinone, 1-benzamidoanthraquinone, 1:5-bisbenzamidoanthraquinone, 1:4-bisbenzamidoanthraquinone, pyranthrone, and lastly flavanthrone. The leuco compounds of 1-amino- and 2-benzamidoanthraquinone are known to have no affinity for cellulose and hence have the least adsorbability. The order of the adsorbabilities of the remaining five compounds corresponds to the order of the affinity of the leuco derivatives for cellulose as determined by Vickerstaff et al (loc. cit.).

The adsorption sequence of mixtures of vat dyes reported earlier (Rao, Shah and Venkataraman, Current Sci., 1951, 20, 66) also lead to a similar conclusion. It is well known that the leuco derivatives of acylamidonathraquinones have less affinity than those of the vat dyes obtained from condensed polynuclear ring systems; Caledon Yellow 3G (1:5-bisbenzamidoanthraquinone) has less adsorbability than dibenzanthrone or Caledon Brilliant Purple 4R (dichloroisodibenzanthrone). An increase in the number of benzene rings in a polynuclear vat dye generally
increases the affinity of the leuco derivative for cellulose; Caledon Gold Orange G (pyranthrone; 8 rings) has less adsorbability than dibenzanthrone (9 rings). The adsorbability increases in general with the depth of the colour. However, it is found that the leuco derivative of Caledon Jade Green has less adsorbability than that of the dark blue dibenzanthrone; this may be due to the steric hindrance of the methoxyl groups in the Caledon Jade Green molecule.

The affinity of the leuco salts of acylamidoanthraquinones for cellulose

Anthraquinone and simple derivatives such as the aminoanthraquinones are capable of vatting or undergoing reduction with an alkaline reducing agent, usually aqueous caustic soda and sodium hydrosulphite, to form water-soluble alkali salts; but the alkali salts of the reduced (or leuco) compounds have no affinity for cellulose. Deinet in 1909 made the important observation that benzylation of 1-aminoanthraquinone and its derivatives had the remarkable effect of transforming them into vat dyes with adequate affinity for practical dyeing, and several benzamidoanthraquinones (e.g., 1:4-bisbenzamidoanthraquinone; 4:8-dihydroxy-1:5-dianisoylamidoanthraquinone) are in the commercial range of anthraquinonoid vat dyes. However, many fundamental problems concerning the behaviour of anthraquinone derivatives, including the vat dyes, towards alkaline reducing agents and the affinity of the reduction products for cellulose remain unsolved.

Anthraquinone vats readily, but 1:3:5:7-tetramethylanthraquinone is indifferent to alkaline reduction; the corresponding tetracarboxylic acid gives an intense violet-red solution with alkaline reducing agents (Seer, Monatsh., 1912, 33, 535). 1-Benzylaminoanthraquinone gives a light red vat, but 1:5-bisbenzylaminoanthraquinone is not reduced by alkali and hydrosulphite or zinc dust; replacement of the phenyl by carboxyl groups as in (I) again leads to vattability (Seer and Weitzenbock, Monatsh., 1910, 31, 379). When 1:5-bisbenzylaminoanthraquinone is benzyolated, the product (II) remains unvattable. 1:4-Dimethylanthraquinone gives a red solution by alkaline reduction, but 1-methyl-4-p-tolylanthraquinone is insoluble in alkaline hydrosulphite; the corresponding dicarboxylic acid produced by oxidation of the methyl groups by means of nitric acid gives a deep red vat.

During the condensation of 4-halogenoalizarins with aniline and p-toluidine (Joshi, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1951, 34A, 304), 1:2:4-
trianilino- and 1 : 2 : 4-tri-p-toluidinoanthraquinones were obtained, together
with 4-anilino- and 4-p-toluidinoalizarins. It was found that the trianilino deriv­
avatives were insoluble in alkaline hydro sulphite even on boiling. Other substituted
aminoanthraquinones were then prepared and examined. 1-Amino-4-anilino-
anthraquinone gave an orange-red vat. 1 : 4- and 1 : 5-di-p-toluidinoanthra-
quinones were unvattable. The former was prepared in the known manner by
reacting leucoquinizarin with p-toluidine. The 1 : 5-compound was prepared by
Kaufler by boiling 1 : 5-dinitroanthraquinone with excess of p-toluidine (Z. Farben-
ind., 1903, 2, 469) and was described as red-violet crystals from dilute alcohol,
m.p. 200-210° (dec.). Joshi prepared the compound from 1 : 5-dichloroanthra-
quinone by condensation with p-toluidine and obtained violet needles, m.p. 294°.
The introduction of sulphonic groups in the 2'- or 3'-positions in 1 : 4-toluidino-
anthraquinone led to ready vattability. 1-Anilino-4-benzamidoanthraquinone
was vattable, but had no affinity for cellulose. Three factors are apparently
involved in the inability of an anthraquinone derivative to undergo reduction by
aqueous alkali and a reducing agent: steric hindrance of the carbonyl groups by
substitution in the a-positions, hydrogen-bonding between a-substituents and
the 9:10-carbonyl groups, and basicity of the molecule.

The general mechanism of the dyeing process and the structural characteristics
of dye molecules favourable to substantivity towards cellulose have been recently,
discussed (Venkataraman, The Chemistry of Synthetic Dyes, Vol. II, Academic
Press, New York, 1952 ; Vickerstaff, The Physical Chemistry of Dyeing, Oliver
and Boyd, London, 1950). Two types of substantive dyes are known: an elongated
molecule, such as a disazo dye from benzidine, which orients parallel to the cellu­
lose chain, and a large flat planar molecule which can attach itself to two or more
cellulose chains. The size of the molecule is limited on the one hand by the dia-
meter of the channels in the cellulose substrate and on the other by the require­
ments of a diffusion process in which the dye molecules are taken up by the fibre
from an aqueous solution and equilibrium is attained.

The dye Indanthrene Khaki GG, prepared by the carbazolization of the pent-
anthrimide from one molecule of 1 : 4 : 5 : 8-tetrachloroanthraquinone and four
molecules of α-aminoanthraquinone, has a length of over 16A along one axis and
over 17A along the perpendicular axis, assuming the molecule to be planar and to
have four carbazole nuclei. This dye therefore appears to represent the limiting
size of a molecule which has affinity for the cellulose fibre. Experiments are in
progress to build flat dye molecules whose dimensions in one or both the perpen­
dicular axes are more than 17A. The condensation product of 1 : 4 : 5 : 8-tetra-
anthraquinone and four molecules of anthraquinone-2-carboxyl chloride was
first prepared. A scale drawing of this molecule, made on the assumption that the
molecule is completely planar and that the NHCO- group has the same configura­
tion as that in the acetylglycine molecule (Carpenter and Donohue, J. Am. Chem.
Soc., 1950, 72, 2315), indicates the dimensions along two perpendicular axes to be
13.6A and 27.2A. The compound dyes cotton a dull violet shade, and qualitatively
has pronounced affinity for cellulose.
The absorption spectra of the leuco derivatives of anthraquinone, 1- and 2-aminoanthraquinones and certain acylamidoanthraquinones

Since vat dyes have affinity for cellulose only in the form of their leuco salts, the absorption spectra of the leuco derivatives may give useful data on the nature of these leuco salts and their affinity for cellulose. The absorption spectra of the leuco derivatives of vat dyes have not been reported so far, but Waters (J. Soc. Dyers Colourists, 1950, 69, 554; Rowe, Colour Index, Society of Dyers and Colourists, Bradford, 1924, lists the wave lengths of absorption maxima of the leuco derivatives of a few vat dyes) has stated, without giving the actual data, that the spectra of the leuco derivatives of benzamidoanthraquinones are characterized by two absorption peaks with maxima in the yellow and blue regions. One difficulty in the determination of the spectra of the leuco derivatives is their ready oxidizability, but this can be overcome by the addition of alcohol or dioxane to the leuco solution.

