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STRUCTURAL PROBLEMS CONCERNING CERTAIN VAT DYES AND THEIR INTERMEDIATES: APPLICATION OF NMR AND MASS SPECTROSCOPY

A THESIS

SUBMITTED BY

T.G. MANJREKAR, M.Sc.

TO THE

UNIVERSITY OF BOMBAY

FOR THE DEGREE OF

Ph.D.

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No part of this thesis has been submitted for a degree or diploma or other academic award. The literature concerning the problems investigated has been surveyed, and all the necessary references are given in the thesis. The present work has been clearly indicated separately. The experimental work has been carried out entirely by me. In accordance with the usual practice, due acknowledgement has been made wherever the work presented is based on the results of other workers.

Tmanjrekar

(T.G. Manjrekar)
CANDIDATE

Poona
17th June 1968

(K. Venkataraman)
RESEARCH GUIDE

C O N T E N T S

PART I

NMR SPECTRA OF REDUCTIVE METHYLATION PRODUCTS OF VIOLANTHRONE DERIVATIVES

INTRODUCTION

Dyes are classified in accordance with their chemical constitution or their application to textile fibers or other colouring purposes. Their dyeing properties are useful for subdivision of a large group of dyes such as azo or anthraquinone dyes. Thus basic classification of the anthraquinonoid dyes indicates the fundamental nucleus from which all the dyes in the series are derived, but for a detailed consideration it is convenient to divide the group into mordant, acid, vat, and disperse dyes.

Vat dyes are organic colouring matters capable of undergoing a reversible reduction-oxidation cycle without colour loss or change of shade. Vat dyes can be reduced by sodium dithionite (hydrosulphite) in presence of alkali. The chemical change in such a process is the reduction of quinone or carbonyl groups to alkali-soluble phenolic or enolic groups ($\rangle C = O \xrightarrow{H} \rangle\!\rangle C - OH \longrightarrow \rangle\!\rangle C - ONa$). The sodium salt of the reduction products (leuco compounds) have affinity for textile fibers, and when the impregnated fiber is exposed to air, the leuco compound reoxidises to the insoluble parent dyes. Vat dyes belong to two main chemical classes: indigoid and anthraquinonoid.

The vat dyes, especially anthraquinonoids, are characterized by their high all-round fastness. The anthraquinonoid vat dyes represent the highest fastness to all agencies so far available among the synthetic dyes, and they are therefore most valuable dyes for cotton.

Many of the dyes are not marketed in the pure form. The manufacturers and users of dyestuffs are interested in products of standard quality giving reproducible results in application, rather than in their chemical purity. Commercial dyes are therefore standardized in shade, concentration and physical form. Two types of impurities (substances other than the main tinctorial constituent) occur in commercial dyes: (1) by-products of the series of reactions by which the dye is synthesized, and (2) substances added subsequently for standardization. Among the latter may be one or more dyes added to the main dyestuff for shading purposes.

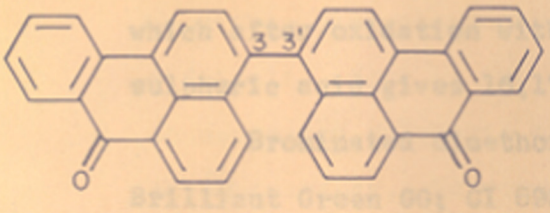
Benzanthrone dyes constitute an extremely important group which includes some of the fastest and most widely used dyes in the entire vat dye range. Ever since their discovery, violanthrones (dibenzanthrones) and isoviolanthrones (isodibenzanthrones)

have been important dyes. The method first used for the preparation of violanthrone consists in the alkali fusion of benzanthrone, which is still commercially important. In another method, benzanthrone is first converted to 4,4'- or 3,3'-dibenzanthronyl, and the intermediate after ring closure gives violanthrone (see Chart 1).

The alcoholic alkali fusion of 3-chloro-benzanthrone gives isoviolanthrone, a violet dye, the halogenated derivatives of which are brighter and faster than the parent quinone.

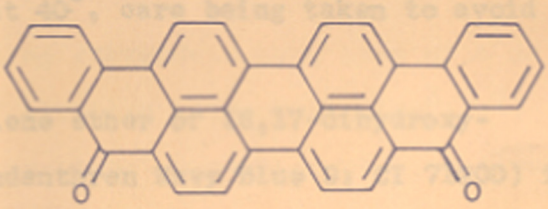
Most important of the violanthrone derivatives are halogenated and nitrated derivatives, as well as alkyl ethers of dihydroxyviolanthrone. Thus 16,17-dimethoxyviolanthrone (Caledon Jade Green; CI 59825), one of the most important of this series, is obtained by oxidation of violanthrone with manganese dioxide and sulphuric acid. The dihydroxy derivative, after methylation in nitrobenzene or other suitable medium with dimethyl sulphate or methyl p-toluenesulphonate in presence of anhydrous potassium carbonate, gives 16,17-dimethoxyviolanthrone, which dyes bright and attractive bluish green shades with excellent fastness[1]. Another commercial method of preparation proceeds through 4,4'-dibenzanthronyl

CHART 1.

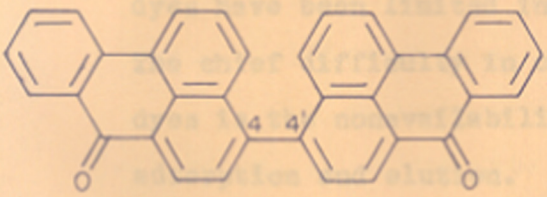


3,3'—Dibenzanthronyl

KOH (alc.)
130–150°



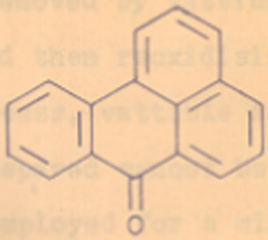
Violanthrone



4,4'—Dibenzanthronyl

$AlCl_3$ or
KOH
200–220°

NaOH, KOH, AcONa, 225–230°



Benzanthrone

which after oxidation with manganese dioxide in sulphuric acid gives 16,17-dihydroxyviolanthrone.

Brominated dimethoxyviolanthrone (Indanthren Brilliant Green GG; CI 59830) is obtained by brominating dimethoxyviolanthrone in a mixture of 96% sulphuric acid and 24% oleum in presence of sodium nitrite at 40°, care being taken to avoid demethylation[2].

The ethylene ether of 16,17-dihydroxy-violanthrone (Indanthren Navy Blue G; CI 71200) is obtained by alkylating it with ethylene dibromide or β-chloroethyl p-toluenesulphonate[3,4].

Applications of chromatography to synthetic dyes have been limited in spite of its enormous scope. The chief difficulty in carrying out chromatography of dyes is the nonavailability of suitable solvents for adsorption and elution. Vat dyes are insoluble in water and therefore water-soluble impurities can be removed by washing with hot water. Non-vattable impurities can be removed by vatting the dye, filtering the vat solution and then reoxidising to the parent dye. But during this process, vattable intermediates from which the dye is prepared cannot be removed, and this process cannot be employed for a mixture of vat dyes. Poor solubility in organic solvents makes purification

by either chromatography or crystallization difficult. Most of the vat dyes are soluble in concentrated sulphuric acid, not suitable for chromatography. However, methods involving fractional crystallization by careful dilution of the sulphuric acid solution with water or alcohol have been mentioned.

Conflicting statements have been made on the separability of alkaline vats on alumina[5,6,7]. Alkaline vat solutions have been chromatographed on bleached saw-dust or disintegrated cotton columns which were then developed in the colours of the oxidised dyes by means of potassium ferricyanide solution[5]. This method is limited for the separation of dyes of widely different substantivity to cellulose.

The chromatographic separation of the leuco derivatives of vat dyes on cellulose has been described by Rao et al.[8] They vatted with aqueous tetraethylenepentamine and sodium hydrosulphite, and carried out the adsorption on a column of cellulose powder, followed by development with aqueous tetraethylenepentamine containing a little sodium hydrosulphite. One part of the organic solvent and four parts of water were employed both for adsorption and development. Separations of various

mixtures of vat dyes were effected, and a relation between the substantivity of the leuco derivatives for cellulose and their adsorbability was observed.

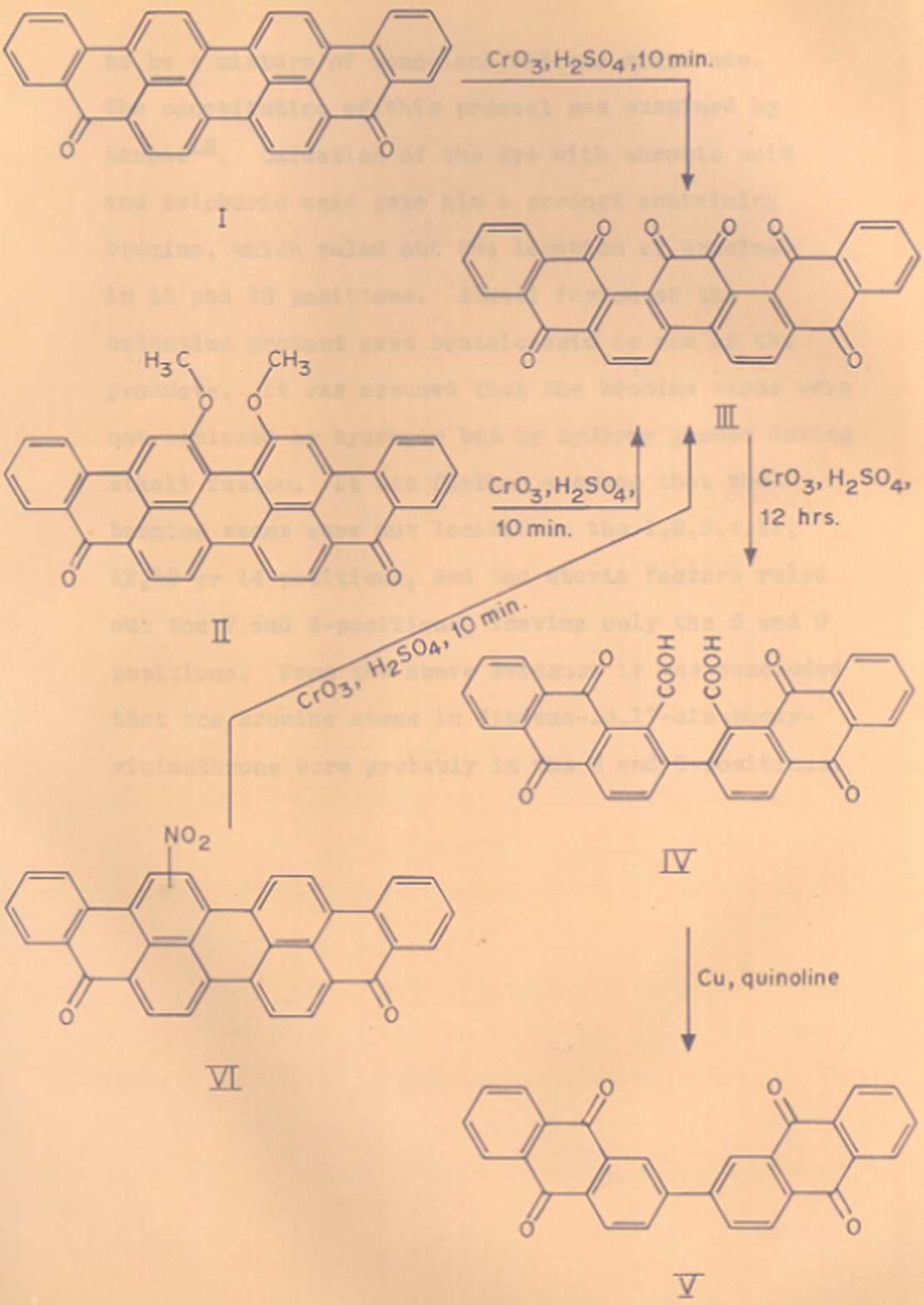
It has been claimed that a mixture of vat dyes can be separated on an alumina column using nitrobenzene as a solvent[5], but most vat dyes are insoluble in nitrobenzene at room temperature. The chromatographic separation of vat dyes at elevated temperature has been carried out by Unni and Venkataraman[9]. Several model separations were carried out in a quantitative manner; but large quantities could not be handled.

The elucidation of the structures of many of the commercially valuable vat dyes by the classical organic methods involves tedious experiments and in some cases leads to erroneous results. The chemical method usually employed is degradation of the molecule, usually by oxidation. Thus oxidation of violanthrone (I) and 16,17-dimethoxyviolanthrone (II) with chromic acid and sulphuric acid gives 1,2,7,8-diphthaloylphenanthraquinone (III). Further oxidation with chromic acid and sulphuric acid gives 2,2'-dianthraquinonyl-1,1'-dicarboxylic acid (IV), from which after decarboxylation 2,2'-dianthraquinonyl (V) can be obtained

(see Chart 2). The constitution of nitroviolanthrone was studied by Unni *et al.*[10]. They obtained a pure nitroviolanthrone from the commercial dye by carrying out chromatography at elevated temperature. From the analysis of C, H and N it was found to be a mononitroviolanthrone. Oxidation of pure mononitroviolanthrone (VI) with chromic acid and sulphuric acid gave nitrogen-free 1,2,7,8-diphthaloylphenanthraquinone (III). It was therefore clear that the nitro group in mononitroviolanthrone is in the 15- or 16-position. The reduction product of the mononitroviolanthrone was found to be identical with an authentic sample of 16-aminoviolanthrone, synthesised by alkali fusion of a mixture of benzanthrone and 2-aminobenzanthrone and chromatographic separation of the mixture of violenthrone, 16-aminoviolanthrone and 16,17-diaminoviolenthrone thus formed. Thus the main constituent of nitrated violanthrone was proved to be 16-nitroviolanthrone.

Brominated 16,17-dimethoxyviolanthrone (Indanthren Brilliant Green GG; CI 59830) is described in the literature[11] as dibromo-16,17-dimethoxyviolanthrone; but the commercial dye does not analyse for two bromine atoms per violanthrone molecule. The product appears

CHART 2.


CrO3, H2SO4, 10 min.
I
III
H3C
CH3
II
CrO3, H2SO4, 10 min.
CrO3, H2SO4, 12 hrs.
CrO3, H2SO4, 10 min.
COOH
COOH
IV
NO2
VI
Cu, quinoline
V

to be a mixture of mono- and dibromo compounds. The constitution of this product was examined by Sampat[12]. Oxidation of the dye with chromic acid and sulphuric acid gave him a product containing bromine, which ruled out the location of bromines in 15 and 18 positions. Alkali fusion of the oxidation product gave benzoic acid as one of the products. It was assumed that the bromine atoms were not replaced by hydrogen but by hydroxy groups during alkali fusion. It was further assumed that the bromine atoms were not located in the 1,2,3,4,11, 12,13 or 14 positions, and the steric factors ruled out the 7 and 8-positions, leaving only the 6 and 9 positions. From the above evidence it was concluded that the bromine atoms in dibromo-16,17-dimethoxy-violanthrone were probably in the 6 and 9-positions.

PRESENT WORK

As most anthraquinonoid vat dyes are sparingly soluble in organic solvents even at boiling temperature, the purification by chromatography and crystallization is difficult. It was found that the reductive methylation derivatives (methyl ethers of the leuco compounds) of quinones were much more soluble in organic solvents (such as benzene) than the parent quinones. These derivatives have the additional value of being amenable to thin layer and column chromatography, and they can be very easily crystallized from common organic solvents. A convenient method for the isolation of complex quinonoid vat dyes in pure form thus becomes available, because the reductive methylation products are readily oxidizable to the parent quinones. Although, the reductive methylation of quinones has been known in the literature for many years,[13] it has not been used as a method of purification of polycyclic quinones such as the anthraquinonoid vat dyes.

The general procedure for obtaining the reductive methylation product was to reduce the vat dyes with aqueous sodium dithionite and sodium hydroxide at 60 - 70°, cool to room temperature (25 - 30°), and shake the solution vigorously with dimethyl sulphate (about

6 mols) for 30 minutes when the product separated. In a second method, the calculated amount of hydrogen was absorbed in a suspension of the quinone in a mixture of dimethylacetamide and triethylamine in presence of Adams platinum oxide catalyst. The mixture was treated with sodium hydroxide solution and dimethyl sulphate under stirring when the reductive methylated product separated.

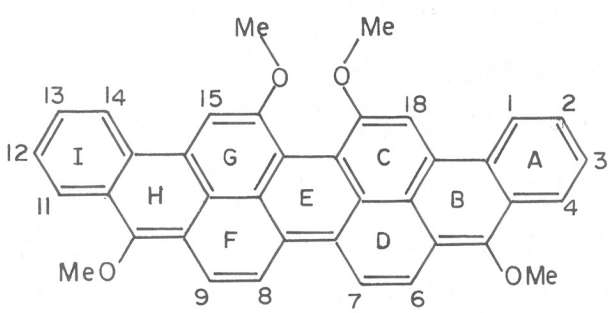
Purification of violanthrone from commercially available violanthrone was carried out by the new procedure. It was observed that violanthrone underwent reductive methylation by shaking the alkaline vat with dimethyl sulphate, whereas isoviolanthrone did not react under the same conditions. It is known in the literature that reductive methylation of isoviolanthrone can be effected under drastic conditions by boiling it in trichlorobenzene with zinc dust, sodium carbonate and methyl p-toluenesulphonate[13]. The reductive methylation product of violanthrone obtained as above was crystallized from nitrobenzene, in which isoviolanthrone was sparingly soluble. The parent violanthrone was recovered by precipitation of the reductive methylation product from sulphuric acid at room temperature. Crystallization from nitrobenzene finally yielded pure violanthrone.