Rao (Ph.D. Thesis, Bombay University, 1953) has determined the absorption spectra of the leuco derivatives of anthraquinone, 1- and 2-aminoanthraquinones and a few acylamidoanthraquinones, and Table I lists the wave lengths and intensities of the absorption maxima. The spectra of these leuco derivatives are similar in nature, having two regions of absorption maxima, one at about 425 m$_\mu$ (A band) and the other at about 155 m$_\mu$ (B band). The spectra are reported between 400-600 m$_\mu$, since the solution of caustic soda and sodium hydrosulphite is not transparent below 380 m$_\mu$.

The spectrum of anthraquinone in the reduced state shows one sharp peak of high intensity at 420 m$_\mu$ and another broad diffuse band at 506 m$_\mu$. On the introduction of an amino group in the 1- and 2-positions, no major change in the nature of the spectra of the reduced compounds is observed, while the oxidized compounds behave very differently, profound changes in the absorption spectra occurring when anthraquinone is substituted by an amino group in the 1- and 2-position (Suthan- kar, Ph.D. Thesis, University of Bombay, 1947; see also Morton and Earlam, J. Chem. Soc., 1941, 159). This is understandable if we associate the colour of the aminoanthraquinones with the contribution of low energy structures such as (I)

(I) \[ \text{O}^- \text{NH}_2 \text{O} \]

and (II) to the excited states of the molecules. In the alkaline solutions of the leuco or dihydro derivatives of anthraquinone and the aminoanthraquinones, the absorption spectra are those of the anions of anthrahydroquinones. The negatively charged oxygen atoms inhibit the contribution of structures involving
Table I

Wave lengths and intensities of absorption maxima of the leuco derivatives of anthraquinone, 1- and 2-aminoanthraquinone, and acylamidoanthraquinones

<table>
<thead>
<tr>
<th>Leuco derivative of</th>
<th>A band λ max. in μ</th>
<th>log ε</th>
<th>B band λ max. in μ</th>
<th>log ε</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anthraquinone</td>
<td>420</td>
<td>8,700</td>
<td>506</td>
<td>3,130</td>
</tr>
<tr>
<td>1-Aminoanthraquinone</td>
<td>430</td>
<td>12,820</td>
<td>499</td>
<td>4,709</td>
</tr>
<tr>
<td>2-Aminoanthraquinone</td>
<td>418</td>
<td>11,920</td>
<td>510</td>
<td>4,340</td>
</tr>
<tr>
<td>1-Benzamidoanthraquinone</td>
<td>425</td>
<td>14,800</td>
<td>532</td>
<td>6,920</td>
</tr>
<tr>
<td>2-Benzamidoanthraquinone</td>
<td>485</td>
<td>9,770</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>1:4-Bisbenzamidoanthraquinone</td>
<td>488</td>
<td>18,800</td>
<td>528</td>
<td>6,920</td>
</tr>
<tr>
<td>1:5-Bisbenzamidoanthraquinone</td>
<td>437</td>
<td>9,770</td>
<td>545</td>
<td>4,190</td>
</tr>
<tr>
<td>Bis-α-anthraquinonylamide of isophthalic acid</td>
<td>424</td>
<td>22,610</td>
<td>544</td>
<td>11,230</td>
</tr>
<tr>
<td>Bis-α-anthraquinonylamide of terephthalic acid</td>
<td>424</td>
<td>31,430</td>
<td>542</td>
<td>15,800</td>
</tr>
<tr>
<td>Bis-α-anthraquinonylamide of azobenzene-4:4'-dicarboxylic acid</td>
<td>426</td>
<td>30,380</td>
<td>535</td>
<td>16,400</td>
</tr>
<tr>
<td>Bis-α-anthraquinonylamide of adipic acid</td>
<td>424</td>
<td>28,440</td>
<td>514</td>
<td>11,320</td>
</tr>
<tr>
<td>Bis-α-anthraquinonylamide of sebacic acid</td>
<td>424</td>
<td>26,580</td>
<td>512</td>
<td>10,470</td>
</tr>
</tbody>
</table>

positively charged nitrogen, and as a result there is little or no spectral interaction between the amino group and the anthraquinone nucleus as in structures (I) and (II). The amino group will then show presumably an effect like the anilinium ion or the amino group in 2 : 6-dimethylaniline, because of restricted electron mobility. The A band of leucoanthraquinone is shifted to 430 μ in leuco 1-aminoanthraquinone; in leuco 2-aminoanthraquinone there is hypsochromic shift to 418 μ. The B band of the leucoanthraquinone spectrum at 506 μ undergoes reverse changes, the 1-amino compound showing a hypsochromic shift, and the 2-amino compound a bathochromic shift.

The introduction of one or more benzamido groups in the α- or β-position does not effect any change in the nature of the spectrum, except for shifts in the wave lengths of maximum absorption. The spectrum of leuco 1-benzamidoanthraquinone shows that the A band is at about 425 μ, as in the spectrum of leuco
1-aminoanthraquinone, and has the same order of intensity. The B band, which does not show an appreciable shift in the 1-amino compound as compared with anthraquinone, has shifted considerably to the longer wave length side and has a slightly greater intensity than the corresponding band for leuco 1-aminoanthraquinone. The A band of leucoanthraquinone shows a much greater bathochromic shift in the 2-benzamido derivative than in the 1-benzamido derivative, but there is little increase in intensity. There is no distinct B band in the spectrum of leuco 2-benzamidoanthraquinone corresponding to the B band of leucoanthraquinone, although there is a flat absorption in this region, which shows the presence of this band. In leuco 2-benzamidoanthraquinone the A band, which does not show any shift in leuco 2-aminoanthraquinone as compared with leucoanthraquinone, shows a considerable shift and has about the same order of intensity. Thus it is principally one of the two bands (A or B) of leucoanthraquinone which shifts on substitution of an amino group in the 1- or 2-position; on benzoylation, the position of the displaced band remains nearly the same, but the second band undergoes a bathochromic shift. The further introduction of a benzamido group in the 4- or 5 position of 1-benzamidoanthraquinone decreases the intensity of absorption, this decrease being considerable in the case of leuco 1:5-bisbenzamidoanthraquinone; the wave lengths of the absorption maxima are also shifted, although not very significantly.

The spectra of the leuco derivatives of the bis-a-anthraquinonylamides of a few aliphatic dicarboxylic acids indicate the extent of insulation effected by the alkyylene or arylene groups in these compounds. It is found that there is no appreciable change in the spectra in comparison with the spectrum of leuco 1-benzamidoanthraquinone as far as the positions of the maxima are concerned. The A band of 1-benzamidoanthraquinone is practically at the same position in all the compounds, and the B band also does not show any significant shift. Talavdekar (Ph.D. Thesis, University of Bombay, 1951) has discussed the spectra of acetanilide and benzanilide and has drawn attention to the lack of interaction between the two benzene rings in benzanilide, indicating the insulating effect of the -NHCO- group. Moreover, it has been shown that this insulating effect depends on the character of the intervening groups and also on the electron mobility of the chromophores which are bridged by the -NHCO- group (Braude et al, J. Chem. Soc., 1946, 45, 47; see also Cromwell and Watson, J. Org. Chem.; 1949, 14, 413; Venkataraman, The Chemistry of Synthetic Dyes, Vol. I, Academic Press, New York, 1951).

When two 1-benzamidoanthraquinone nuclei are joined through meta positions of the phenyl ring, the insulating effect of the -NHCO- group is clearly observed, the spectrum of leuco 1-benzamidoanthraquinone (ε ×2) being nearly identical with that of the bis-a-anthraquinonylamide of isophthalic acid. In the terephthalic and azobenzenedicarboxylic acid derivatives, the intensity is much more than twice that of leuco 1-benzamidoanthraquinone, showing thereby that there is apparently some electronic interaction between the two aminoanthraquin-
one residues. The insulating effect is almost complete in the adipic acid derivative and the intensity is exactly twice that of leuco 1-benzamidoanthraquinone; a further increase of -CH₂-groups between the -NHCO-groups as in the sebacic acid derivative has no effect on the spectrum.

**Steric hindrance in dibenzanthronyls and dibenzanthrones**

There are many examples of the effects of steric hindrance to the planarity of organic molecules on their absorption spectra. A common influence of such steric hindrance is a reduction in the intensity of maximum absorption, usually but not invariably accompanied by a hypsochromic shift in the long wave length absorption. Changes in the absorption spectra as a result of steric hindrance to planarity can be related to its interference with the resonance of the molecule either in the ground or excited states. Steric hindrance in the excited state decreases the resonance stabilization of that state and increases the transition energy, leading therefore to a hypsochromic shift in the absorption spectrum. On the other hand, steric hindrance in the ground state decreases the energy of transition because of the reduced resonance stabilization of the ground state, and the consequence is a bathochromic shift in the absorption spectrum. Brooker et al, (Chem. Revs., 1947, 41, 325), while studying the effects of steric hindrance to planarity of dye molecules, have discussed two distinct types of behaviour. In the great majority of cases the compounds studied are characterized by a single low energy resonance structure. As a rule the crowding substituent does not affect this single dominant structure, which is usually benzenoid and contributes principally to the ground state, but affects other higher energy structures, which contribute mostly to the excited states of the molecule, resulting in a hypsochromic shift of the spectrum. If the molecule, however, can be represented by two identical structures of low energy, the effect of steric hindrance will be to decrease the contribution of these identical structures to the ground state of the molecule, thereby leading to a bathochromic shift.

The effect of steric hindrance to the planarity of an aromatic ring system may be of varied character. In the simplest o-disubstituted benzene derivatives, the benzene nucleus, due to its high energy of resonance stabilization, will remain planar and the substituent groups will twist about the connecting bond to attain a state of least strain within the molecule.

The usual effect of introducing two substituent groups in such positions as to make them sterically hinder each other is to twist the substituent group around the bond connecting the group to the parent nucleus, or to twist two parts of the molecule around a bridging linkage. The effect of introducing two crowding substituents in vicinal positions in a polynuclear aromatic ring system, which has an overriding tendency to remain planar, does not appear to have been studied. Table II gives the wave lengths and intensities of the maxima in the absorption spectra of dibenzanthrone (I; R = H), 16 : 17-dihydroxydibenzanthrone (I; R = OH), 16 : 17-dimethoxydibenzanthrone (I; R = OMe), 3 : 12-dimethoxydibenzathrone (II),
benzanthrone, 9-methoxybenzanthrone, 3 : 3'-dibenzanthronyl (IV) and 4 : 4'-
dibenzanthronyl (V). The spectrum of 16 : 17-dihydroxydibenzanthrone shows a
slight decrease in the intensity and a very insignificant increase in the wave-length

![Diagram](https://via.placeholder.com/150)

of maximum absorption, whereas the 16 : 17-dimethoxy compound exhibits a con­siderable decrease in intensity and a large bathochromic shift in comparison with
the spectrum of dibenzanthrone. The bathochromic shift of the spectrum as we
pass from dibenzanthrone to 16 : 17-dimethoxydibenzanthrone may be due to two
reasons. The first obvious reason is the introduction of the two auxochromic metho­xyl groups; but the methoxyl groups can exercise their normal auxochromic effect
only if they can enter into electronic interaction with the dibenzanthrone ring system
which in turn is contingent on the coplanarity of the methoxyl groups and the diben­zanthrone system. Since there is no pronounced shift of the spectrum on the
introduction of two hydroxyl groups in the 16:17-positions, the shift in the spectrum
of the 16 : 17-dimethoxy compound may be mainly due to the effect of steric hind­rance of the vicinal methoxyl groups. This is also supported by the fact that
there is a considerable decrease in the intensity of maximum absorption.

We have no data on the planarity of dibenzanthrone and its derivatives. How­ever, the larger the number of benzene rings in a polynuclear aromatic ring
system, the larger is the resonance stabilization energy of the molecule and one
effect of this increased resonance will be an increased tendency for the ring system
to retain planarity. It is therefore reasonable to assume that the dibenzanthrone
molecule is planar. Disubstitution at the 16 : 17-positions of dibenzanthrone
will lead to steric interference between the two substituent groups. A scale drawing
of the 16 : 17-dimethoxydibenzanthrone molecule clearly shows the overlap of the
van der Waals radii of the vicinal methoxyl groups. If the molecule is constructed
with Fisher-Hirschfelder-Taylor models, the interference is less obvious, but as
Jones (J. Am. Chem. Soc., 1943, 65, 1815) has pointed out, very great care has to be
taken in making deductions from these models in border line cases.

One effect of steric hindrance between the two substituent methoxyl groups
in the 16 : 17-positions of dibenzanthrone can be to twist the methoxyl groups out
of the plane of the aromatic ring system around the bonds connecting the substi­tuent groups to the ring system. If this happened, the absorption spectrum of the
TABLE II

Wave-lengths and intensities of absorption maxima of dibenzanthrone and certain related compounds