Similarly pure 16,17-dimethoxyviolanthrone was obtained by carrying out the reductive methylation of commercial Caledon Jade Green (CI 59825). The product was chromatographed on a short silica gel column using benzene as solvent, when single red band was eluted as a highly fluorescent red solution. Concentration gave pure 5,10,16,17-tetramethoxy-violanthrene (VII)as fine red needles with a greenish lustre. 16,17-Dimethoxyviolanthrone was obtained by precipitation of the tetramethoxy compound from concentrated sulphuric acid at room temperature, followed by crystallization from nitrobenzene. Under prescribed conditions, there was no demethylation of the 16,17-methoxyl groups.

An important part of the present work is the application of NMR spectroscopy for investigating structural (and especially orientation) problems concerning violanthrone derivatives. The orientation of bromine atoms in brominated 16,17-dimethoxy-violanthrone (Indanthrene Brilliant Green GG, CI 59830) was first studied.

Reductive methylation of the commercial dye was carried out as mentioned earlier. TLC of the product on silica gel (solvent acetone-hexane, 15:85) showed two spots, one major, having very close Rf values.

The faster moving major component was obtained in pure form by passing the mixture through a short column of silica gel, using chloroform as solvent, followed by repeated crystallization from chloroform; analysis indicated that it was a dibromo derivative (VIII). Several other violanthrone derivatives were reductively methylated and purified by chromatography. The NMR spectra of all the products were obtained at 60 Mc in tetramethyl urea, using TMS as an internal reference. The spectra were fairly well resolved and they could be readily analysed with the qualitiative use of simple notions of ring currents. In addition to the large π-electron rings that may be considered for these systems, benzenoid ring currents may be expected for several rings and phenanthrene-type character may be expected for the ring systems ABC, DEF and GHI.



VII

In the spectrum of 5,10,16,17-tetramethoxyviolanthrene VII (Fig. 1) the two-proton singlet absorption at 1.27* was readily assigned to the C(15) and C(18) protons. Since the ring system DEF is a phenanthrene type of unit the C(7) and C(8) protons may be expected to absorb at lower field than the C(6) and C(9) protons. In phenanthrene the 4- and 5-protons are observed as a multiplet at 1.3; the singlet absorption at 2.28 is due to the 9- and 10-protons, and the remaining protons appear as a multiplet centred at 2.3. The pair of doublets in the spectrum of (VII) (J = 9 cps) at 1.08 and 1.62 can therefore be assigned to the 7,8-protons and 6,9-protons respectively.

The methoxyl groups in the 5- and 10-positions will deshield the protons at 6 and 9. In anthracene the α-protons appear at 2.09; but in 9,10-dimethoxyanthracene (the reductive methylation product of anthraquinons), the corresponding protons appear at 1.68 (Fig. 2) because of the deshielding influence of the methoxyl groups on the peri- protons as in 1-methoxynaphthalene. The assignments for the three multiplet absorptions, representing the four spin systems of the terminal rings A and I, indicated in

*Chemical shifts on the τ scale

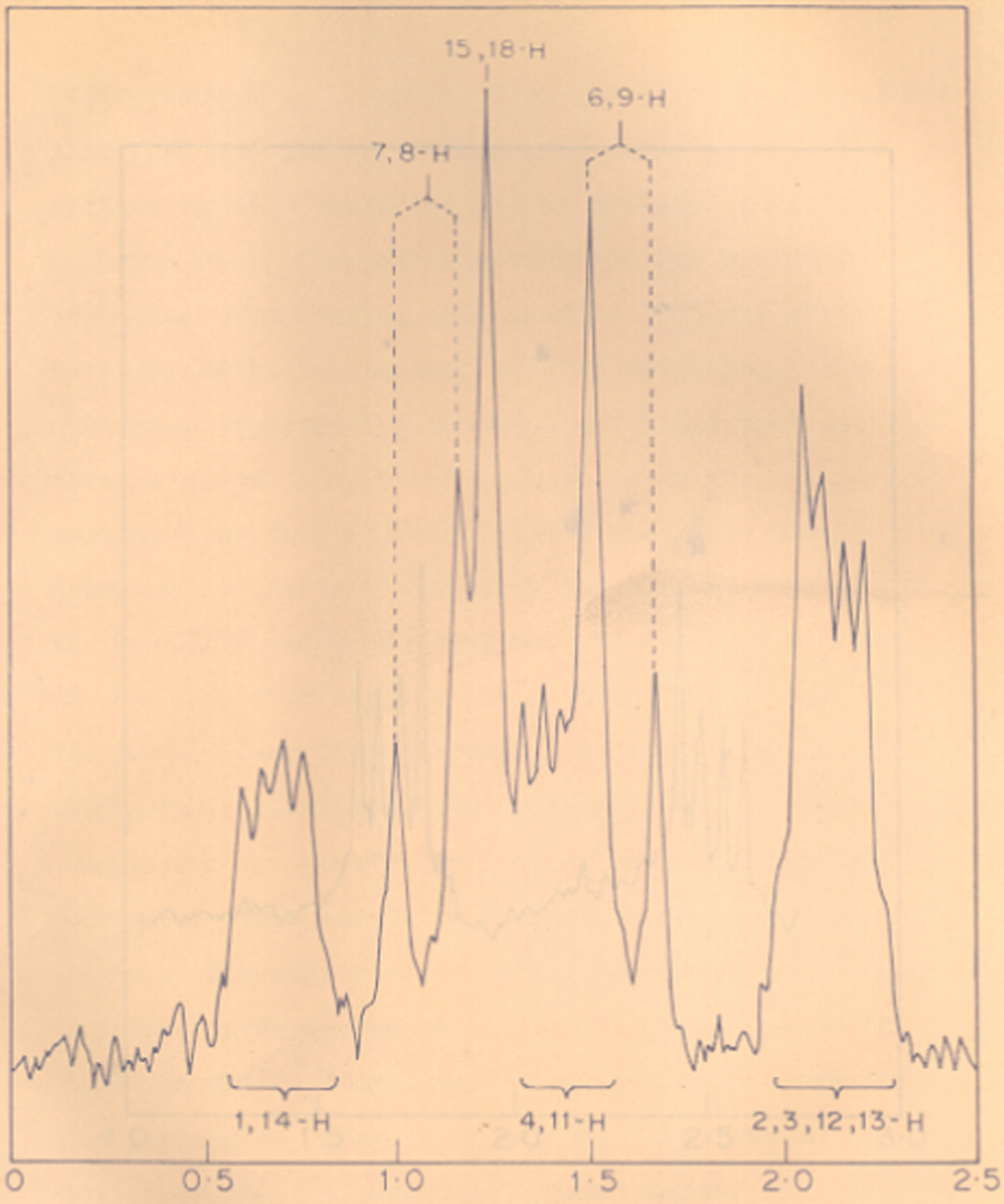


FIG. 1

NMR SPECTRUM OF 5,10,16,17-TETRAMETHOXYVIOLANTHRENE.

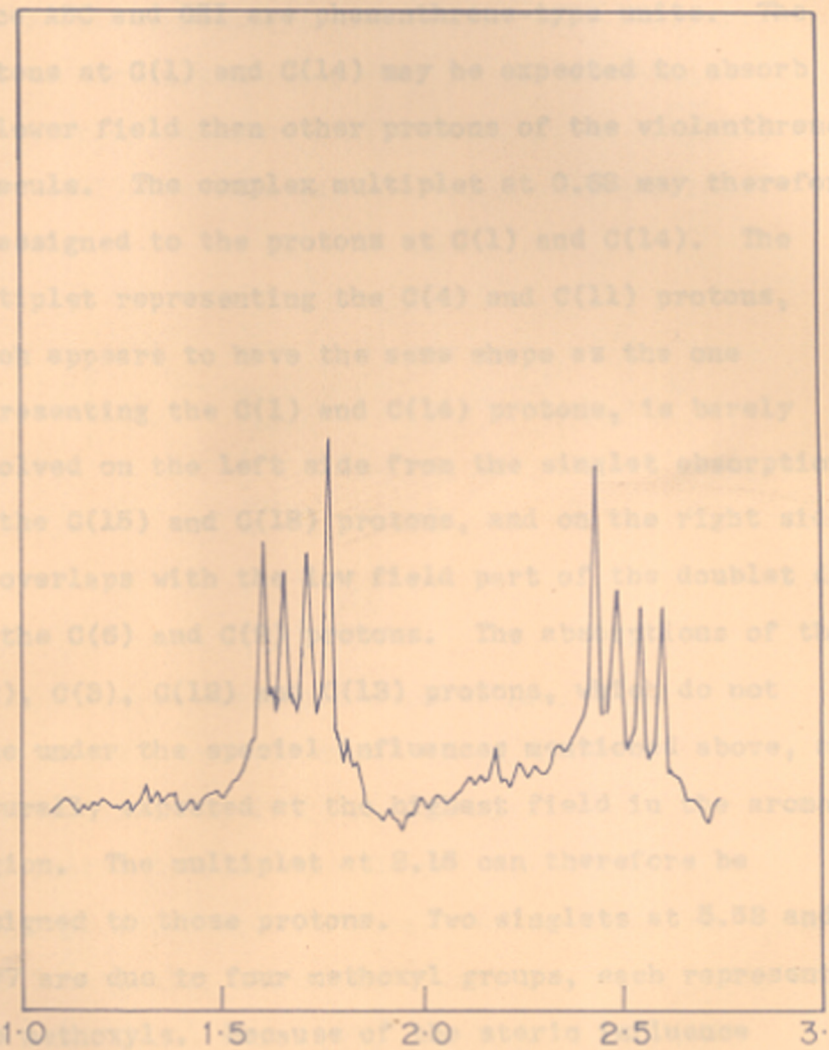


FIG. 2.

NMR SPECTRUM OF 9,10-DIMETHOXYANTHRACENE IN $CDCl_3$.

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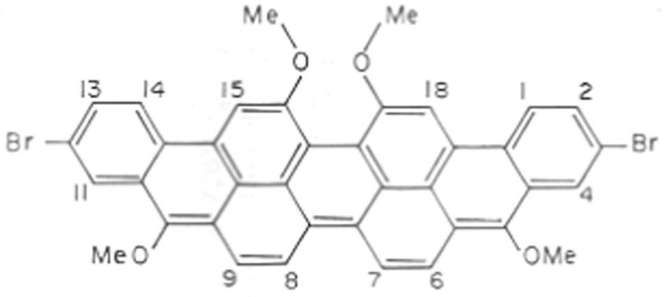
Table 1 and Fig. 1, follow from the same considerations since ABC and GHI are phenanthrene-type units. The protons at C(1) and C(14) may be expected to absorb at lower field than other protons of the violanthrene molecule. The complex multiplet at 0.68 may therefore be assigned to the protons at C(1) and C(14). The multiplet representing the C(4) and C(11) protons, which appears to have the same shape as the one representing the C(1) and C(14) protons, is barely resolved on the left side from the singlet absorption of the C(15) and C(18) protons, and on the right side it overlaps with the low field part of the doublet due to the C(6) and C(9) protons. The absorptions of the C(2), C(3), C(12) and C(13) protons, which do not come under the special influences mentioned above, are naturally expected at the highest field in the aromatic region. The multiplet at 2.15 can therefore be assigned to those protons. Two singlets at 5.53 and 5.77 are due to four methoxyl groups, each representing two methoxyls. Because of the steric influence methoxyls at C(16) and C(17) positions are expected to absorb at lower field than the C(5) and C(10) methoxyls. The singlets at 5.53 and 5.77 can therefore be assigned to the former and latter pair of methoxyls respectively, which also agreed with the values

obtained for the C(5) and C(10) methoxyls in other 5,10-dimethoxyviolanthrenes (see Table 1).

The only changes seen in the spectrum of the dibromo compound (VIII) (Fig. 3) in comparison with (VII) are that (a) the two-proton multiplet



VIII

at the lowest field has changed into a doublet (J = 9 cps), and (b) the four-proton multiplet at highest field in (VII) is replaced by a broad two-proton doublet (J = 9 cps) indicating meta as well as ortho coupling. In other features the two spectra are identical. Since the signal for the protons at C(1) and C(14) show ortho coupling (J = 9 cps) and there is a decrease in the number of protons in the high-field part of the aromatic region, it is clear that the bromine atoms in (VIII) are in the 3- and 12-positions.

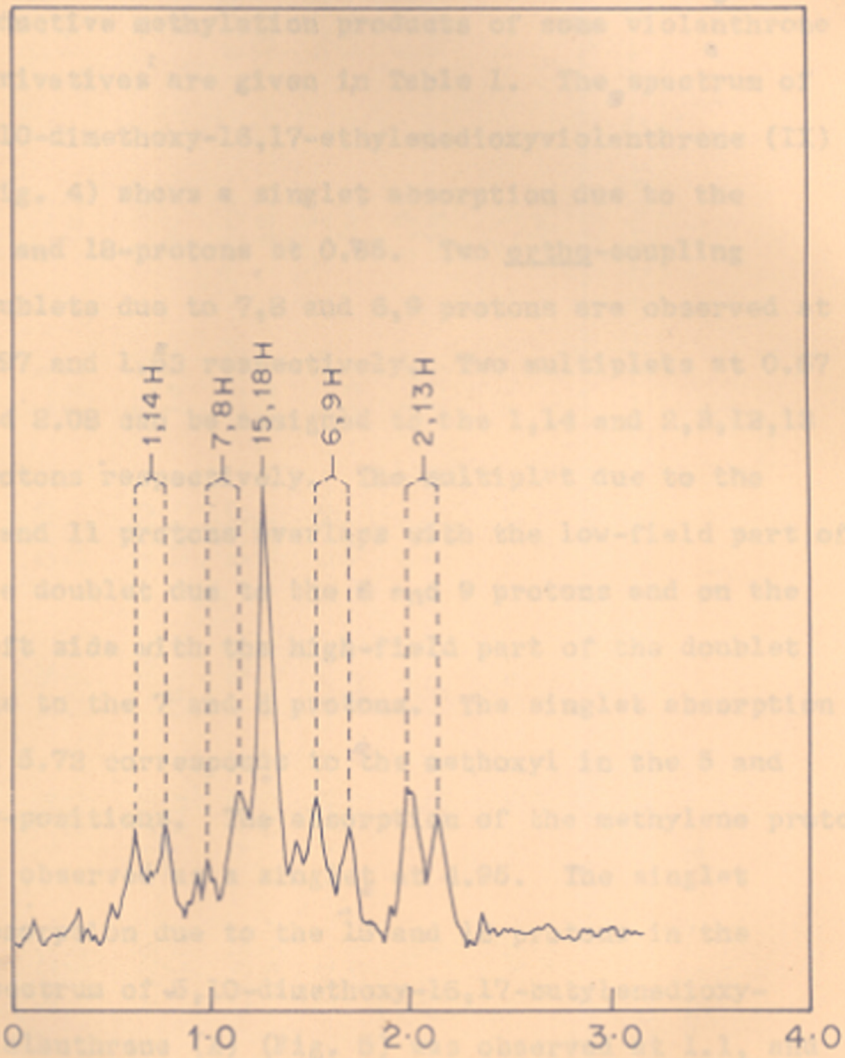


FIG. 3.

NMR SPECTRUM OF 3,12-DIBROMO-5,10,16,17-TETRAMETHOXYVIOLANTHRENE.

The chemical shifts of the protons in the reductive methylation products of some violanthrone derivatives are given in Table 1. The spectrum of 5,10-dimethoxy-16,17-ethylenedioxyviolanthrene (IX) (Fig. 4) shows a singlet absorption due to the 15 and 18-protons at 0.85. Two ortho-coupling doublets due to 7,8 and 8,9 protons are observed at 0.97 and 1.53 respectively. Two multiplets at 0.67 and 2.08 can be assigned to the 1,14 and 2,3,12,13 protons respectively. The multiplet due to the 4 and 11 protons overlaps with the low-field part of the doublet due to the 6 and 9 protons and on the left side with the high-field part of the doublet due to the 7 and 8 protons. The singlet absorption at 5.72 corresponds to the methoxyl in the 5 and 10-positions. The absorption of the methylene protons is observed as a singlet at 4.85. The singlet absorption due to the 15 and 18 protons in the spectrum of 5,10-dimethoxy-16,17-butylenedioxy-violanthrene (X) (Fig. 5) was observed at 1.1, and the absorption due to the methylene protons appeared as a broad triplet at 4.85. In other features the spectrum was identical with the spectrum of 5,10-dimethoxy-16,17-ethylenedioxyviolanthrene (IX). The spectrum of 5,10-dimethoxy-16,17-dimethyl-

Table 1

Substitution in violanthrene	Chemical shifts							
	15,18-H	7,8-H	6,9-H	1,14-H	4,11-H	2,3,12,13-H	5,10-OMe	Other groups
5,10,16,17-$(OMe)_4$ (VII)	1.27 (s)	1.08 (d)	1.62 (d)	0.68 (m)	1.4 (m)	2.15 (m)	5.77 (s)	5.53 (s) OMe at 16,17
" " Br_2 (VIII)	1.32 (s)	1.08 (d)	1.65 (d)	0.73 (d)	1.32 (s)	2.08 (bd)	-	-
5,10-$(OMe)_2$-16, 17-O-$(CH_2)_2$-O- (IX)	0.85 (s)	0.97 (d)	1.53 (d)	0.67 (m)	1.32 (m)	2.08 (m)	5.72 (s)	4.95 (s) -O-CH_2-
5,10-$(OMe)_2$-16,17-O-$(CH_2)_4$-O- (X)	1.1 (s)	1.02 (d)	1.57 (d)	0.65 (m)	1.33 (m)	2.1 (m)	5.74 (s)	4.95(bt) O-CH_2
5,10-$(OMe)_2$-16,17-$(Me)_2$ (XI)	0.78 (s)	1.0 (d)	1.50 (d)	0.7 (m)	1.37 (m)	2.05 (m)	5.67 (s)	6.85 (s); Me at 16,17 (in pyridine)
5,10,16,17-$(OEt)_4$ (XII)	1.27 (s)	0.98 (d)	1.53 (d)	0.68 (m)	-	2.1 (m)	-	-

s = singlet; d = doublet (J = 9 cps); m = multiplet; bd = broad doublet (J = 9 cps) indicating meta as well as ortho coupling.