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\lambda_{\text{max.}}$ in $\mu m$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max.}}$ in $\mu m$</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\lambda_{\text{max.}}$ in $\mu m$</th>
<th>$\varepsilon_{\text{max}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dibenzanthrone</td>
<td>642</td>
<td>63,810</td>
<td>365</td>
<td>15,540</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>594</td>
<td>44,810</td>
<td>355</td>
<td>15,540</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>16:17-Dihydroxydibenzanthrone</td>
<td>647</td>
<td>47,600</td>
<td>395</td>
<td>16,000</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>16:17-Dimethoxydibenzanthrone</td>
<td>685</td>
<td>37,000</td>
<td>400</td>
<td>15,380</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>3-12-Dimethoxydibenzanthrone</td>
<td>650</td>
<td>23,160</td>
<td>472</td>
<td>28,800</td>
<td>463</td>
<td>28,800</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>285</td>
<td>7,940</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>276</td>
<td>8,130</td>
</tr>
<tr>
<td>Benzanthrone</td>
<td>394</td>
<td>10,000</td>
<td>306</td>
<td>8,510</td>
<td>254</td>
<td>20,890</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>285</td>
<td>7,940</td>
<td>220</td>
<td>34,670</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>276</td>
<td>8,130</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>9-Methoxybenzanthrone</td>
<td>420</td>
<td>7,760</td>
<td>315</td>
<td>9,930</td>
<td>260</td>
<td>25,120</td>
</tr>
<tr>
<td></td>
<td>364</td>
<td>3,310</td>
<td></td>
<td></td>
<td>231</td>
<td>34,670</td>
</tr>
<tr>
<td></td>
<td>361</td>
<td>3,390</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>365.5</td>
<td>3,310</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3:3'-Dibenzanthronyl</td>
<td>415</td>
<td>54,950</td>
<td>307</td>
<td>38,020</td>
<td>253</td>
<td>83,180</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>288</td>
<td>42,660</td>
<td>230</td>
<td>162,200</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>276</td>
<td>40,740</td>
<td>213</td>
<td>177,800</td>
</tr>
<tr>
<td>4:4'-Dibenzanthronyl</td>
<td>411</td>
<td>69,500</td>
<td>323</td>
<td>46,770</td>
<td>255</td>
<td>126,500</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>313</td>
<td>54,480</td>
<td>228</td>
<td>195,000</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>284</td>
<td>37,840</td>
<td>214</td>
<td>214,900</td>
</tr>
</tbody>
</table>

The dimethoxy compound must be similar to that of dibenzanthrone, because of the absence of resonance interaction between the ring system and the substituent groups. However, this is not true since the spectrum of the dimethoxy derivative is markedly different from that of the parent dibenzanthrone. A second possibility, that the methoxyl groups tend to twist the whole molecule out of planarity, is highly improbable, because the high energy of resonance stabilization of the dibenzanthrone molecule will not allow such distortion. The most probable explanation seems to be that, on account of the high energy of resonance stabilization, the polynuclear ring system of dibenzanthrone undergoes a slight adjustment of the bond angles and remains coplanar with the two methoxyl groups. Extra energy is needed to force the methoxyl groups into the same plane as the ring system in this manner. Westheimer and Mayer (J. Chem. Phys., 1946, 14, 733) have made theoretical calculations regarding the rate of racemization of sterically hindered (optically active) diphenyl derivatives. They assume, as suggested by Hill, that the energy of a strained molecule is distributed among many bonds and by no-
means concentrated in the energy of repulsion of the groups. On this basis they calculate the activation energy of racemization which is the excess energy of the sterically hindered planar configuration over the non-hindered planar configuration. This excess energy, they show, depends upon the angle between the hindered substituent and the phenyl ring. They find, however, that the true activation energy can be found by subtracting the resonance energy from the calculated energy of activation. Since it is assumed that the 16:17-dimethoxydibenzanthrone molecule remains planar by adjustments in bond lengths and angles, the true activated complex state may be identified with the ground state, the ground state thus being raised from its normal level. The small decrease in the intensity, as well as a small increase in the wave length of maximum absorption in the spectrum of 16:17-dihydroxydibenzanthrone, as compared to the greater reduction in absorption intensity and a large bathochromic shift of the longest wave length band of dimethoxydibenzanthrone, clearly indicates the more pronounced effects of steric hindrance in the dimethoxy compound in comparison with the dihydroxy analogue.

Among the spectra of the alkyl derivatives of various polycyclic aromatic hydrocarbons reported so far, it is only the data for the methylchrysenes that provide a similar example. Brode and Paterson (J. Am. Chem. Soc., 1941, 63, 3252) have shown that among the methylchrysenes the greatest bathochromic shift is found in the 4- and 5-methylchrysenes, although by analogy with 1:2-benzanthracene the greatest bathochromic shift was predicted for 5- and 6-methylchrysenes (Jones, J. Am. Chem. Soc., 1941, 63, 133; see also Chem. Revs., 1943, 32, 1), and they suggest that this shift is due to steric hindrance between the methyl groups and the hydrogen atoms in the 4- and 5- positions and consequent distortion of the planar nature of the molecule. Such hindrance will be greatly enhanced in 4:5 dimethylchrysenes (III), the absorption spectrum of which shows changes of greater magnitude. From a scale drawing of the 4:5-dimethylchrysenes molecule, Newman has suggested three alternatives for the location of the methyl groups in such aromatic ring systems: (1) the methyl groups are coplanar with the ring system but bent away from one another; (2) the aromatic rings are distorted; or (3) the ring system and the methyl groups are not in the same plane. Newman considers the last as the most probable explanation (J. Am. Chem. Soc., 1940, 62, 2295). However, in the light of the present treatment of the absorption spectrum of dimethoxydibenzanthrone, it is suggested that the dimethylchrysenes molecule as a whole, by adjustments in the bond lengths and angles, is coplanar, and since the energy required for achieving coplanarity decreases the energy of resonance stabilization, the potential energy of the molecule is increased, resulting in a greater bathochromic shift in 4:5-dimethylchrysenes in comparison with the isomeric dimethyl chrysenes which were examined by Jones (loc cit).
The spectrum of 3:12-dimethoxydibenzanthrone (II) shows a small bathochromic shift and a considerable decrease in the intensity of maximum absorption in comparison with dibenzanthrone. In the case of 16:17-dihydroxy- and dimethoxydibenzanthrone the decrease in the intensity of maximum absorption has been associated with the steric hindrance between the vicinal substituent groups; but no such hindrance occurs in the 3:12-dimethoxy compound, and the decrease in the intensity of absorption must be due to the specific effect of substitution in the 3- and 12-positions. Comparing the absorption spectra of benzanthrone and 9-methoxybenzanthrone, the methoxy substituent effects a bathochromic shift of the benzanthrone spectrum, simultaneously with a considerable decrease in the intensity of maximum absorption.

In connection with the present study of dibenzanthrone and its derivatives the spectra of 3:3'- and 4:4'-dibenzanthronyls (IV and V) were determined. There is a remarkable degree of resemblance between the spectra of benzanthrone and the 3:3'- and 4:4'-derivatives; comparing the latter with benzanthrone there is no change at all in the nature of the curve and the bathochromic shift with respect to benzanthrone is of the order which an alkyl substituent may effect. The intensities of the absorption maxima of the dibenzanthronyls are approximately double those of benzanthrone. The complete similarity between the spectra of benzanthrone and the two dibenzanthronyls indicates that there is no new chromophoric system formed and that there are no possibilities of extended conjugation across the C-C bond connecting the two benzanthronyl residues, because of the effect of steric hindrance of the hydrogen atoms in the 4:4'- and 3:3'-positions. These two dibenzanthronyls can be considered to be derivatives of 1:1'-dinaphthyl which is known to exhibit steric hindrance due to the 8:8'-hydrogen atoms interfering with each other (Friedel et al., J. Am. Chem. Soc., 1948, 70, 199).

The constitution of a dinitrodibenzanthrone

Nitration of dibenzanthrone with nitric acid in acetic acid, nitrobenzene or chloracetic acid (the last being used in one of the I.G. processes) gives a mixture of mono- and dinitrodibenzanthrones, which forms a blue vat with alkaline hydrosulphite and dyes an unlevel green (Indanthrene Green B) of no practical value. Since the nitro groups are reduced during vatting, the product on the fibre is a mixture of aminodibenzanthrones. When the green dye is oxidized on the fibre with hypochlorite, a deep fast black is obtained. Nitrodibenzanthrone is marketed under the name of Indanthrene Black B, Caledon Black NB, etc., and is an important and largely used dye. The position of the nitro groups and the constitution of the black dye produced on the fibre are still undetermined. The nitrogen content
(4.0%) of purified Caledon Black 2B indicates that it is approximately a 50% mixture of mononitro and dinitro derivatives (Calc. N, 2.7% and 5.1% respectively).

The available data on the constitution of dinitrodibenzanthrone, obtained by nitration of dibenzanthrone, are conflicting and inconclusive. Maki (J. Soc. Chem. Ind., Japan Suppl. binding, 1935, 38, 710B) has suggested that the nitro groups are in the 16:17-positions (I) since the corresponding diamino compound, on oxidation with chromic acid and sulphuric acid, gave first a brown alkali-soluble product (II) and ultimately a dicarboxylic acid (III); the proposed structures (II and III), however, were based mainly on nitrogen estimation. On the assumption of the 16:17-orientation for the nitro groups, Maki concluded that the black dye, produced by the hypochlorite oxidation of the diamine on the fibre, is the pyridazine derivative (IV). Maki considered that the structure (IV) for the black dye was supported by its reversion to green on treatment with alkaline hydrosulphite, followed by air oxidation; the green shade again changed to black on treatment with hypochlorite. However, the pyridazine ring is unlikely to undergo reductive fission by the usual vatting process; and if diaminodibenzanthrone is formed by alkaline reduction of the black dye, the structure of the latter is probably that of a polyazo compound formed by oxidative polymerisation of diaminodibenzanthrone.

Other evidence cited by Maki in favour of the 16:17-orientation of the nitro groups in dinitrodibenzanthrone cannot be regarded as valid. One example is his generalization that, in contrast to the blue vat formed by dinitrodibenzanthrone, all dibenzanthrone derivatives substituted in the anthrone rings give violet vats, although he had only two or three dibenzanthrone derivatives in his hands for comparison. It may be conceded that the green colour of 16:17-dihydroxy- and dimethoxydibenzanthrone lends some support to Maki's structure for dinitro-
dibenzanthrone on grounds of analogy, but there is no reason to conclude that other diamino- and dihydroxydibenzanthrones (e.g. the 7:8-derivatives) cannot be green in colour.

Bennett, Pritchard and Simonsen (J. Chem. Soc., 1943, 31) obtained a nitrogen-containing carboxylic acid by the chromic acid oxidation of dinitrodibenzanthrone, and this rules out the 16:17-orientation (I), since the oxidation of benzanthrone leads to anthraquinone-1-carboxylic acid. However, Bennett et al. obtained 0.5 g. of dinitrodianthraquinonyl-1:1’-dicarboxylic acid from 6 g. of dinitrodibenzanthrone and they did not disprove the formation of dianthraquinonyl-1:1’-dicarboxylic acid, which might have been eliminated during purification. By analogy with other substitution reactions in the benzanthrone series, they regard dinitrodibenzanthrone as the 3:12-compound. Oxidation gave a dinitrodianthraquinonyl dicarboxylic acid, which on reduction and deamination via the diazonium salt gave 2:2’-dianthraquinonyl-1:1’-dicarboxylic acid, identical with the product of oxidation of dibenzanthrone itself.

The products of the oxidation of commercial Caledon Black 2B, purified to remove water-soluble material, have been examined by Pandit (Ph.D. Thesis, Bombay University). In addition to a dinitrodianthraquinonyl dicarboxylic acid, an acid free from nitrogen was isolated. Decarboxylation of the crude acid gave 2:2’-dianthraquinonyl, thus demonstrating the presence in Caledon Black 2B of either the parent dibenzanthrone or a nitrated dibenzanthrone containing one or two nitro groups in the 15, 16, 17 or 18-positions.

3:12-Diaminodibenzanthrone (V) has now been synthesized by two routes (Pandit, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1950, 32A, 39) and it has been found to be different from the reduction product of dinitrated dibenzanthrone, which therefore cannot have the nitro groups in the 3:12-positions as suggested by Bennett et al.

Dinitration according to the method of Maki, Nagai and Hayashi (J. Soc. Chem. Ind., Japan, Suppl. binding, 1935, 38, 710B) does not give a homogeneous or
crystalline dinitro derivative. It is necessary to use dibenzanthrone, free from isodibenzanthrone. Maki purifies the dye by vatting and by treatment with boiling chlorobenzene; Bennett et al (J. Chem. Soc., 1943, 31) extract crude dibenzanthrone successively with pyridine and water in a Soxhlet, crystallize the residue from cresol, and repeat the crystallization until the product has a constant magnetic susceptibility. Pandit prepared pure dibenzanthrone from 3 : 3'-dibenzanthronyl, m.p. 410-12°, by cyclization with methanolic caustic potash in presence of glucose; the dye was then repeatedly crystallized from nitrobenzene. Nitration of dibenzanthrone, prepared in this manner, in nitrobenzene solution proceeds readily, and the greyish brown by-product (apparently a hydroxydibenzoanthrone), to which Maki and Bennett et al. refer, was not formed. Nitration of benzanthrone in acetic acid gave a mixture of the 2- and 3-nitro compounds, and nitration of 3 : 3'-dibenzoanthronyl in acetic acid gave an intractable mixture; on the other hand nitration of benzanthrone, 3-bromobenzanthrone and 3 : 3'-dibenzoanthronyl in nitrobenzene solution proceeded smoothly and homogeneous products were obtained. Nitrating pure dibenzanthrone in nitrobenzene solution with a slightly larger amount of nitric acid than that required for dinitration, the nitrogen content of the product indicated a mixture of mono- and dinitrodibenzanthrones. When nitration was carried out with a large excess of fuming nitric acid (d 1.55) in nitrobenzene at 50 to 55° a crystalline and apparently homogeneous trinitrodibenzanthrone, analysing correctly, was obtained. However, oxidation showed that the substance was a mixture, since two dianthraquinonyl dicarboxylic acids were obtained. One of the acids analysed for a dinitro derivative. One of the constituents of the trinitrated dibenzanthrone therefore carried a nitro group in the 15- or 16-position, probably the latter on grounds of analogy with the oxidation of 4 : 4'-dibenzoanthronyl and dibenzanthrone to 16 : 17-dihydroxydibenzoanthrone. The second dianthraquinonyl dicarboxylic acid analysed for three nitro groups. The dyeing properties of the trinitrated dibenzanthrone were similar to those of the commercial nitrated dibenzanthrones, and it may be reasonably assumed that two nitro groups in dinitrated dibenzanthrone and the trinitrated dibenzanthrone are in the same positions.