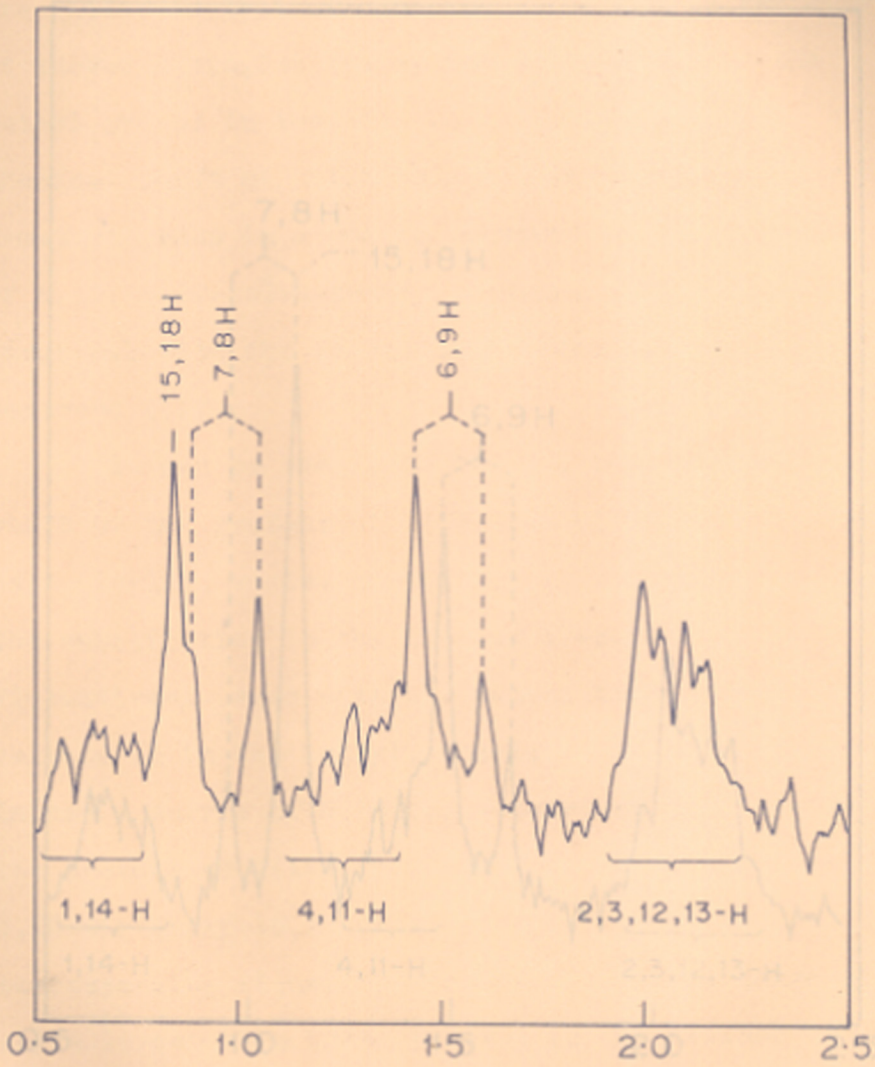


FIG. 4

NMR SPECTRUM OF 5,10-DIMETHOXY-16,17-ETHYLENE-DIOXYVIOLANTHRENE.

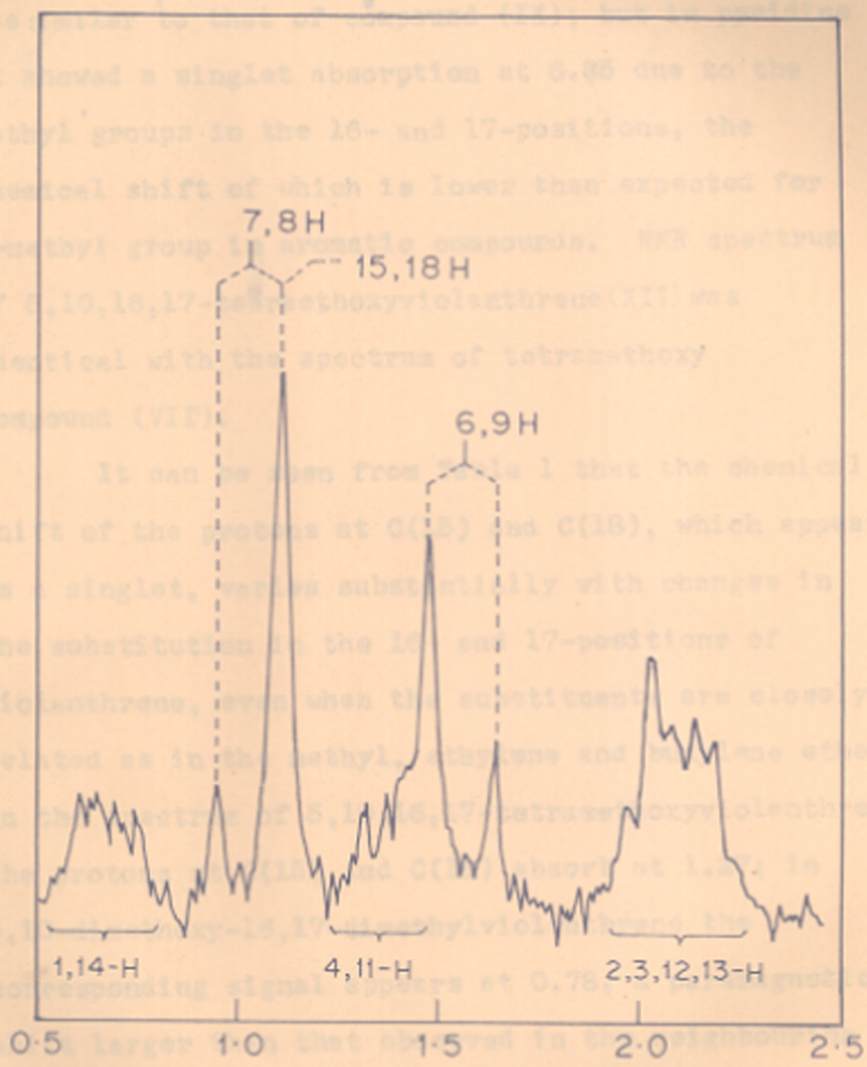


FIG. 5.

NMR SPECTRUM OF 5,10-DIMETHOXY-16,17-BUTYLENE-DIOXYVIOLANTHRENE.

violanthrene (XI) (Fig. 6) in tetramethyl urea was similar to that of compound (IX); but in pyridine it showed a singlet absorption at 6.85 due to the methyl groups in the 16- and 17-positions, the chemical shift of which is lower than expected for C-methyl group in aromatic compounds. NMR spectrum of 5,10,16,17-tetraethoxyviolanthrene (XII) was identical with the spectrum of tetramethoxy compound (VII).

It can be seen from Table 1 that the chemical shift of the protons at C(15) and C(18), which appears as a singlet, varies substantially with changes in the substitution in the 16- and 17-positions of violanthrene, even when the substituents are closely related as in the methyl, ethylene and butylene ethers. In the spectrum of 5,10,16,17-tetramethoxyviolanthrene, the protons at C(15) and C(18) absorb at 1.27; in 5,10-dimethoxy-16,17-dimethylviolanthrene the corresponding signal appears at 0.78, a paramagnetic shift larger than that observed in the neighbouring aromatic protons of anisole and toluene. Attention has already been drawn to the appearance of the methyl singlet in a lower field than the methyl signal in toluene. From this it can be inferred that the effect of methyl groups on the adjacent

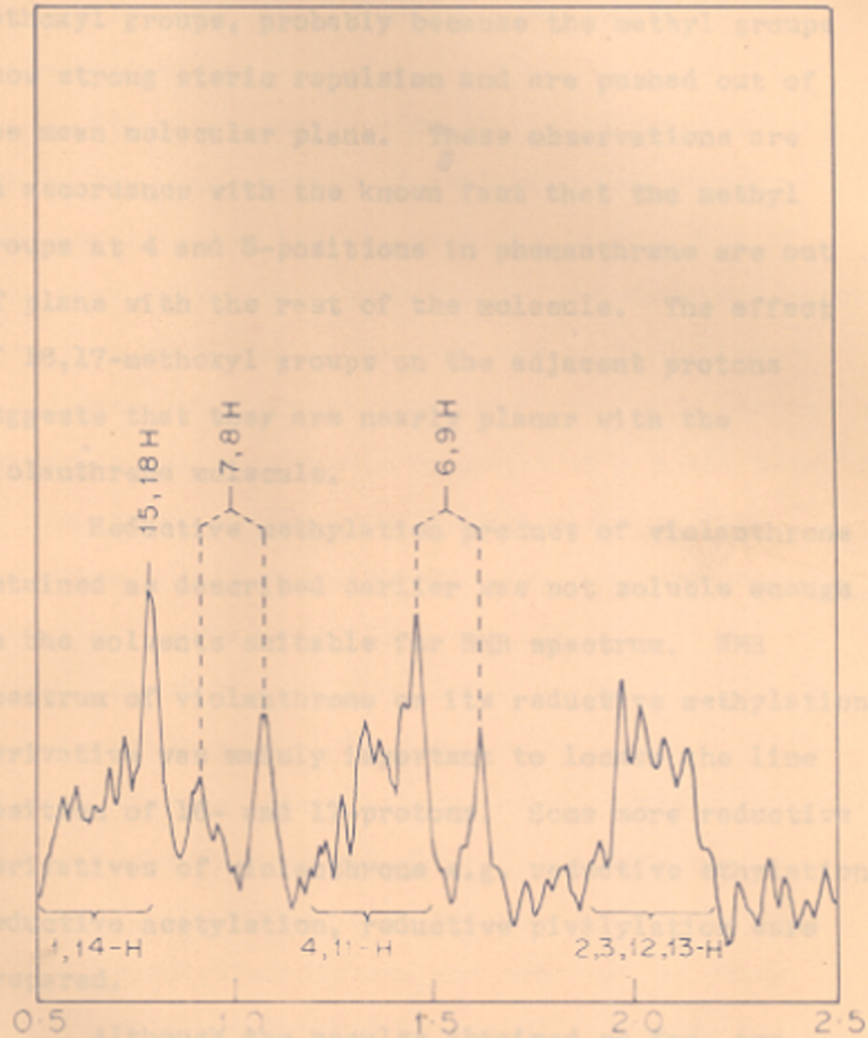


FIG. 6

NMR SPECTRUM OF 5,10-DIMETHOXY-16,17 DIMETHYL-VIOLANTHRENE

protons is insignificant as compared to that of methoxyl groups, probably because the methyl groups show strong steric repulsion and are pushed out of the mean molecular plane. These observations are in accordance with the known fact that the methyl groups at 4 and 5-positions in phenanthrene are out of plane with the rest of the molecule. The effect of 16,17-methoxyl groups on the adjacent protons suggests that they are nearly planar with the violanthrene molecule.

Reductive methylation product of violanthrone obtained as described earlier was not soluble enough in the solvents suitable for NMR spectrum. NMR spectrum of violanthrone or its reductive methylation derivative was mainly important to locate the line position of 16- and 17-protons. Some more reductive derivatives of violanthrone e.g. reductive ethylation, reductive acetylation, reductive pivalylation were prepared.

Although the results obtained so far are adequate to show the value of NMR spectroscopy in the investigation of structural problems concerning anthraquinonoid vat dyes, one direction in which progress has to be made before undertaking more elaborate studies on other dyes of this type is to

find derivatives more soluble than the reductive methylation products in solvents suitable for NMR spectroscopy.

Reductive acetylation of violanthrone carried out by the usual method of refluxing the quinone with acetic anhydride and pyridine in presence of zinc dust gave a very poor yield. Two improved methods were then developed. The acid vat of violanthrone (5,10-dihydroxyviolanthrene), refluxed with acetic anhydride and pyridine in presence of a small quantity of zinc dust, gave a quantitative yield of the diacetate. This was also obtained when the calculated amount of hydrogen (1 mole) was absorbed in a suspension of the dye in dimethylacetamide and triethylamine solvent in presence of Adams catalyst, and the mixture after decantation from the catalyst, was refluxed with acetyl chloride in pyridine. Similarly, the trimethylacetyl (pivalyl) ether of 5,10-dihydroxyviolanthrene was prepared by using pivalyl chloride instead of acetyl chloride. Unsuccessful attempts were then made to prepare benzyl and trityl ethers of 5,10-dihydroxyviolanthrene. The pivalate was much more soluble in arsenic trichloride than the other derivatives, but the NMR spectrum could not be obtained.

Since no derivative of violanthrone with adequate solubility for NMR spectroscopy has yet been obtained, the benzyl and trityl ethers of anthrahydroquinone were prepared and they were found to be much more soluble than methyl ether. Their NMR spectra have been determined and are tabulated (Table 2).

Table 2

Compound	Solvent	α-protons	β-protons	Other groups
Anthraquinone	DMSO	1.78 (m)	2.03 (m)	-
9,10-Dimethoxy -anthracene	$CDCl_3$	1.68 (m)	2.52 (m)	OMe - 5.88 (s)
Ditrityl ether of 9,10-dihydroxyanthracene	$CDCl_3$	1.70 (m)	2.25 (m)	Trityl - 2.7 (s)
Dibenzyl ether of 9,10-dihydroxyanthracene	$CDCl_3$	1.67 (m)	2.27 (m)	Phenyl - 2.53 (m) CH_2 - 5.72 (s)

Attempts are being made to prepare benzyl and trityl ethers of leucoviolanthrone.

EXPERIMENTAL

5,10-Dimethoxyviolanthrene

The commercial product Indanthren Dark Blue BOA (2.0 g) was dissolved in concentrated sulphuric acid and precipitated by pouring on ice. The precipitated product was filtered washed with water free from acid. The wet cake was then suspended in sodium hydroxide solution (5% solution; 30 ml) at 60-70°. The vat was prepared by adding sodium dithionite (3.0 g) under shaking. Dimethyl sulphate (12 ml) was then added at room temperature and shaking continued for half an hour when red coloured precipitate separated (excess alkali and sodium dithionite were tested with phenolphthalein and vat papers respectively). The red residue (2.1 g) was filtered, washed with water and dried.

After three crystallizations from nitrobenzene, it gave chromatographically homogeneous product, which did not melt upto 360° (Found: C, 88.5; H, 4.5%. $C_{36}H_{22}O_2$ requires C, 88.9; H, 4.5%).

Reductive methylation of isoviolanthrone

Alkaline vat of isoviolanthrone (1 g) was prepared as above. To the clear vat solution, dimethyl sulphate (6 ml) was added and continued shaking at

room temperature for 30 minutes. No colour change was observed. More of dimethyl sulphate and alkali was added, and shaken for further 30 minutes. The residue was filtered, washed with water and dried. The product showed reddish blue colouration with sodium dithionite in alkali indicating that the compound did not undergo reductive methylation.

Demethylation of 5,10-dimethoxyviolanthrene

Pure 5,10-dimethoxyviolanthrene (500 mg) was dissolved in concentrated sulphuric acid (5 ml) under stirring at room temperature and left for ten minutes. The clear solution was then poured on ice (50 g). The blue precipitate separated (450 mg) was filtered, washed with water and dried. It was crystallized from nitrobenzene to obtain pure violanthrene in blue needles.

5,10,16,17-Tetramethoxyviolanthrene (VII)

16,17-Dimethoxyviolanthrone (Caledon Jade Green; 5 g) was first dissolved in concentrated sulphuric acid and precipitated by pouring on ice. The alkaline vat of the wet cake free from acid was prepared as described earlier. Dimethyl sulphate (25 ml) was added to the solution under stirring. The red product then separated (4.5 g) was filtered, washed with water and dried. The product was then passed through a short column of alumina using benzene as a solvent when single

red highly fluorescent band was eluted. The solvent was removed and the product was crystallized from benzene in red plates having green lustre, m.p. 276-8° (dec.) (Found: C, 83.2; H, 4.6; OMe, 20.6%. $C_{38}H_{26}O_4$ requires C, 83.5; H, 4.8; OMe, 22.7%).

Selective demethylation of 5,10,16,17-tetramethoxyviolanthrene

Demethylation was carried out by dissolving the product in concentrated sulphuric acid at room temperature and precipitating it by pouring on ice. The compound obtained was crystallised from nitrobenzene in greenish blue needles. The IR spectrum of this product is superposable with the spectrum of a pure sample of jade green.