By assuming that one or both the nitro groups in dinitrodibenzanthrone are in the 7 : 8-positions it may be possible to reconcile the experimental results of both Maki and Bennett et al, the former obtaining the oxidation products (II) and (III) from dianiminodibenzanthrone and the latter a dinitrodianthraquinonyl dicarboxylic acid by oxidation of dinitrodibenzanthrone. Methods for the synthesis of 7 : 8-dinitro- and diamino-dibenzanthrone are therefore being investigated by Malhotra. These positions in dibenzanthrone correspond to the 5-position in benzanthrone and 5-substituted benzanthrones have the additional interest that the only 5-substituted derivative to which a reference can be found in the literature is 5-nitrobenzanthrone (VI), prepared by Boyes, Grieve and Rule (J. Chem. Soc., 1938, 1841) by a tedious route. Methyl 8-bromo-3-nitro-1-naphthoate was condensed with methyl o-iodobenzoate to form 3-nitro-8-(o-carbomethoxyphenyl)-1-naphthoate; cyclization with sulphuric acid gave 5-nitrobenzanthrone-11-carboxylic acid, which was finally decarboxylated to 5-nitrobenzanthrone. This
compound (VI) has now been prepared by Malhotra by taking advantage of the powerful directing influence of the acetamido group. Nitration of 4-acetamido-benzanthrone with fuming nitric acid in glacial acetic acid gave 4-acetamido-5-nitro-benzanthrone (VII), which was deacetylated to 4-amino-5-nitrobenzanthrone. The adjacent orientation of the amino and nitro groups was established by reduction to a diamine, which condensed with phenanthraquinone to a quinoxaline and with benzoyl chloride to a phenylimidazole. Deamination of 4-amino-5-nitro-benzanthrone by heating the diazonium sulphate with alcohol yielded 5-nitrobenzanthrone (VII), from which 5-amino- and 5-chlorobenzanthrone were then prepared by the usual methods. The position of the chlorine atom was confirmed by oxidation to 3-chloroanthraquinone-1-carboxylic acid, which was prepared by Pandit from 1-amino-3-chloroanthraquinone via the diazonium salt and nitrile. Malhotra has also converted 4-amino-5-nitrobenzanthrone into 4-iodo-5-nitrobenzanthrone, and the latter into 5 : 5'-dinitro-4 : 4'-dibenzanthronyl by the action of copper powder in nitrobenzene. So far it has not been possible to cyclize this dibenzanthronyl to 7 : 8-dinitrodibenzanthrone or the corresponding diamine.

The constitution of the products of the Skraup reaction on \( \beta \)-aminoanthraquinone

By the action of glycerol and sulphuric acid on \( \beta \)-aminoanthraquinone in the absence of an oxidizing agent Bally (1905) obtained as the major product a "benzanthronequinoline," to which he assigned the structure (I); he also isolated 1-azanaphthacene-6 : 11-dione (III). Bally proved the angular orientation of the pyridine ring in (I) by the fact that the same compound was obtained by the action of glycerol and sulphuric acid on 4-azabenzenzanthraquinone (IV), which Graebe had prepared from Alizarin Blue (the product of the Skraup reaction on 8-aminoalizarin) by distillation with zinc dust, followed by chromic acid oxidation. It was shown recently (Pandit, Tilak and Venkataraman, *Proc.*
Indian Acad. Sci., 1950, 32, 39) that Bally’s “benzanthronequinoline” is constituted as (II) and not as (I), since it is identical with the product of the Skraup reaction on 9-aminobenzanthrone; this amine, obtained by Copp and Simonsen (J. Chem. Soc., 1942, 209) in low yield by a lengthy synthesis, can be prepared by nitration of 3-bromobenzanthrone, reduction and debromination with palladium on calcium carbonate activated by hydrazine hydrate in methanolic caustic potash (Busch, Weber and Zink, J. prakt. Chem., 1940, 155, 163).

Cyananthrene (Indanthrene Dark Blue BT; Bally and Isler, 1904), prepared by alkali fusion of Bally’s benzanthronequinoline (II), is no longer used commercially. By analogy with the formation of dibenzanthrone (violanthrone) from benzanthrone, but without a re-examination of the preparation and properties of Cyananthrene, Pandit, Tilak and Venkataraman assigned to the dye the structure (V). Bradley and Sutcliffe (J. Chem. Soc. 1952, 2118) repeated the preparation of Cyananthrene with a slight modification of Bally’s conditions, and submitted the crude product (16 g.) to a process of purification, involving extraction with 1:2:4-trichlorobenzene and chromatography of the soluble fraction. A minute amount of a dye was thus isolated, which exhibited in conc. sulphuric acid solution an absorption spectrum corresponding to an isodibenzanthrone (isoviolanthrone), and not to a dibenzanthrone derivative. They then concluded that Cyananthrene has the isodibenzanthrone structure (VI). It would appear, however, that the presence of (V) in crude Cyananthrene has not been excluded by Bradley and Sutcliffe’s work, which has only provided evidence of the fact that crude Cyananthrene contains a substance which probably has the isodibenzanthrone structure (VI). Bradley and Sutcliffe attempted to prepare a dye with the authentic structure (V) by the action of copper on 3-bromopyridino (3':2':8:9):benzanthrone (3-bromo derivative of II), but the only isolable product was the debrominated pyridinobenzanthrone. Other methods for the synthesis of (V) are also being explored. Pandit found that no crystalline material could be
isolated from the product of the Skraup reaction on 9:9'-diamino-3:3'-dibenzanthronyl, which he prepared by the nitration and reduction of 3:3'-dibenzanthronyl. By the action of palladized calcium carbonate, hydrazine and methanolic caustic potash on the 3-bromo derivative of (II) Malhotra has obtained a dark blue, difficultly vattable compound, which is under examination. He is also attempting the conversion of (II) into (V) in two stages via the 3:3'- or 4:4'-dibenzanthronyl derivative.

When the product of the action of glycerol and sulphuric acid on β-aminanthraquinone is repeatedly crystallized from xylene, pure (II), m.p. 251-2°, is obtained in about 20% yield. By evaporation of the xylene mother liquor and fractional precipitation of the residue from sulphuric acid 1-azanaphthacene-6:11-dione can be obtained. Chromatographic analysis of a benzene solution of the residue on alumina leads to five compounds, one of which (m.p. 234-5°) has the structure (VII), since it is identical with the product of the Skraup reaction on 4-aminobenzanthrone.