3,12-Dibromo-5,10,16,17-tetramethoxyviolanthrene (VIII)

Indanthren Brilliant Green GG (2 g) free from water solubles was reductively methylated as described earlier. The red residue (2.1 g) showed two spots after two developments on TLC plates (silica gel) using hexane:acetone (85:15) as a solvent system. Both the spots were almost overlapping and therefore preparative layer chromatography was not possible. The compound was chromatographed over a short column of

silica gel using chloroform for development and elution. The faster moving major band, on removal of solvent separated as a red product, crystallized from chloroform in red needles, m.p. above 360°. It moved as a single spot on TLC (silica gel) using the same solvent system (Found: C, 64.4; H, 3.8; Br, 25.4%. $C_{38}H_{24}O_4Br_2$ requires C, 64.8; H, 3.4; Br, 22.7%).

5,10-Dimethoxy-16,17-ethylenedioxyviolanthrene (IX)

16,17-Ethylenedioxyviolanthrone (Indanthren Navy Blue G; 1.5 g) free from water and alcohol solubles was reductively methylated as described in the earlier experiment. The crude red product (1.4 g) was passed through a short column of silica gel using benzene as solvent. The single red band was eluted. The solvent was removed and product crystallised from benzene in shining red needles, m.p. 286-7° (dec.). The compound showed single spot on TLC (silica gel) using acetone:hexane (2:8) as a solvent system (Found:C, 84.1; H, 4.7; OMe, 9.9% in o-cresol. $C_{38}H_{24}O_4$ requires C, 83.8; H, 4.4; OMe, 11.4%).

Methoxyl estimation could not be carried out in regular solvents (phenol and propionic anhydride) as these compounds are insoluble in the medium. o-Cresol and propionic anhydride mixture has been

tried and found to be quite satisfactory. The number of methoxyl groups in these products has been confirmed from their NMR spectra.

5,10-Dimethoxy-16,17-butylenedioxyviolanthrene (X)

16,17-Butylenedioxyviolanthrone (0.85 g, supplied by BASF) free from water and alcohol soluble impurities was reductively methylated. The crude red product (0.8 g) was passed through a short column of alumina using benzene: acetone mixture (9:1) for development and elution. The single red band was eluted as a red fluorescent solution. The solvent was removed and the product was crystallised from benzene in red needles having green lustre with m.p. 285-7° (dec.). (Found: C, 84.2; H, 5.2; OMe, 11.6% in o-cresol. $C_{40}H_{28}O_4$ requires C, 83.9; H, 4.9, OMe, 10.8%).

5,10-Dimethoxy-16,17-dimethylviolanthrene (XI)

16,17-Dimethylviolanthrone was prepared by alkalifusion of 2-methylbenzanthrone.[14]

16,17-Dimethylviolanthreone (0.5 g) was first precipitated from concentrated sulphuric acid. The wet cake free from acid was reductively methylated by the method described above. The crude red product (0.55 g) was passed through a short column of silica gel

using benzene as solvent, when bright yellowish red fluorescent band was eluted as red solution which finally crystallised from benzene in red plates, m.p. 283° (dec.). The compound moves as a single spot on TLC plate (silica gel) using acetone: hexane (2:8) as a solvent system. (Found: C, 88.9; H, 5.1%. $C_{38}H_{26}O_2$ requires C, 88.7; H, 5.1%).

5,10,16,17-Tetraethoxyviolanthrene (XII)

16,17-Diethoxyviolanthrone (Atic Vat Jade Green 3 B, supplied by Atic, 1.2 g) free from water and alcohol solubles was suspended in sodium hydroxide solution (5% solution; 15 ml) and vat was prepared with sodium dithionite (1.5 g). It was then treated with diethyl sulphate (8 ml) at room temperature and stirred for one hour. The red coloured precipitate separated was filtered, washed with water free from alkali and dried. The residue (1 g) was passed through a short column of alumina using benzene as solvent. The single red band was eluted as red solution which showed yellow fluorescence under ultra violet light. The product was crystallised from benzene and petroleum ether mixture in red microscopic needles, m.p.228-30°. (Found: C, 83.7; H, 5.8; OC_2H_5, 29.3%. $C_{42}H_{34}O_4$ requires C, 83.7; H, 5.7; OC_2H_5, 29.9%).

5,10-Diethoxyviolanthrene

Reductive ethylation of Indanthren Dark Blue BOA (1.0 g) was carried out as described in the previous experiment. The chocolate red precipitate (1.05 g) obtained was crystallised from o-dichlorobenzene in chocolate coloured needles, m.p.294-6°(dec.) (Found: C, 86.8; H, 4.8%. $C_{38}H_{26}O_2$ requires C, 88.7; H, 5.1%)

5,10-Diacetoxyviolanthrene

a) The commercial product Indanthren Dark Blue BOA (1.0 g) was first precipitated from concentrated sulphuric acid. The alkaline vat solution was acidified with acetic acid when red coloured leuco compound separated which was filtered at the pump, washed with acetic acid first and then with acetic anhydride (care being taken to avoid reoxidation).

The red residue was refluxed with acetic anhydride (25 ml) in presence of pyridine (0.5 ml) and zinc dust (1.0 g) for two hours. The solution after cooling poured on ice (250 g). The red precipitate (1.1 g) was filtered, washed with water and dried and crystallized from nitrobenzene in red needles. It did not melt upto 360° (Found:C, 83.5; H, 4.1%. $C_{38}H_{22}O_4$ requires C, 84.1; H, 4.1%).

b) Violanthrone (0.18 g) was reduced with hydrogen (1 mole) in dimethylacetamide (3 ml) and triethylamine (1.5 ml) in presence of platinum oxide (5 mg). The mixture was decanted from the catalyst and treated with acetyl chloride (1 ml) and refluxed for two hours. After cooling the solution was poured on ice (100 g). The red coloured precipitate (0.17 g) was filtered and crystallized from nitrobenzene in red needles m.p. above 360°.

Dipivalyl ether of 5,10-dihydroxyviolanthrene

The 5,10-dihydroxy-violanthrene was prepared by absorbing 1 mole of hydrogen as described in the previous experiment. Trimethylacetyl chloride (pivalyl chloride) was used instead of acetyl chloride. The product crystallized from o-dichlorobenzene in red needles. It did not melt up to 360° (Found: C, 84.0; H, 5.6%. $C_{42}H_{34}O_4$ requires C, 83.7; H, 5.6%).

Attempts to prepare dityrityl ether of 5,10-dihydroxy-violanthrene

a) Violanthrone (182 mg) was reduced to dihydroxy-violanthrene by hydrogen absorption method as mentioned in the previous experiment. The resultant solution was treated with trityl chloride (0.5 g) and kept on shaker for 24 hrs. No colour change was observed. The residue, separated after pouring the above mixture

on water, showed positive vat colouration, indicated that the compound had not undergone reductive tritylation.

b) Violanthrone (0.5 g) was refluxed with dimethylacetamide (25 ml), zinc dust (0.5 g), pyridine (2 ml) and trityl chloride (1.5 g) for two hours. The cooled solution was poured on water. The residue obtained showed violet colouration with sodium hydroxide and sodium dithionite, indicating thereby the failure of the reaction.

An attempt to prepare dibenzyl ether of 5,10-dihydroxy violanthrene

The mixture of violanthrone (0.5 g), zinc dust (1 g), sodium carbonate (anhydrous; 1 g), dimethylacetamide (15 ml) and pyridine was refluxed for 15 minutes. Cooled it partially and introduced leukotrope W (a quaternary ammonium salt of phenyl-benzyldimethylammonium chloride; 2 g) and refluxed for two hours. The residue obtained after pouring the mixture on water, gave positive vat colouration with alkaline sodium dithionite, indicates the presence of starting material.

9,10-Dimethoxyanthracene

Hydrogen (0.001 mole) was absorbed in a suspension of anthraquinone (0.208 g; 0.001 mole)

in dimethylacetamide (3 ml) and triethylamine (3 ml) in presence of platinum oxide catalyst (5 mg). The reddish yellow solution decanted from the catalyst in a flask containing sodium hydroxide solution (5% solution; 10 ml). To the red solution dimethyl sulphate (2 ml) was added under vigorous stirring and stirred for 1/2 hr at room temperature. The light yellow precipitate (0.2 g) was filtered, washed with water and dried. The product was crystallized from petroleum ether in light yellow plates with blue fluorescence, m.p. 201° (lit.[15]; m.p. 202°).

Ditrityl ether of 9,10-dihydroxyanthracene

Anthraquinone (0.083 g; 0.0004 mole) was reduced to anthrahydroquinone by the method described earlier in dimethylacetamide (1.5 ml) and triethylamine (1.5 ml) in presence of platinum oxide (5 mg). The mixture was decanted from the catalyst and treated with trityl chloride (0.667 g; 0.0024 mole) at room temperature. The mixture was left on shaker for 24 hrs. The yellow product separated after pouring the mixture on water (0.68 g) was filtered and crystallized from petroleum ether in light yellow needles m.p. 162° (Found:C, 89.2; H, 6.1%. $C_{52}H_{38}O_2$ requires C, 89.9; H, 5.5%).

Dibenzyl ether of 9,10-dihydroxyanthracene

A mixture of dimethylacetamide (10 ml), pyridine (1 ml), zinc dust (2 g), sodium carbonate (anhydrous, 1 g) and anthraquinone (1 g) was refluxed for fifteen minutes when colour of the solution changed to red. To the partially cooled solution, leukotrope W (2 g) was added and refluxed for 2 hrs. The product was isolated by pouring the mixture on water. It was crystallized from petroleum ether in light yellow needles, m.p. 196-7°. (Found: C, 85.9; H, 5.0%. $C_{28}H_{22}O_2$ requires C, 86.1; H, 5.6%).

REFERENCES

1. BASF, DRP 411,013.
2. BIOS 987, p.70; Colour Index (Vat Green 2),3487.
3. BIOS 987
4. Stallmann and Du Pont, B.P. 546, 997; Maki, J.Soc.Chem.Ind.Japan, 46, 1256 (1943).
5. Johnson, quoted in Vicketstaff, The Physical Chemistry of Dyeing, Oliver Boyd, London, 1954.
6. Fox, Vat Dyestuffs and Vat Dyeing, Chapman and Hall, London, 1946.
7. Bilik, Novosti Tekhniki, 1936, No.42-43, 42.
8. N.R. Rao, K.H. Shah and K. Venkataraman, Curr.Sci.(India) (1950) 19, 149; (1951) 20, 66.
9. M.K. Unni and K. Venkataraman, J.Sci.Ind.Res.(India) 19B, 355 (1960).
10. S.S. Malhotra, M.K. Unni and K. Venkataraman, J.Sci.Ind.Res.(India), 19B, 382 (1960).
11. Colour index (CI 59830), 3487.
12. N.K. Sampat, M.Sc.(Tech.) Thesis, Bombay University (1960).
13. DRP 470, 184; Frdl. 16, 1133.
14. D.H. Hey, R.J. Nicholls and C.W. Pritchett, J.Chem.Soc. (1944), 97.
15. K.H. Meyer, J.Chem.Soc., 100(I), 193 (1911).

PART II

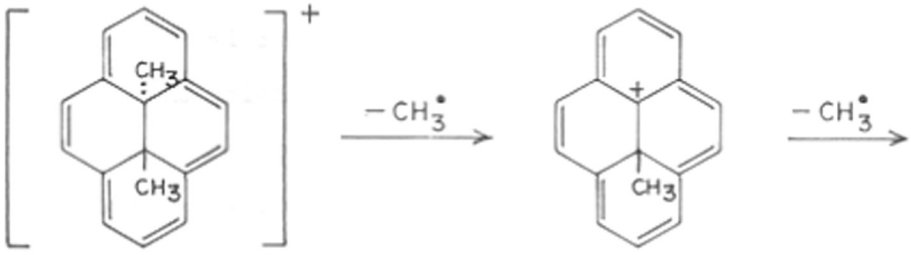
ELECTRON IMPACT STUDIES OF SOME VIOLANTHRENE DERIVATIVES

INTRODUCTION

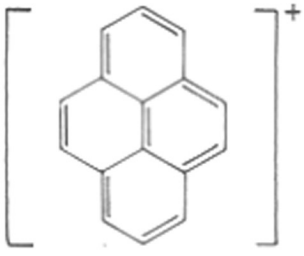
Petroleum chemists were the first to realize the use of mass spectroscopy as an analytical tool in organic chemistry[1]. Unlike aliphatic hydrocarbons where bond fission occurs simultaneously at various positions accompanied by extensive rearrangements which are difficult to rationalise, the aromatic hydrocarbons give well defined spectra. In aromatic compounds the initial ionization can take place with the loss of an electron from the π system and the charge is stabilized by resonance.

The mass spectra of alkylbenzenes were extensively studied by Meyerson and coworkers[2]. The most characteristic cleavage of alkylbenzenes is β-cleavage resulting in the rupture of the benzylically activated bond. Polyalkylated benzenes decompose in the same manner to provide substituted tropylium ions by ring expansion. Like benzene, biphenyl undergoes very little fragmentation; the main product is the $C_6H_4^+$ ion (m/e 76) accompanied by benzene; a smaller m/e 77 peak is also observed, but it is not certain if it represents the doubly charged molecular ion ($C_{12}H_{10}^{++}$) or the $C_6H_5^+$ ion[1]. Alkylated biphenyls and polyphenyls are similar in their behaviour to alkylbenzenes.

Relatively little work has been done on polycyclic hydrocarbons. Unsubstituted aromatic hydrocarbons such as naphthalene, chrysene and pyrene show[3] only very little fragmentation. Loss of acetylene is the major fragmentation mode. In trans-15,16-dimethyl-15,16-dihydropyrene (I)[4], the only significant fragment, besides the molecular ion, corresponds to the successive loss of two methyl groups.



I



The mass spectra of various quinones and polycyclic ketones have been studied by Beynon and Williams[5]. Loss of carbon monoxide has been shown to be a preferred fragmentation mode in quinones.

Using the vacuum spark mass spectrograph, Hodgson *et al.*[6], studied the fragmentation of a few polycyclic aromatic hydrocarbons. Contrary to previous reports that only atomic species can be observed in the spark, they recorded ions of masses up to and above the molecular weights and also distinct groups of lines equal to the number of carbon atoms in the molecule. Van Brunt and Wacks[7] reported the ionization energies of some polynuclear hydrocarbons and compared them with the values obtained from molecular orbital calculations. Multiply charged ions are characteristic of the mass spectra of polynuclear aromatic hydrocarbons[8,9] and compounds containing hetero atoms[10,11].

The mass spectral fragmentation of dyes has not been studied so far, probably because of the difficulty in handling them in the mass spectrometer.

The limited number of aliphatic methyl ethers which have been studied[12] show fission on both sides of the oxygen to give ions having masses of 15 and 31 units less than the molecular weight. Fragmentation of anisole occurs by fission of either C-O bond to give ions due to loss of a methyl radical or a formaldehyde molecule[13].

2-Methoxynaphthalene and methyl-substituted methoxynaphthalenes behave like the benzene analogues, necessarily losing CH_3, CO and finally a hydrogen molecule[1].

PRESENT WORK

The mass spectum of 16,17-dimethoxyviolanthrone (CI Vat green 1 ; CI 59825) (II) was recorded, although the compound was not volatile enough to give a perfect spectrum, a significant peak due to the molecular ion was observed at m/e 516. This symmetrical compound fragments in a random way. Very insignificant fragments due to loss of methyls from methoxyls were observed. No peak due to loss of carbon monoxide or acetylene from the molecular ion was significant. Doubly charged ions as well as singly charged ions due to the cleavage of the molecule into two halves were absent.

By reductive methylation of (II), 5,10,16,17-tetramethoxyviolanthrene (III) was obtained (see Part I). This compound was found to be more volatile than the parent quinone. The molecular ion at m/e 546 (Fig. 1) was very significant (76 per cent of the base peak). Two sets of peaks were observed, one corresponding to the fragments formed directly from the molecular ion,

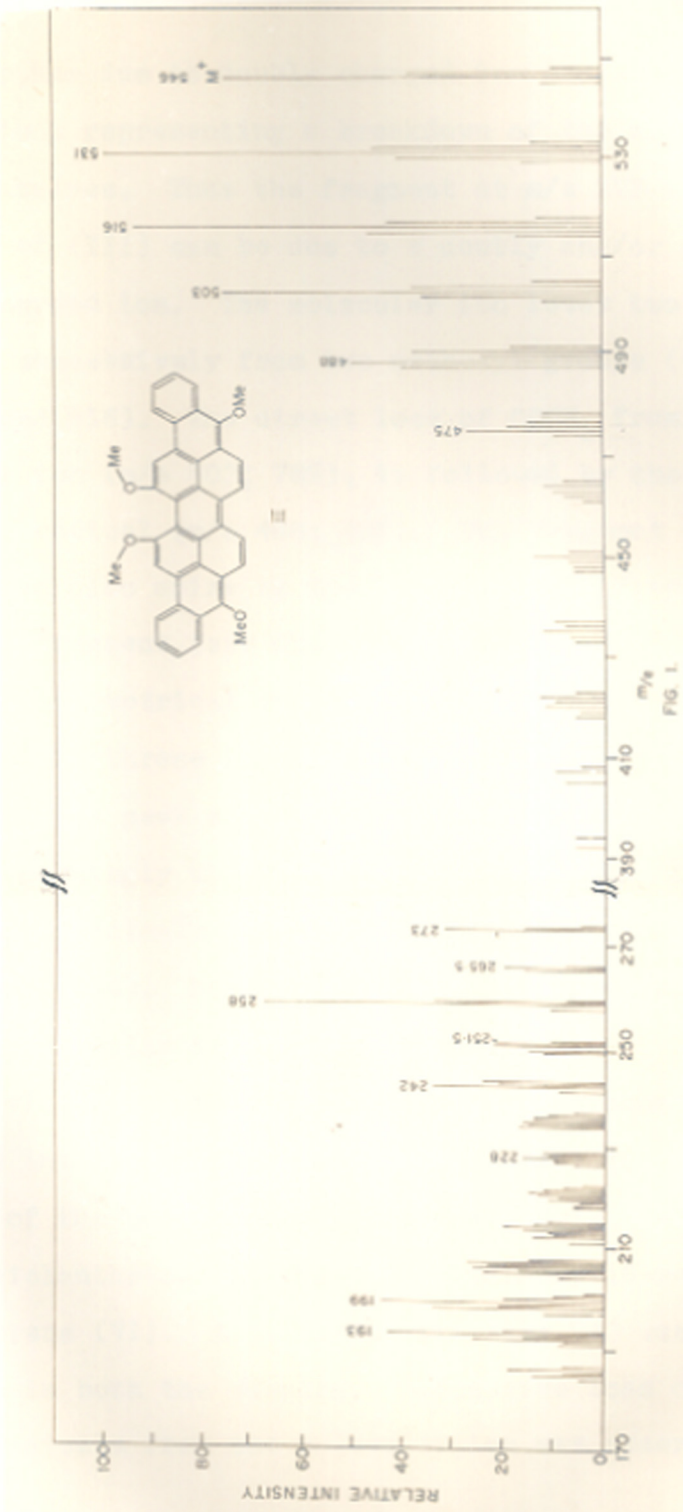
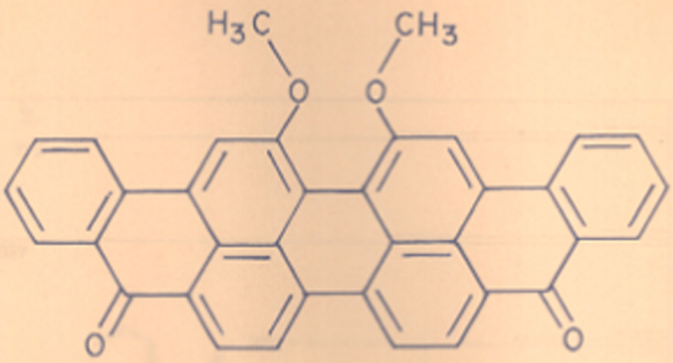

RELATIVE INTENSITY
100
80
60
40
20
0
170
193
199
210
226
242
251·5
258
265·5
273
270
390
410
450
475
480
490
503
516
531
530
M+ 546
OMe
Me
Me
MeO
III
m/e

FIG. 1.

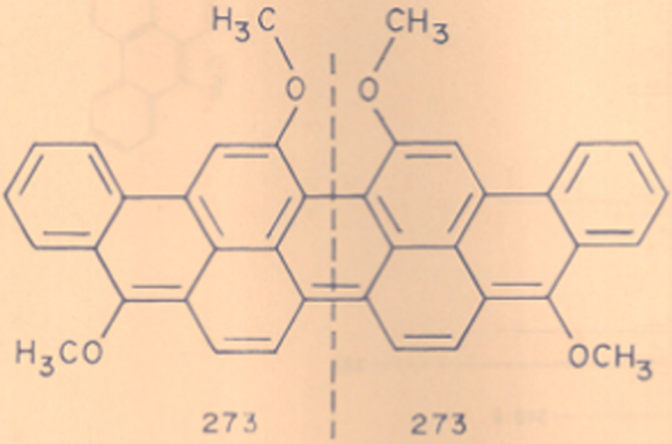
and the other due to doubly charged ions and/or singly charged ions representing a breakdown of the molecule into two halves. Thus the fragment at m/e 273 in the spectrum of (III) can be due to a doubly and/or a singly charged ion. The molecular ion loses two methyl radicals successively from two methoxyl groups (peaks at m/e 531 and 516). The direct loss of $COCH_3$ from the molecular ion (m/e 503; 76%), is followed by the loss of methyl radical (m/e 488; 40%). The fragment at m/e 488 can also arise by the loss of $COCH_3$ from the (M - CH_3) fragment (see Chart I).

The symmetrical compound 5,10-dimethoxy-16,17-dimethylviolanthrene (IV) (Fig. 2) also behaves in the same way. The peak at m/e 257 in the spectrum can be a doubly or singly charged ion. The molecular ion loses four methyl radicals successively (fragments at m/e 499, 484,469 and 454). No loss of $COCH_3$ was observed either from the molecular ion or the fragments.

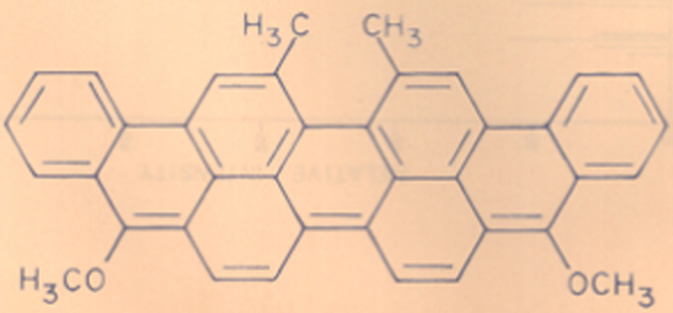
Evidence of the fragmentation of compounds (III) and (IV) into two halves was obtained from the mass spectra of the unsymmetrical compounds 5,10,16-trimethoxyviolanthrene (V) and 5,10-dimethoxy-16-methylviolanthrene (VI). A fragment with mass 243 was observed in both the spectra. Successive loss of three methyl radicals from the molecular ion was observed



II



III



IV

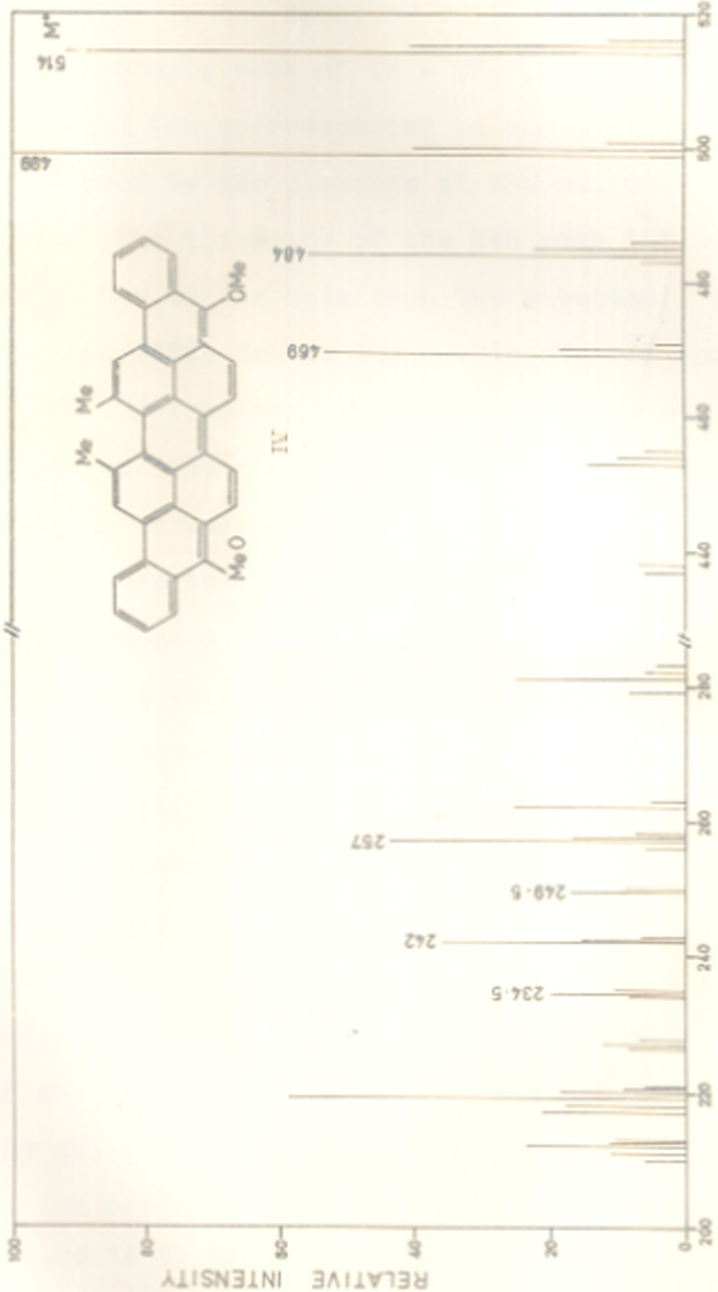

RELATIVE INTENSITY
100
80
60
40
20
0
200
220
240
260
280
440
480
500
520
m/e
M+
514
489
484
469
257
249·5
242
234·5
OMe
Me
Me
MeO

FIG 2.

in the spectrum of compound (VI) (Fig. 3). The peak at m/e 243 in the spectrum of (VI) can be either the isotopic peak of $(M - CH_3)^{2+}$ or the singly charged ion corresponding to one half of the molecule formed by the cleavage of the molecule into two halves. The intensity of the 243 peak (83.3% of the peak at 242.5) was more than the expected isotopic peak (40%) due to the doubly charged ion $(M - CH_3)$. The abundance of the peak at m/e 244 shows that it is the isotopic peak of the singly charged ion corresponding to one half of the molecule. Thus the molecule appears to cleave into two halves. The fragment corresponding to the other half of the molecule is not observed. This is probably due to the fact that the odd-electron molecular ion fragments into an ion with mass 243 and a free radical or neutral molecule. Compound (V) also appears to cleave into two halves under electron impact. The peak at m/e 243 (see Table 1) may be due to the doubly charged (M - 30) ion and/or the singly charged ion corresponding to one half of the molecule. The peak at m/e 228 can only arise by the loss of a methyl radical from the singly charged ion corresponding to half of the molecule. Since there is no peak at m/e 456, the fragment 228 cannot be a doubly charged ion. However, the peak

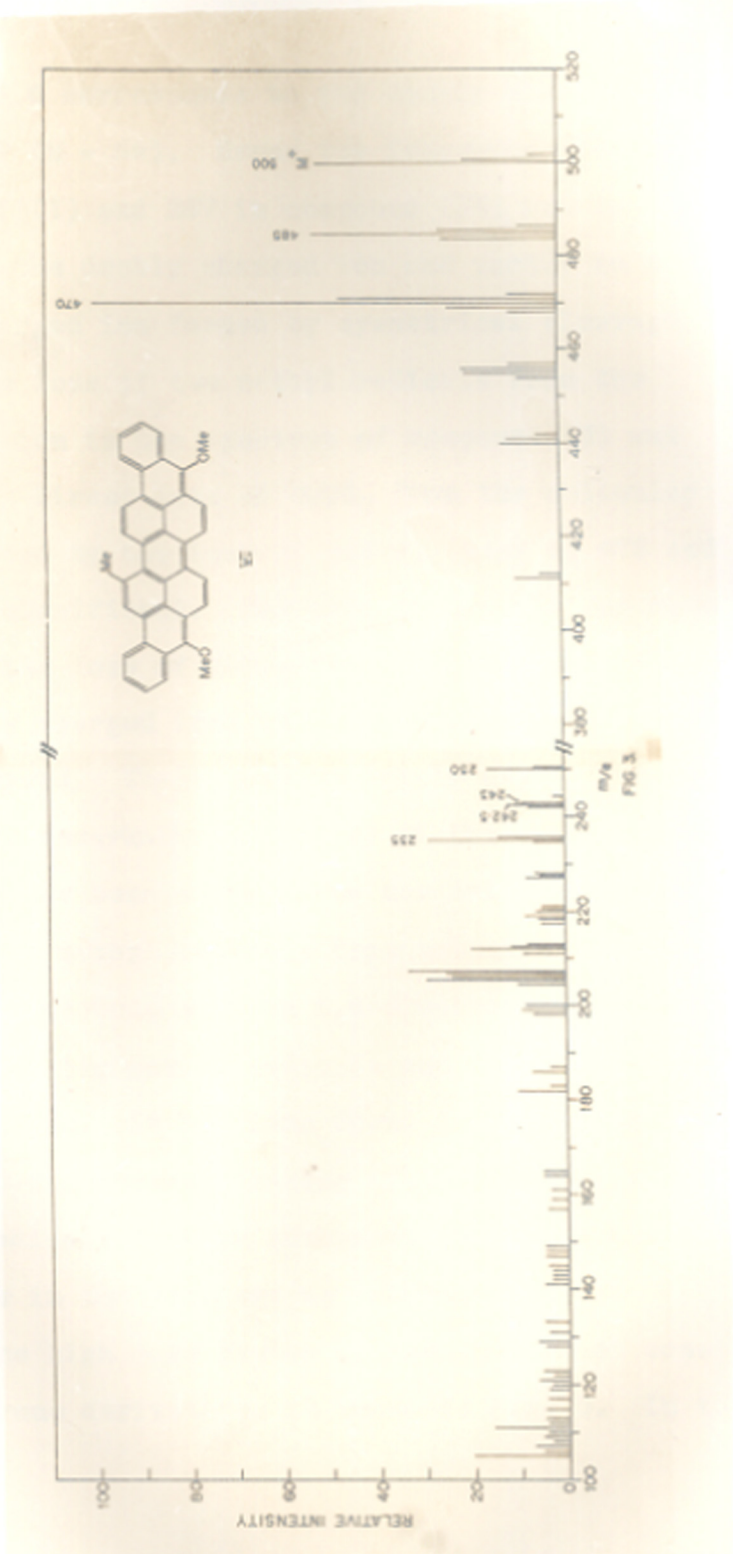

RELATIVE INTENSITY
m/e
M+ 500
485
470
255
243.5
243
230
OMe
Me
MeO

FIG 3

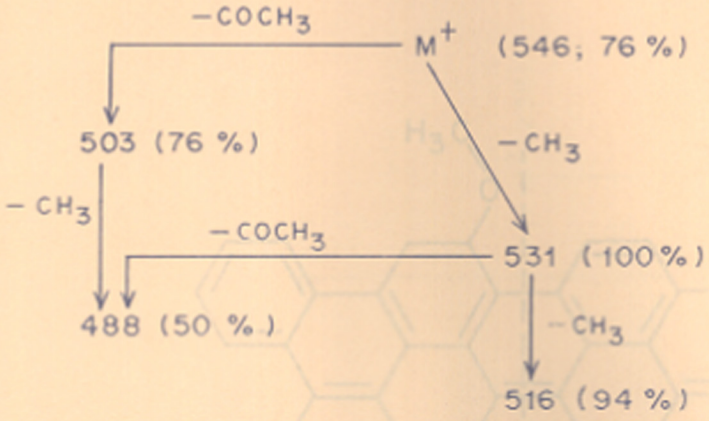
at m/e 228.5 corresponds to the doubly charged ion of m/e 457 (M - 59). Hence the fragments 273 in compound (III) and 257 in compound (IV) can be due partly to the doubly charged ion and partly to the singly charged ion formed by symmetrical cleavage. The successive loss of two methyl radicals from the molecular ion in the spectrum of compound (V) was observed. Direct loss of $COCH_3$ from the molecular ion followed by the loss of methyl (peak at 473 and 458) was significant. The peak at m/e 458 can also arise by the loss of $COCH_3$ from the (M - CH_3) fragment. The doubly charged ions in all the spectra except (II) were observed. There were no triply charged ions.

The remarkable stability of the quinonoid structure has been shown to be the driving force for the loss of methyl radicals from methoxyl groups in aromatic compounds such as 1,4-dimethoxybenzene[14], which loses two methyl radicals and forms a stable p-quinone ion. It has been found in the present work that 9,10-dimethoxyanthracene (VII) (Fig. 4) loses two methyl radicals to form anthraquinone which then fragments in the same way as anthraquinone.