Degradation of anthraquinonoid vat dyes

Methods of degradation of anthraquinonoid vat dyes appear to have been little investigated, although they are of obvious interest in determining their constitution and may also yield useful data on the relative stability of the ring systems by the fusion of which to anthraquinone or anthrone residues various types of vat dyes are obtained. By the prolonged action of chromic acid in acetic acid solution on indanthrone Scholl and Edlbacher (Ber., 1911, 44, 1727) obtained phthalic anhydride and 2:3-dihydroxy-1:4-diazabenz(a)anthraquinone (oxalyl-1:2-diaminoanthraquinone; I). For the purpose of locating the chlorine atoms in dichloroindanthrones prepared by different methods (cf. Bedekar, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1948, 28A, 236) Jayaraman has prepared monochloro derivatives of (I), both by oxidation of the dichloroindanthrones and
by the condensation of chloro derivatives of 1:2-diaminoanthraquinone and oxalic acid. Joshi (Ph.D. Thesis, Bombay University, 1952) has studied the degradation of anthraquinoneacridone (naphth [2, 3-c] acridone-5:14-dione; II), 9:10-benzanthraquinoneacridone (Indanthrene Red RK; Caledon Red BN; III) and anthraquinone-bisacridone (Indanthrene Violet RN; Caledon Violet XBN; IV). The chromic acid treatment by which Scholl degraded indanthrone to (I) left the anthraquinoneacridones unaffected. When a large excess of chlorine is passed into an acetic acid solution of a-aminoanthraquinone, the anthraquinone nucleus breaks down and the final products are phthalic acid and tetrachlorophenol (Fries and Auffenberg, *Ber.*, 1920, 53, 732); similar treatment of (III) resulted only in chlorination of the dye. Oxidation with nitric acid has often been employed for the degradation of hydroxyanthraquinones. Allen, Frame and Wilson (*J. Org. Chem.*, 1941, 6, 732) found that the action of boiling dilute nitric acid on arylaminoanthraquinones was to effect hydrolysis, and they used the method for determining the constitution of certain acid anthraquinone dyes; thus Toluidine Blue and Toluidine Green gave 1:4:5:8-tetrahydroxyanthraquinone. Solway Sky Blue BS (1-amino-2-bromo-4-^p^-toluidinoanthraquinone-2'-sulphonic acid) gave 2-bromoquinizarin, but the acridone (III) gave only a trinitro derivative, which dyed cotton a grey shade from a violet vat.

It is well known that hydroxyanthraquinones break down to benzoic acid derivatives by fusion with caustic potash at about 250°. When (II) was fused with caustic potash at 210° the products were benzoic acid and acridone-3-carboxylic acid (V), characterized as the methyl ester, m.p. 319°. The 4-acid is known, but not the 3-acid (V), and for comparison with the degradation product of (II) it was synthesized from 3-aminoacridone. The same acid (V), together with an unidentified phenolic substance, was obtained by the alkali fusion of the bisacridone (IV). Alkali fusion of (III) took a similar course, the products being benz (a)-acridone-9-carboxylic acid (VI) and benzoic acid. The unknown acid (VI) was
synthesized by the Ullmann condensation of 2-chloro-4-cyanobenzoic acid with 3-naphthylamine, followed by cyclization to the acridone and hydrolysis of the nitrile group.

1:9-Pyrazolanthrone (VII) has recently been shown to undergo fission at the carbonyl group by heating with caustic potash, manganese dioxide and potassium acetate at 200-220°C, the product being 3-o-carboxyphenylindazole (VIII) (Bradley and Geddes, *J. Chem. Soc.*, 1952, 1636). 1:9-Pyrazolanthrone Yellow, the dye prepared by treatment of (VII) with hot alcoholic potash, is usually regarded as 3:3'-dipyrazolanthronyl (IX). Bradley and Geddes obtained a dicarboxylic acid by the alkali fusion of (IX), which they considered to be di-(3-o-carboxyphenylindazol-7-yl), supporting the structure (IX) (see also Maki and Akamatsu, *J. Chem. Soc., Japan, Ind. Chem. Sect.*, 1951, 54, 281; 326). However, the indazole- and diindazolyl-carboxylic acids were not synthesized, and alternative structures for Pyrazolanthrone Yellow cannot be altogether excluded. Syntheses of the dye from an authentic 2:2'-dianthraquinonyl derivative and of a dye possessing the structure (X) appear desirable and are in progress; the N:N'-diethyl derivative of Pyrazolanthrone Yellow is Indanthrene Rubine R, to which the structure of an N:N'-diethyl derivative of (X) has been assigned in FIAT 1313, Vol. II.

**Raney nickel reduction and desulphurization**

*Thioindigoid dyes*

The uses of Raney nickel as a reduction catalyst and as a reagent for the removal of sulphur from sulphur-containing organic compounds have been widely studied in recent years (see Baxtér and Spring, *Ann. Rep. Chem. Soc.*, London, 1945, 42, 100; McOmie, *ibid.*, 1948, 45, 199). Raney nickel desulphurization has proved to be valuable in elucidating the structure of biotin and benzylpenicillin, and it has been used for obtaining data on the constitution of sulphur-containing dyes such as Hydron Blue, Cibanone Yellow R and Cibanone Orange R (Shah, Tilak and Venkataraman, *Proc. Indian Acad. Sci.*, 1948, 28A, 142). For such purposes treatment with Raney nickel can be carried out broadly under two sets of condi-
tions: (1) treatment with a large excess of active Raney nickel in a suitable solvent at temperatures up to the boiling point of the solvent (Mozingo, J. Am. Chem. Soc., 1948, 65, 1013), and (2) treatment with Raney (nickel-aluminium) alloy in hot aqueous alkali (Papa, Schwenk et al, J. Org. Chem., 1942, 7, 587; et sequa). In the thioindigoid series these Raney nickel reactions are useful not only for structural studies, but also for the preparation of otherwise somewhat inaccessible compounds. Thus thioindigo (I) leads to diphenacyl (II) and 6:6'-diethoxythioindigo (Durindone Orange R; III) to 6:6'-diethoxydiphenacyl (IV), the latter conversion proceeding in about 80% yield under specified conditions (Kao, Tilak and Venkataraman, Proc. Indian Acad. Sci., 1950, 32A, 162). The diphenacyls

\[ \text{(I)} \quad \text{(II)} \]

\[ \text{(III)} \quad \text{(IV)} \]

were accompanied by small amounts of bye-products, such as benzoic acid from (I) and \( p \)-ethoxybenzoic acid from (III).

Degradations of thioindigoid dyes by treatment with alcoholic caustic potash (Friedländer and St. Kielbesinski, Ber., 1911, 44, 3098), ozonization (Furst and Pollak, Ber., 1932, 65, 390), and oxidation with fuming nitric acid (Riesz, Ber., 1931, 64, 1893), which have been described in the literature, involve the fission of the carbon chain linking the two aryl residues. Desulphurization of thioindigoid dyes by means of Raney nickel has the distinctive feature that the carbon skeleton of the molecule remains largely intact. When excess of Raney alloy in aqueous alkali is used, thioindigo gives 1:4-diphenylbutane, together with other reduction products. More recently Kao (unpublished work) has found that treatment of thioindigoid dyes with Raney nickel in alcohol gives 1:4-diphenylbutanes in good yields and as the only isolable products. Desulphurization of a chlorine-containing thiondigoid dye can be effected without removal of the halogen; Durindone Red 3BS leads to the chlorine-containing diphenacyls (V) and (VI), together with 1:4-di-\( m \)-tolyl-1-butanol (VII), or to 1:4-di-\( m \)-tolylbutane (VIII), according as Raney alloy and alkali or Raney nickel and alcohol are used. The unsymmetrical dye

\[ \text{(VI)} \]

\[ \text{(V)} \]

\[ \text{(VII)} \]

\[ \text{(VIII)} \]
(IX) gives 2:4-diphenyl-1-butanol (X) or 1:3-diphenylbutane (XI) under the two sets of conditions.