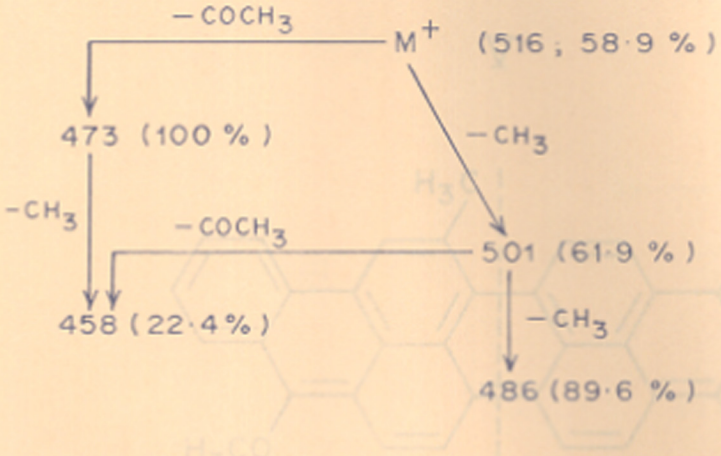
The high mass region in the spectra of some violanthrone derivatives is shown in Fig. 5. In the

CHART - 1

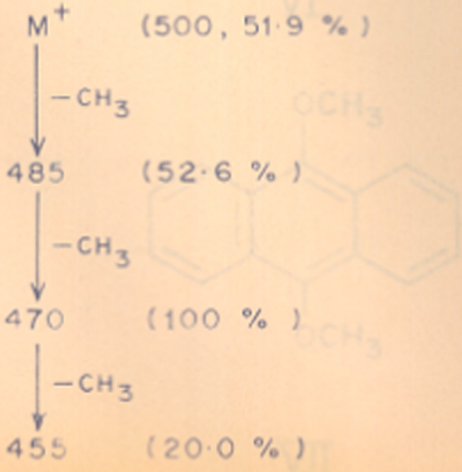
COMPOUND III

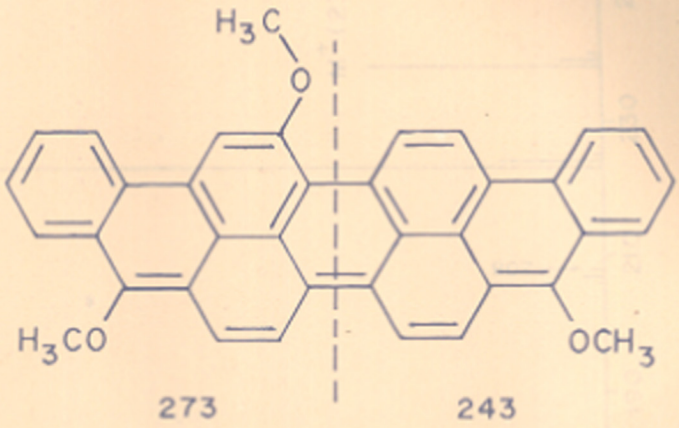


COMPOUND V

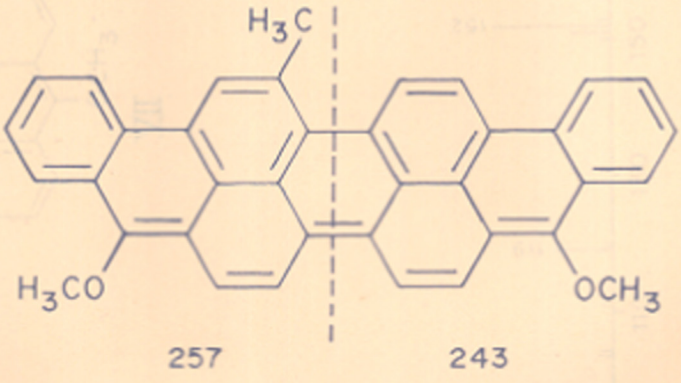


COMPOUND VI

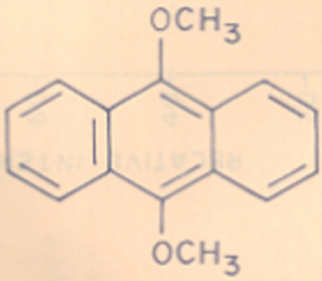




V



VI



VII

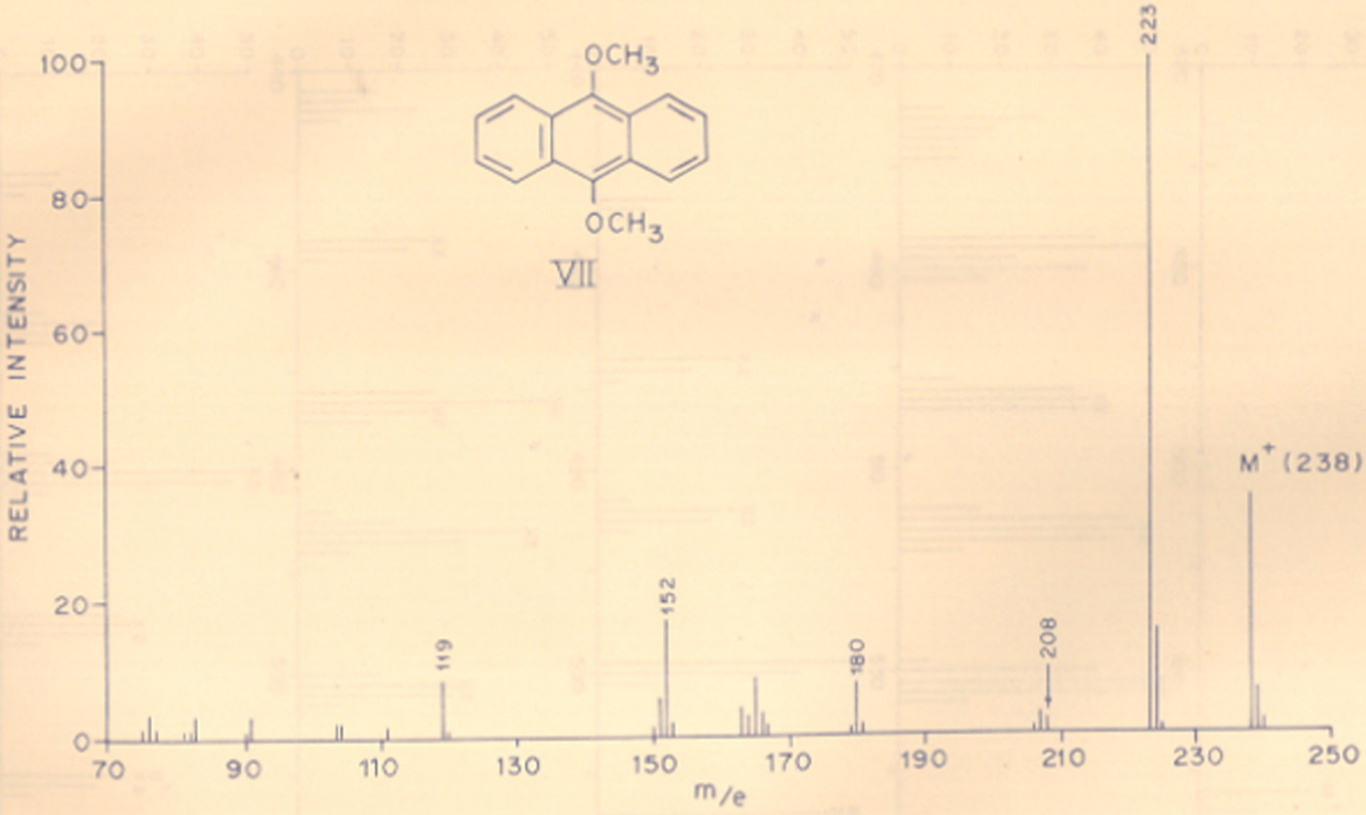

OCH3
OCH3
VII
RELATIVE INTENSITY
100
80
60
40
20
0
70
90
110
130
150
170
190
210
230
250
m/e
119
152
180
208
223
M+ (238)

FIG. 4.

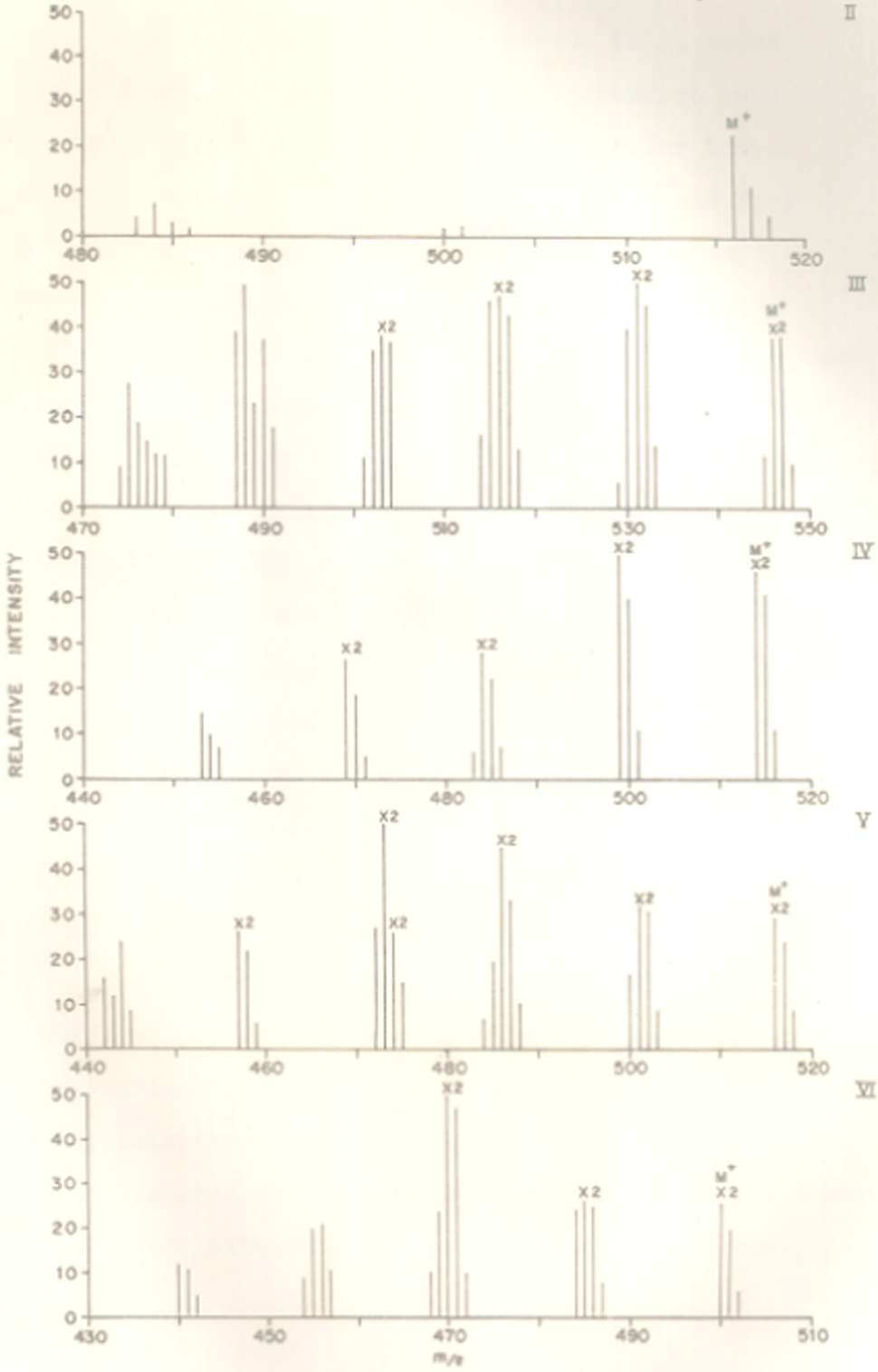


FIG. 5.

spectra of all the derivatives except (II), peaks are observed corresponding to the successive loss of only two methyl radicals from the molecular ion. Though compounds (VI) and (IV) lose three and four methyl radicals, no loss of a third methyl was observed in the case of the trimethoxy and tetramethoxy compounds (V) and (III). It appears that the loss of a third methyl in (VI) and third and fourth methyl radicals in the spectrum of (IV) is from C-methyl groups. A comparison of these spectra therefore showed that methyl radicals are preferentially lost from the methoxyl groups in the C-5 and C-10 positions, the driving force being to the formation of the corresponding violanthrone derivatives of great stability. The loss of a formaldehyde molecule from a methoxyl group cannot result in as stable an ion as the quinonoid structure formed by the loss of two methyl radicals; hence the former appears to be a less significant fragmentation mode.

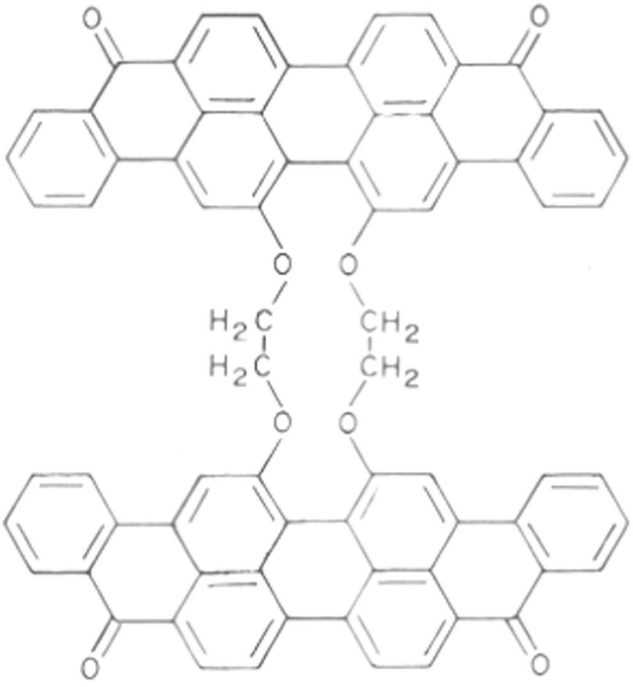
The study of the fragmentation pattern of methyl ethers of polynuclear hydrocarbons has been extended to the confirmation of the monomeric nature of 16,17-ethylenedioxyviolanthrone (Indanthren Navy Blue G; CI 71200).

Indanthren Navy Blue G is prepared by the action of ethylene dibromide or 2-chloroethyl p-toluene-

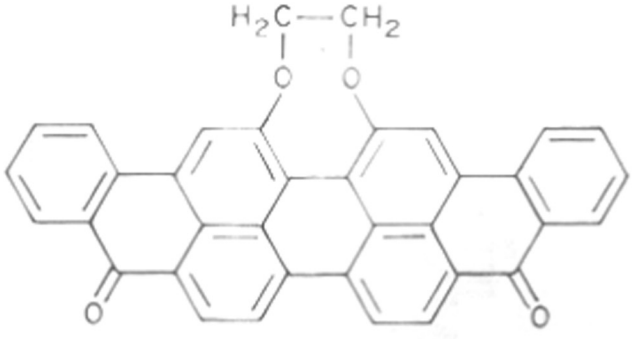
sulphonate on 16,17-dihydroxyviolanthrone. The dimeric structure (VIII)was assigned to this dye earlier[15]. In the new Colour Index (1956) it is formulated as the monomeric compound (VIXI) with the note, for which no reference or reason is cited that "the dimeric formula postulated for this dye is believed to be incorrect". Nair et al.[16] have studied this problem in the light of absorption spectra and concluded that the compound is monomeric (VIXI).

The monomeric nature of 16,17-ethylene-dioxyviolanthrone has been established from the mass spectrum of its reductive methylation product (X) (Fig. 6). The molecular ion was observed at m/e 544. It is evident from the previous discussion that doubly charged ions are very characteristic of these compounds. If the compound is a dimer, a peak at m/e 544.5, corresponding to the doubly charged ion of M + 1 (1089) should be observed. The absence of a peak at m/e 544.5 rules out the dimeric structure. The peak at m/e 545 (14.6% of base peak) appears to be the isotopic peak of the molecular ion 544. Additional peaks above m/e 544 are to be expected if the compound (X) has a dimeric structure. The absence of such peaks further supports the monomeric nature of the compound. Successive loss of two methyl radicals from the molecular ion is significant (peaks

59



VIII



IX

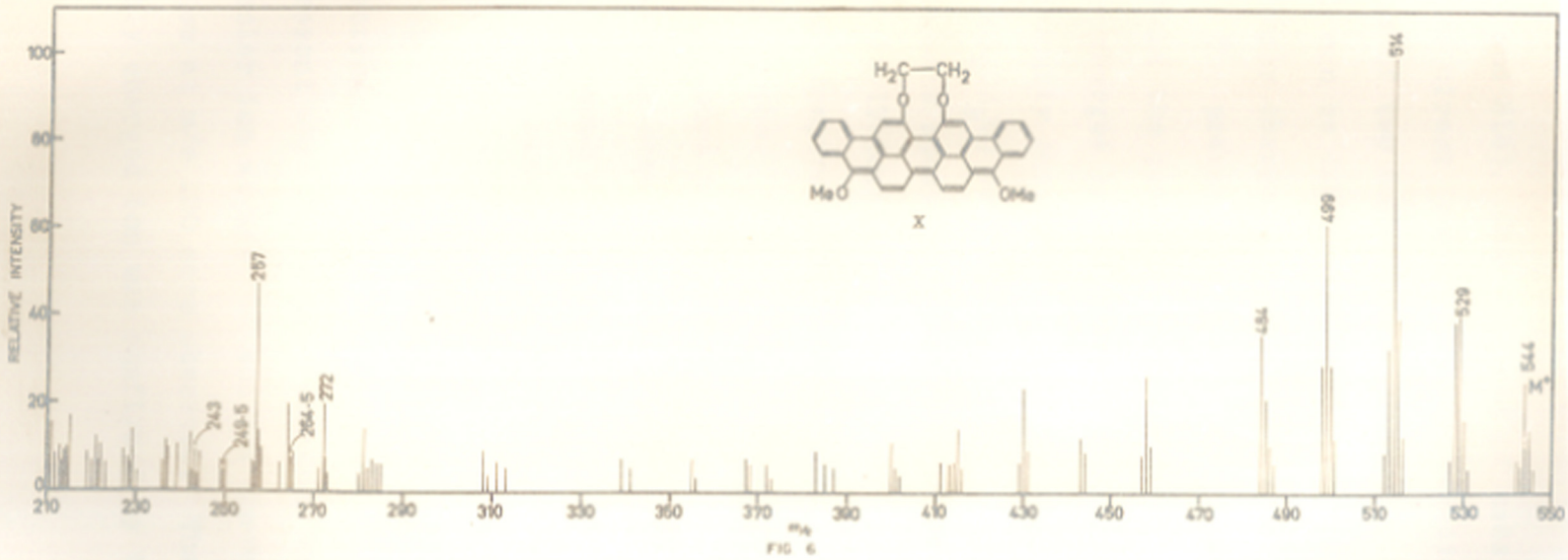
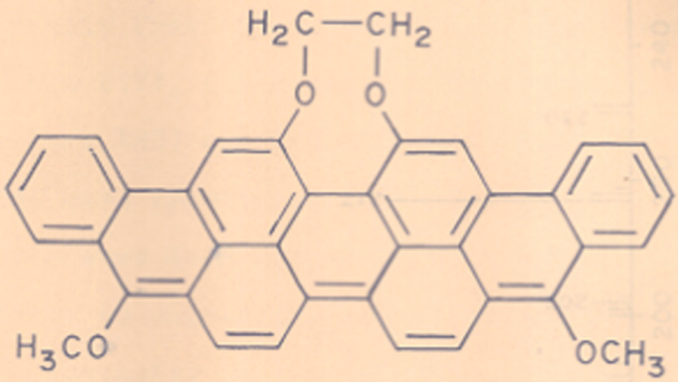

RELATIVE INTENSITY
100
80
60
40
20
0
243
249·5
257
264·5
272
484
499
514
529
544
X_2
210
230
250
270
290
310
330
350
370
390
410
430
450
470
490
510
530
550
m/e
H_2C—CH_2
MeO
OMe
X

FIG 6

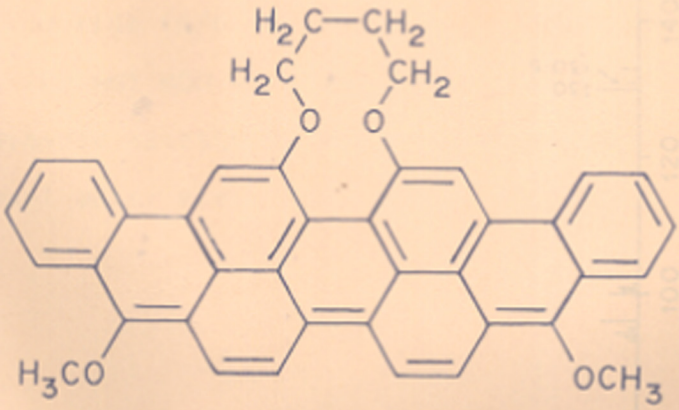
at m/e 529 and 514). The fragment of mass 484 can arise by the direct loss of the ethylenedioxy group or the loss of two formaldehyde molecules. The peak at m/e 272 can be due to the doubly charged ion of M^+ or a singly charged ion formed by symmetrical cleavage. The presence of the peaks at m/e 272.5 and 273 show that the peak at m/e 272 may be partly due to the doubly charged ion and partly to the singly charged ion. The doubly charged ions of M - CH_3, M - 2 CH_3 and (M - OCH_2CH_2O) were observed in the spectrum.

The mass spectrum of the reductive methylation product of 16,17-butylenedioxyviolanthrone (XI) was recorded and compared with the analogue from 16,17-ethylenedioxyviolanthrone. The molecular ion was observed at m/e 572. It loses two methyl radicals successively.

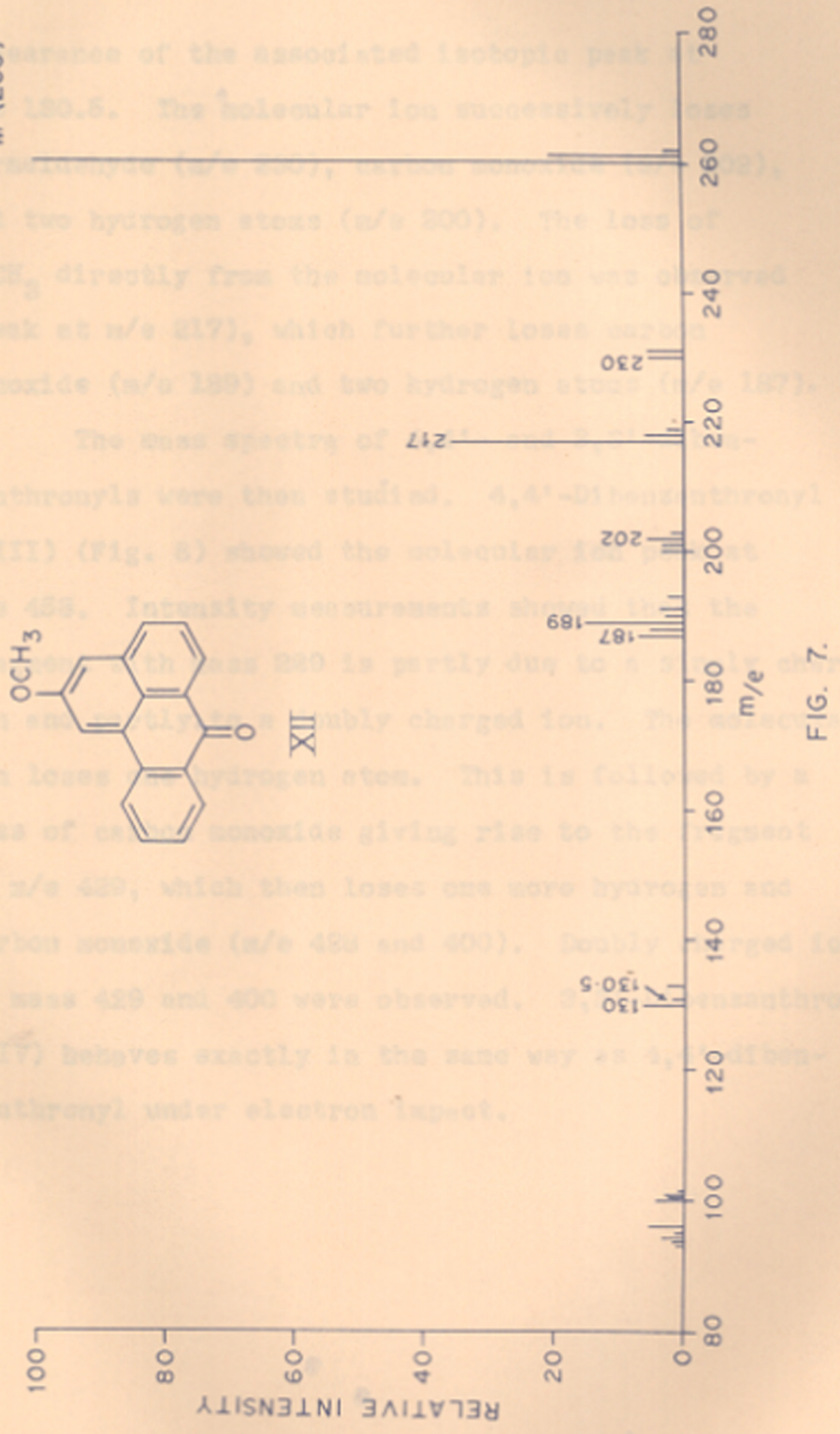
The mass spectrum of benzanthrone has been recorded by Beynon and Williams[5], who found that the loss of carbon monoxide is a significant fragmentation mode. The resulting fragment ion then loses two hydrogen atoms forming a new ring. The mass spectrum of 2-methoxybenzanthrone (XII) (Fig. 7) was recorded in the present work for comparison with benzanthrone. The molecular ion at m/e 260 and the corresponding doubly charged ion at m/e 130 were observed. The presence of a doubly charged ion was confirmed by the



X



XI

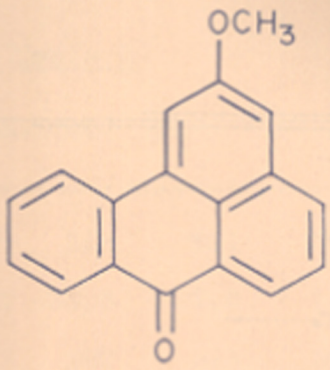

RELATIVE INTENSITY
100
80
60
40
20
0
80
100
120
140
160
180
200
220
240
260
280
m/e
M+(260)
230
217
202
189
187
130
130·5
OCH3
O

XII

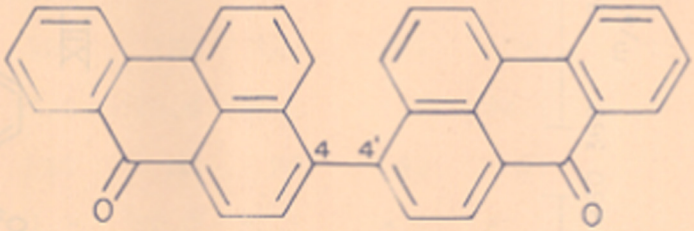
FIG. 7.

appearance of the associated isotopic peak at m/e 130.5. The molecular ion successively loses formaldehyde (m/e 230), carbon monoxide (m/e 202), and two hydrogen atoms (m/e 200). The loss of $COCH_3$ directly from the molecular ion was observed (peak at m/e 217), which further loses carbon monoxide (m/e 189) and two hydrogen atoms (m/e 187).

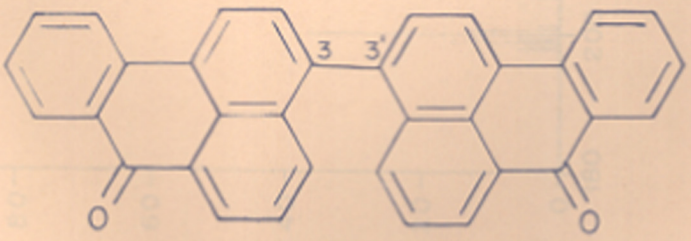
The mass spectra of 4,4'- and 3,3'-dibenzanthronyls were then studied. 4,4'-Dibenzanthronyl (XIII) (Fig. 8) showed the molecular ion peak at m/e 458. Intensity measurements showed that the fragment with mass 229 is partly due to a singly charged ion and partly to a doubly charged ion. The molecular ion loses one hydrogen atom. This is followed by a loss of carbon monoxide giving rise to the fragment at m/e 429, which then loses one more hydrogen and carbon monoxide (m/e 428 and 400). Doubly charged ions of mass 429 and 400 were observed. 3,3'-Dibenzanthronyl (XIV) behaves exactly in the same way as 4,4'-dibenzanthronyl under electron impact.



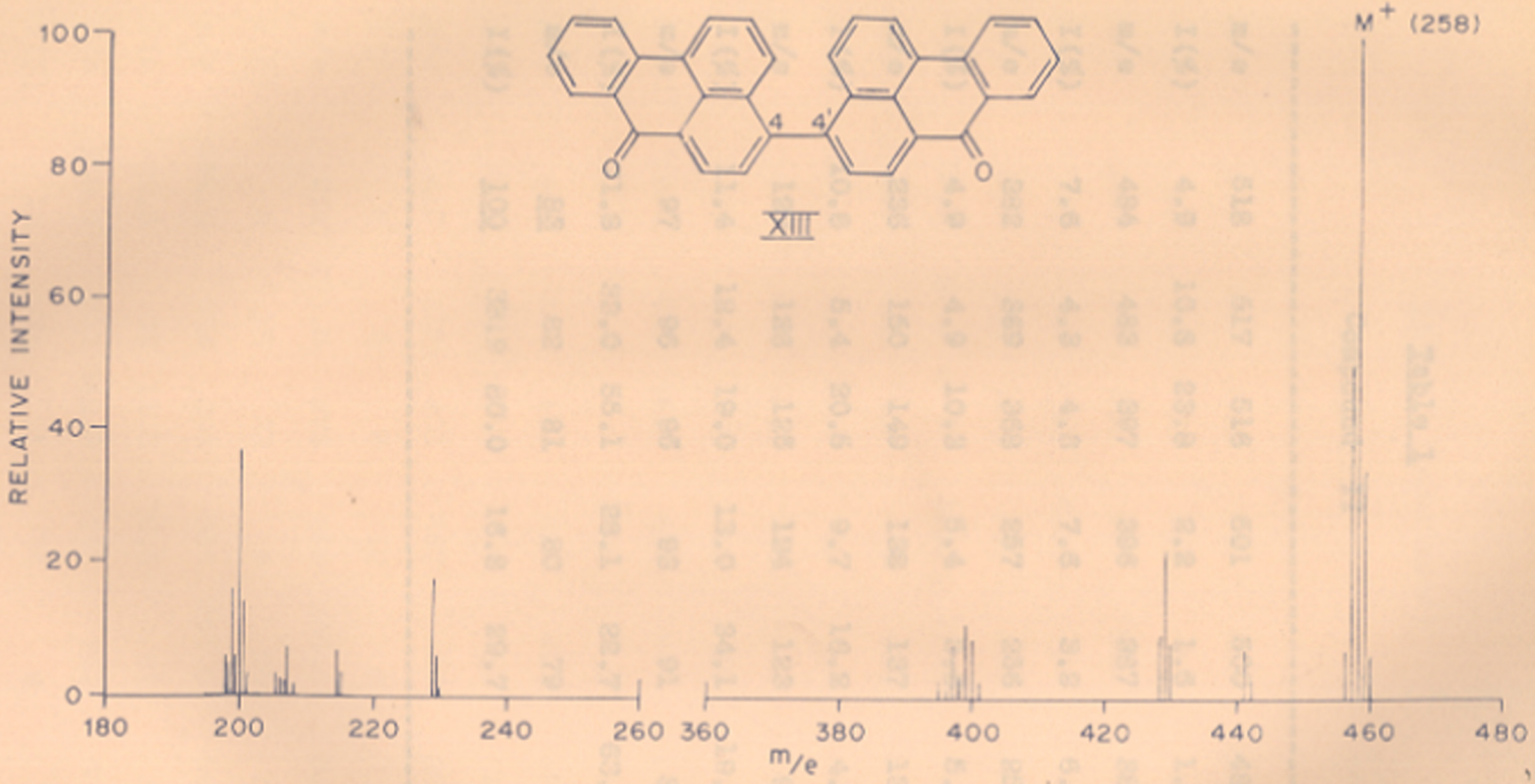
XII



XIII



XIV


100
80
60
40
20
0
RELATIVE INTENSITY
180
200
220
240
260
360
380
400
420
440
460
480
m/e
M+ (258)
4
4'
O
O

XIII

FIG. 8.

Table 1

Compound II

m/e	518	517	516	501	500	486	485
I(%)	4.9	10.8	23.8	2.2	1.6	1.6	3.2
m/e	484	483	397	396	387	386	383
I(%)	7.6	4.3	4.3	7.6	3.2	6.5	2.5
m/e	382	369	368	257	256	255	237
I(%)	4.9	4.9	10.3	5.4	3.8	5.4	5.4
m/e	236	150	149	138	137	130	129
I(%)	10.8	5.4	20.5	9.7	16.2	4.9	21.6
m/e	127	126	125	124	123	99	98
I(%)	11.4	12.4	19.0	13.0	34.1	19.5	34.9
m/e	97	96	95	93	91	85	84
I(%)	71.8	33.0	55.1	28.1	22.7	63.2	45.9
m/e	83	82	81	80	79		
I(%)	100	38.9	80.0	16.8	29.7		

Table 1 (continued)

Compound III

m/e	548	547	546	545	533	532	531
I(%)	10	38	76	12	14	45	100
m/e	530	529	518	517	516	515	514
I(%)	40	16	13	42.5	94	46	16.5
m/e	505	504	503	502	501	491	490
I(%)	13.5	37.5	76	35.5	11.5	18	37.5
m/e	489	488	487	479	478	477	476
I(%)	23.5	50	39.5	12	12	15	19
m/e	475	474	465	464	463	462	461
I(%)	27	9.5	8	12	10	8	4
m/e	451	450	449	448	447	437	436
I(%)	7	14	7	6	6	10	8
m/e	435	434	433	423	422	421	420
I(%)	12	7	6	6	13	10	12
m/e	419	418	408	407	405	394	392
I(%)	5	6	5	10	8	6	6
m/e	274	273.5	273	266	265.5	265	259
I(%)	5	16	32	8	20	16	7
m/e	258.5	258	257	252	251.5	251	250
I(%)	33.5	68	11.5	10.5	21	22	15
m/e	249.5	243	242.5	242	241	237	236.5
I(%)	12	24	21	34	9	6	11

Table 1 (continued)

Compound III (continued)

m/e	236	235.5	235	234.5	234	229	228.5
I(%)	14	14	16	15	17	12	11
m/e	228	227.5	227	226.5	222.5	222	221.5
I(%)	16	10	10	6	4	8	12
m/e	221	220.5	220	219.5	219	218.5	218
I(%)	15	13	9	11	5	6	6
m/e	215	214.5	214	213.5	213	212.5	212
I(%)	11	14	20	16	11	10	14
m/e	211	207.5	207	206.5	206	205.5	205
I(%)	7	15	27	23	26	17	24
m/e	204	201	200.5	200	199	198.5	198
I(%)	9	4	10	20	44	21	34
m/e	197	193.5	193	192.5	192	191.5	191
I(%)	12	20	43	16	26	8	9
m/e	186.5	186	185.5	185	184		
I(%)	8	19	8	14	5		

Table 1 (continued)

Compound IV

m/e	516	515	514	501	500	499	486	485
I(%)	11.5	40.8	92.3	11.5	40.0	100	7.7	22.3
m/e	484	483	471	470	469	455	454	453
I(%)	56.2	6.2	4.6	18.5	53.1	6.9	10.0	14.6
m/e	438	437	283	282	281	279	263	262
I(%)	6.9	6.2	4.6	6.2	25.4	8.5	5.4	25.4
m/e	258	257.5	257	256	250	249.5	243	242.5
I(%)	7.7	16.9	43.9	6.2	9.2	16.9	6.9	15.4
m/e	242	235	234.5	234	228	227	226.5	
I(%)	36.2	10.8	20.0	8.5	6.9	12.3	8.5	
m/e	221	220.5	220	219	218	217	213	
I(%)	6.2	9.2	18.5	59.2	17.7	21.5	10.8	
m/e	212.5	212	211	210				
I(%)	11.5	23.8	11.5	6.2				