Blicke and Sheets (J. Am. Chem. Soc., 1949, 71, 4010) obtained ethylbenzene by the action of Raney nickel on thionaphthene, thioindoxyl, acetophenone or methyl phenyl carbinoil in boiling alcohol. Kao has found that thioindoxyl gives acetophenone in 72% yield on treatment with Raney nickel in aqueous caustic soda at 0 to 5°. Thioindoxyl acid (XII) is completely desulphurized in five minutes by Raney nickel in ice-cold aqueous caustic soda with the formation of β-phenyl-β-hydroxypropionic acid as the main product, together with β-phenylpropionic acid and acetophenone as minor products. Rabindran and Tilak (unpublished work) synthesized 1:2-benzo-9-thiafluorene (XIII) and 3:4-benzo-9-thiafluorene (XIV), and Kao has confirmed the structures of these compounds by desulphurizing them with Raney nickel and alcohol to 2-phenylnaphthalene and 1-phenylnaphthalene respectively.

**Anthraquinone derivatives**

With the object of using Raney nickel for the desulphurization of sulphurized vat dyes derived from anthraquinone and for the determination of their constitution Ramanathan and Tilak made a careful study of the action of Raney alloy and aqueous caustic soda on anthraquinone, 2-methylanthraquinone, 2-mercaptomethylanthraquinone (AQ-CH₂SH; AQ = 2-anthraquinonyl), bis-2-anthraquinonylmethyl sulphide (I; AQ-CH₃-S-CH₃-AQ) and bis-2-anthraquinonylmethyl disulphide (II; AQ-CH₃-S-S-CH₃-AQ). Anthraquinone gave the 1:2:3:4-tetrahydro derivative, which is structurally allied to 2:3-diyethyl-1,4-naphthoquinone, resembles such 2-alkyl- and 2:3-dialkylnaphthoquinones very closely in its absorption spectrum, and may have useful vitamin K activity. With varying amounts of Raney alloy 2-methylanthraquinone gave a dihydro derivative (m.p. 126—127°), 1:2:3:4-tetrahydro-6-methylanthraquinone (m.p. 170—171°), the constitution which was proved by oxidation to adipic and 4-methylphthalic acids, and three octahydroanthraquinones (m.p. 164°; 146°; 126°). Desulphurization of 2-mercaptomethylanthraquinone gave 2-methylanthraquinone, 2-hydroxymethylantha-
quinone and anthraquinone-2-carboxylic acid, together with some bis-2-anthra-
quinonylmethyl sulphide (I). The formation of (I) is apparently due to the poison-
ing effect of the thiol on the nickel catalyst (Cf. Fel’dman, Doklady Akad. Nauk
S.S.S.R., 1949, 65, 857). The sulphide (I) yielded 2-methylanthraquinone and
traces of Anthraflavone. The products obtained from the disulphide (II) were
identical with those from 2-mercaptomethylanthraquinone, except that the sulphide
(I) was not formed; desulphurization of the disulphide apparently proceeded with­
out the prior formation of the thiol. Papa, Schwenk and Ginsberg, (J. Org. Chem.,
1949, 14, 723) obtained toluene as the only product by treatment of benzyl mer-
captan and di-p-tolyl sulphide with Raney alloy and aqueous caustic soda, and the
isolation of 2-hydroxymethylanthraquinone and anthraquinone-2-carboxylic acid,
in addition to 2-methylanthraquinone, indicates the distinctive behaviour of an-
thraquinone derivatives in Raney nickel desulphurizations.

Anthraflavone gave by Raney nickel reduction the decahydroderivative, to­
gether with a small amount of 1:2:3:4-tetrahydro-6-methylanthraquinone. The
formation of the latter substance is noteworthy, since there are few examples on
record of the fission of a carbon-carbon linkage by Raney nickel reduction.

The hydrogenated anthraquinone derivatives are somewhat difficult to separ­
ate and characterize, while the parent anthraquinones are readily crystallizable, and
easy to identify. When tetrahydroanthraquinone was fused with caustic potash, no
tetrahydrobenzoic acid was isolable, the products being anthraquinone and a small
amount of benzoic acid. Alkali fusion was thus valueless for determining the
constitution of tetrahydroanthraquinone derivatives. Methods of dehydrogena­
tion of the hydrogenated anthraquinones were therefore examined. Treatment
with boiling aniline and with sulphur at high temperature are known methods,
which were found to be applicable, but the most suitable procedure has been found
to be treatment with iodine and sodium acetate in boiling nitrobenzene. Tetra­
hydroanthraquinone was also dehydrogenated to anthraquinone in good yield by
prolonged boiling with pyridine. Chloranil in boiling xylene was ineffective.

Pinckard, Chatterjee and Zechmeister (J. Amer. Chem. Soc., 1952, 74, 1608)
have reported the conversion of anthrone to anthraquinone by passage of a benzene
solution through an alumina-Celite column. Ramanathan and Tilak had observed
earlier that 1:2:3:4-tetrahydroanthraquinone and its 6-methyl derivative under­
went dehydrogenation to anthraquinone and 2-methylanthraquinone in 95% yield,
when a hexane solution was passed through a column of alumina (Brockmann
standard activity I). Light did not play a part in the reaction, and dehydrogena­
tion did not take place when hexane was replaced by benzene and alumina by
Fuller’s earth or calcium sulphate.

The action of iodine and sodium acetate in boiling nitrobenzene on deca-
hydroanthraflavone results in dehydrogenation of the hydrogenated anthraquinone
nuclei, but the bridging alkylene group remains unaffected. Dihydroanthraflavone
(α:β-bis-2-anthraquinonylethane) thus obtained can be further dehydrogenated
to Anthraflavone by treatment with selenium dioxide in boiling nitrobenzene. When 1:2:3:4-tetrahydroanthraquinone is heated with a molar proportion of selenium dioxide, the main products are anthraquinone and α-hydroxyanthraquinone. With excess of the oxidizing agent quinizarin is also formed.

Many anthraquinonoid vat dyes are insoluble or very sparingly soluble in organic solvents and are therefore difficult to purify by chromatography and by crystallization. Conversion of the anthraquinone to the corresponding anthracenederivatives, which have much greater solubility in organic solvents, can be effected smoothly by treatment of the sodium salts of the leuco sulphuric esters (“Indigosols” or “Soledons”) in aqueous solution with Raney nickel. Thus Indigosol Golden Yellow IGK gives on Raney nickel reduction a mixture of products, consisting of

![Indigosol Golden Yellow IGK](image1)

the hydrogenated vat dye and hydrogenated hydrocarbon; dehydrogenation by means of iodine and sodium acetate in nitrobenzene and chromatography on alumina lead to the parent hydrocarbon 2:3:7:8-dibenzpyrene in 40% yield (Ramanathan, unpublished work). Such hydrocarbons and their derivatives containing heterocyclic ring systems, which are of interest in chemical carcinogenesis, can thus be readily prepared from commercially available anthraquinonoid vat dyes. The reduction procedure is also applicable to the leuco sulphuric esters of indigoid and thioindigoid dyes.

An interesting use of Raney nickel reduction, unrelated to vat dyes, is in the preparation of 2:6-dihydroxybenzoic acid from phloroglucinol carboxylic acid via the mono-Ο₆-toluenesulphonyl derivative (Ramanathan and Venkataraman, 1952, 21, 283; cf. Kenner and Murray, J. Chem. Soc., 1949, S178); sodium γ-resorcylate has recently been found to be more active than sodium salicylate as a therapeutic agent in rheumatic fever.