Table 1 (continued)

Compound V

m/e	518	517	516	503	502	501	500	488
I(%)	9.0	23.9	58.9	9.0	31.3	61.9	17.2	10.5
m/e	487	486	485	484	475	474	473	472
I(%)	33.6	89.6	20.2	7.5	14.9	52.2	100	27.5
m/e	459	458	457	445	444	443	442	430
I(%)	6.0	22.4	52.2	9.0	23.9	11.9	16.0	14.9
m/e	429	428	427	415	414	413	412	408
I(%)	36.0	11.2	13.4	11.2	28.4	6.0	8.2	9.7
m/e	400	399	283	282	281	268	263	262
I(%)	6.0	13.4	6.7	9.0	26.8	8.2	7.5	19.4
m/e	258.5	258	251	250.5	250	244	243.5	243
I(%)	9.0	23.9	11.2	13.4	7.5	8.2	16.4	47.8
m/e	237	236.5	236	229	228.5	228	222	221.5
I(%)	11.9	17.9	13.4	9.7	9.7	23.9	6.7	8.2
m/e	221	220	219	218	217	216	214.5	214
I(%)	11.9	16.4	52.2	18.7	23.7	10.5	11.9	28.4
m/e	213.5	213	212	206.5	206	205.5	204.5	202
I(%)	11.9	13.4	16.5	32.8	14.9	26.9	11.2	12.7
m/e	201	200.5	200	199.5	199	198	197	194
I(%)	10.5	16.0	55.2	18.7	44.8	17.9	8.2	14.9
m/e	193.5	193	192.5	192	191.5	191	189	187
I(%)	25.4	16.4	18.7	7.5	11.2	14.9	7.5	11.2
m/e	186	185	184	183	180	179	178	177
I(%))	25.4	10.5	7.5	9.0	10.5	8.2	7.5	8.2

Table 1 (continued)

Compound VI

m/e	502	501	500	487	486	485	484
I(%)	5.9	20.0	51.9	8.1	25.2	52.6	24.4
m/e	472	471	470	469	468	457	456
I(%)	10.4	46.7	100	23.7	10.4	10.4	20.7
m/e	455	454	442	441	440	412	411
I(%)	20.0	8.9	4.8	11.1	12.6	4.4	9.6
m/e	250.5	250	244	243	242.5	242	235.5
I(%)	6.3	16.3	2.2	9.3	11.1	7.8	14.1
m/e	235	234.5	228	227.5	227	221	220.5
I(%)	28.9	6.7	6.7	5.6	8.1	5.2	5.2
m/e	220	219	218.5	217.5	213	212.5	212
I(%)	6.3	8.9	5.9	5.2	8.1	11.8	20.0
m/e	211	207	206.5	206	205.5	204.5	200
I(%)	8.9	33.3	25.2	24.1	29.6	10.4	8.5
m/e	199	198	187	186	183	182	165
I(%)	9.6	7.0	3.7	7.4	3.7	10.4	5.2
m/e	164	161	159	157	149	148	147
I(%)	5.2	3.7	3.7	4.4	5.2	5.2	5.2
m/e	145	144	143	142	141	133	131
I(%)	4.4	3.7	3.7	3.7	5.2	5.2	4.8
m/e	129	128	123	122	121	120	119
I(%)	6.7	5.2	5.9	3.7	6.7	3.7	4.4
m/e	117	115	113	112	111	110	109
I(%)	4.8	5.2	5.2	4.8	16.3	4.8	5.9
m/e	108	107	106	105			
I(%)	3.7	7.4	5.6	20.7			

Table 1 (continued)

Compound VII

m/e	240	239	238	225	224	223
I(%)	0.82	6.5	35.3	1.6	15.4	100
m/e	221	208	207	206	181	180
I(%)	1.1	1.7	2.1	1.2	1.0	6.5
m/e	179	167	166	165	164	163
I(%)	1.0	1.4	3.4	7.8	3.1	4.6
m/e	153	152	151	150	119.5	119
I(%)	2.2	16.5	5.7	1.7	0.8	8.0
m/e	111	105	104	91	90	82.5
I(%)	1.8	1.7	1.9	3.2	1.0	2.7
m/e	82	81.5	77	76	75	
I(%)	1.1	1.0	1.2	3.5	1.4	

Table 1 (continued

Compound X

m/e	546	545	544	543	542	531
I(%)	5.4	14.6	25.4	6.2	7.7	5.4
m/e	530	529	528	527	516	515
I(%)	16.9	40.8	39.2	7.7	13.1	40.0
m/e	514	513	512	501	500	499
I(%)	100	33.1	9.2	12.3	29.2	61.6
m/e	498	487	486	485	484	459
I(%)	29.2	6.9	10.8	21.6	36.2	10.8
m/e	458	457	444	443	431	430
I(%)	26.9	8.5	9.2	12.3	8.5	23.9
m/e	429	416	415	414	413	411
I(%)	6.9	5.4	14.6	6.9	6.2	6.9
m/e	402	401	400	387	385	383
I(%)	3.8	5.4	11.5	5.4	6.2	9.2
m/e	373	372	368	367	356	355
I(%)	3.1	6.2	6.2	7.7	3.1	7.7
m/e	341	339	313	311	309	308
I(%)	5.4	7.7	5.4	6.9	3.8	9.2
m/e	285	284	283	282	281	280
I(%)	6.2	6.2	7.7	5.4	14.6	4.6
m/e	273	272.5	272	271	265	264.5
I(%)	4.6	7.7	20.0	5.4	9.2	7.7
m/e	264	262	258	257.5	257	256.5
I(%)	20.0	6.9	10.0	13.9	47.7	6.2
m/e	256	250	249.5	249	244	243.5
I(%)	6.9	6.9	5.4	6.9	8.5	3.8
m/e	243	242.5	242	239	237	236.5
I(%)	9.2	4.6	13.1	10.8	10.0	11.5
m/e	236	230	229	228.5	228	227
I(%)	10.8	4.6	13.9	6.2	7.7	9.2
m/e	223	222	221.5	221	220	219
I(%)	6.2	10.8	6.9	12.3	6.9	8.5
m/e	215	214.5	214	213.5	213	212
I(%)	16.9	10.0	9.2	6.9	10.0	8.5
m/e	211					
I(%)	15.4					

Table 1 (continued)

Compound XI

m/e	574	573	572	571	570	559
I(%)	2.5	5.0	6.9	5.0	8.8	10.0
m/e	558	557	556	555	545	544
I(%)	14.4	25.6	8.8	7.5	6.3	14.1
m/e	543	542	541	540	520	519
I(%)	20.0	46.3	21.2	28.8	11.3	14.1
m/e	518	517	516	506	505	504
I(%)	28.8	43.8	77.5	5.0	16.3	12.5
m/e	503	502	501	491	490	489
I(%)	20.0	43.8	100	11.3	20.0	21.2

Compound XII

m/e	262	261	260	231	230	219
I(%)	2.8	20.5	100	5.4	4.6	1.9
m/e	218	217	203	202	201	200
I(%)	6.2	34.9	1.6	5.6	2.9	3.5
m/e	193	191	190	189	188	187
I(%)	2.5	3.8	2.4	14.9	4.6	6.8
m/e	133	130.5	130	101.5	101	100.5
I(%)	2.9	1.1	6.0	0.73	2.9	1.7
m/e	100	96	95	94.5	94	93.5
I(%)	4.1	5.2	0.79	4.4	2.5	2.2

Table 1 (continued)

Compound XIII

m/e	460	459	458	457	456	442
I(%)	6.4	34.8	100	50.4	7.3	3.3
m/e	441	430	429	428	401	400
I(%)	7.4	8.7	22.6	9.9	2.4	8.9
m/e	399	398	397	396	395	230
I(%)	10.4	3.1	7.8	1.6	2.4	2.1
m/e	229.5	229	215	214.5	208	207
I(%)	5.9	17.4	3.8	6.6	1.7	7.0
m/e	206.5	206	205.5	201	200.5	
I(%)	2.3	2.4	3.7	3.4	14.4	
m/e	200	199.5	199	198.5	198	
I(%)	36.5	6.1	15.7	3.5	5.6	

Compound XIV

m/e	460	459	458	457	456	447
I(%)	7.4	35.5	100	29.0	6.8	1.6
m/e	446	442	441	430	429	428
I(%)	4.5	2.3	5.5	6.5	19.7	10.0
m/e	401	400	399	398	230	229.5
I(%)	9.4	17.4	2.6	5.6	2.6	7.9
m/e	229	215	214.5	208	207	202
I(%)	18.7	5.2	8.4	3.9	14.8	4.5
m/e	201.5	201	200.5	200	199.5	199
I(%)	17.4	40.3	9.4	22.3	3.6	7.7
m/e	188	187	114	113	112	
I(%)	4.8	6.1	18.7	4.5	51.5	

E X P E R I M E N T A L

5,10,16-Trimethoxyviolanthrene

Pure 16-methoxyviolanthrone was prepared by the method described by Sanchorawala[17].

16-Methoxyviolanthrone (150 mg) was treated with sodium hydroxide solution (2% solution; 10 ml) and sodium dithionite (200 mg) at 60-70°, cooled to room temperature and treated with dimethyl sulphate (2 ml), and stirred vigorously for half an hour. The red product separated was filtered, washed with water and dried (130 mg). The product showed two spots on TLC over silica gel using acetone-petroleum ether (2:8) as a solvent system. By repeated crystallization from benzene major product was obtained in the pure form, m.p. 308-10° (dec.).

Preparation of 16-methylviolanthrone

A melt of potassium hydroxide (8 g), sodium hydroxide (2 g), sodium acetate (1 g) and naphthalene (10 g) was prepared at 200° and a homogeneous mixture of benzanthrone (1 g), 2-methylbenzanthrone (1 g) and naphthalene (10 g) was added and raised the temperature of the melt to 220-230° under stirring during 30 minutes and maintained the same temperature for one hour. The

colour of the melt changed from yellow to deep blue. The melt was poured into water (400 ml). Naphthalene was removed by steam-distillation. The blue residue separated was filtered, washed with water (1.4 g). The product (1 g) was chromatographed on a column of alumina (2 x 30 cm) at 110° with o-dichlorobenzene which eluted a yellow band giving unconverted benzanthrone and 2-methylbenzanthrone. Further development of the column was carried out with o-dichlorobenzene containing phenol (1%) to elute greenish blue band giving a reddish blue solution (500 ml) which on concentration gave blue microscopic needles (300 mg) of 16,17-dimethyl-violanthrone. The next bluish green band which was separated from the faster moving band by colourless fraction (200 ml) was then eluted with the same solvent system (2.1 l) which on concentration gave blue microscopic needles (250 mg) of 16-methyl-violanthrone. The dark black band of violanthrone was strongly held at the top of the column and was not eluted.

5,10-Dimethoxy-16-methylviolanthrene

The reductive methylation of pure 16-methyl-violanthrone (50 mg) was carried out as described in the earlier experiment. The red product (40 mg)

was crystallized twice from benzene in red needles, m.p. 310-12° (dec.).

REFERENCES

1. H. Budzikiewicz, C. Djerassi and D.H. Williams "Interpretation of Mass Spectra of Organic Compounds", Holden-Day Inc., San Francisco, (1964), p. 162.

2. H.M. Grubb and S. Meyerson in (F.W. McLafferty ed.) Mass Spectrometry of Organic Ions, Academic Press, New York, 1963, Chapter 10.

3. See Catalog of Mass Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa. Spectra No.410, 1486 and 959.

4. V. Boekelheide and J.B. Phillips, J.Am.Chem.Soc. 85, 1545 (1963).

5. J.H. Beynon and A.E. Williams, Appl.Spectroscopy 14, 156 (1960).

6. F.N. Hodgson, M. Desjardins and W.L. Baun, J.Phy.Chem., 67, 1250 (1963).

7. R.J. Van Brunt and M.E. Wacks, J.Chem.Phys., 41, 3195 (1964).

8. M.I. Bruce, Chem.Comm., 593 (1967).

9. F.W. McLafferty and M.M. Bursey, Chem.Comm., 533 (1967).

10. J.H. Beynon and A.E. Williams, Appl.Spectroscopy, 13, 101 (1959).
ibid., 14, 27 (1960).

11. V.H. Dibeler, F.L. Mohler and R.M. Reese, J.Chem.Phys., 21, 180 (1953).

12. F.W. McLafferty, Anal.Chem., 29, 1782 (1957).

13. C.S. Barnes and J.L. Occolowitz, Aust.J.Chem., 16, 219 (1963).

14. H. Budzikiewicz, C. Djerassi and D.H. Williams, "Interpretation of Mass Spectra of Organic Compounds" Holden-Day Inc., San Francisco, 1964, p.181.

15. K. Venkataraman, The Chemistry of Synthetic Dyes, Acad. Press, New York, p.972 (1952) and FIAT 1313, Vol. II, p.134.

16. P.M. Nair, C.J. Sanchorwala and M.K. Unni, Ind.J.Chem. (in press).

17. C.J. Sanchorawala, Ph.D. (Tech.) thesis, University of Bombay (1963), 76.

PART III

NMR SPECTRA OF SOME BENZANTHRONE DERIVATIVES

Benzanthrone is a very important dye intermediate from which largely used vat dyes with excellent all-round fastness properties, such as violanthrone (C.I. Vat Blue 20; C.I. 59800) and its 16,17-dimethoxy derivative (C.I. Vat Green 1; C.I. 59825), are prepared. There are very few substituted benzanthrones which are used as dye intermediates, but a scrutiny of the patent literature shows that many of them have potential value and deserve to be investigated further. In this connection the orientation of the substituents in a few benzanthrone derivatives has now been examined in terms of their NMR spectra.

The programme, of which the present work represents a preliminary part, has acquired additional interest in view of the fact that the NMR spectrum of benzanthrone itself does not appear to have been recorded so far. Benzanthrone and benzanthrene have not been included in such recent studies as those of Martin[1] on numerous polycyclic hydrocarbons and of Batterham[2] on benzanthracene and its derivatives.

In the present work an attempt is made to study the products formed when benzanthrone condensation was carried out on different alkyl substituted anthraquinones. The NMR spectra of the products were obtained and the

substitution of the alkyl groups in the benzanthrone has been discussed. Since the work described in this part of the thesis is restricted to the NMR spectra of a few benzanthrone derivatives, and does not represent a study of substitution in benzanthrone, it has not been considered necessary to review methods for the synthesis of benzanthrone derivatives or the course of electrophilic and nucleophilic substitution in benzanthrone[3].

Benzanthrone condensation on 2-methylanthraquinone was carried out[4]. The reaction product on crystallization from benzene gave 4-methyl-benzanthrone, m.p. 198-9°. It's constitution was confirmed by chromic acid oxidation to give 2-methylanthraquinone-1-carboxylic acid. The mother liquor after obtaining 4-methyl-benzanthrone was chromatographed on an alumina column. Three different yellow crystalline products were obtained with m.ps. 110°, 159° and 199°. The last two were identified as 10-methyl and 4-methylbenzanthrones respectively.

Benzanthrone condensation on 2-ethylanthraquinone gave a product which found to be a mixture of three compounds having very close Rf values. Faster moving two components were isolated in pure forms by carrying out PLC on silica gel using benzene-hexane (1:1) as

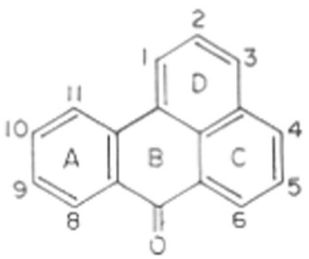
solvent system. The major product (75%) obviously be unknown 4-isomer, m.p. 147°. The NMR spectrum of the other component when recorded showed to be a mixture of at least two components, though it behaves as single component on TLC.

When benzanthrone condensation was carried out on 1,3-dimethyl and 2,3-dimethylanthraquinones, only one dimethylbenzanthrone is obtained in each case. The products were formulated as 4,6-dimethyl[5] and 4,5-dimethylbenzanthrones respectively and confirmed by their NMR spectra. The m.p. of 9,10-dimethyl-benzanthrone[6] prepared earlier from perinaphthen-7-one-8-carboxylic acid on refluxing with 2,3-dimethyl-1,3-butadiene in acetic acid was identical with the m.p. of the product obtained from 2,3-dimethyl-anthraquinone.

It was of interest to examine the products formed by carrying out the benzanthrone condensation on 2-t-butylanthraquinone because of the possible steric effect. The crude reaction product showed to be a mixture of at least two compounds, one being major. Two products were isolated by PLC over silica gel using benzene-hexane (1:1) as solvent. The major product (85%) was identified as 9-t-butylbenzanthrone and other product though showed single spot on TLC found to be

a mixture of at least two components when recorded in NMR spectrum.

The NMR spectra of benzanthrone and its alkyl derivatives have been recorded in $CDCl_3$ except 4-methylbenzanthrone which is recorded in arsenic trichloride. NMR spectrum of benzanthrone in $CDCl_3$ or $AsCl_3$ represents an extremely complex pattern (see Fig. 1) because of the aromatic protons appearing in a very narrow range. However, it can be treated as a number of independent overlapping zones.



BENZANTHRONE

The protons of the ring A will give rise to ABCD pattern, while the protons of the rings C and D form typical ABC patterns. The protons at 1 and 11 of ABD ring system may be expected to come under ring current effects as is the case of similarly placed protons of phenanthrene type system, i.e. proton 1 would come under deshielding influences of ring current influence of A and the proton at 11 of ring D.

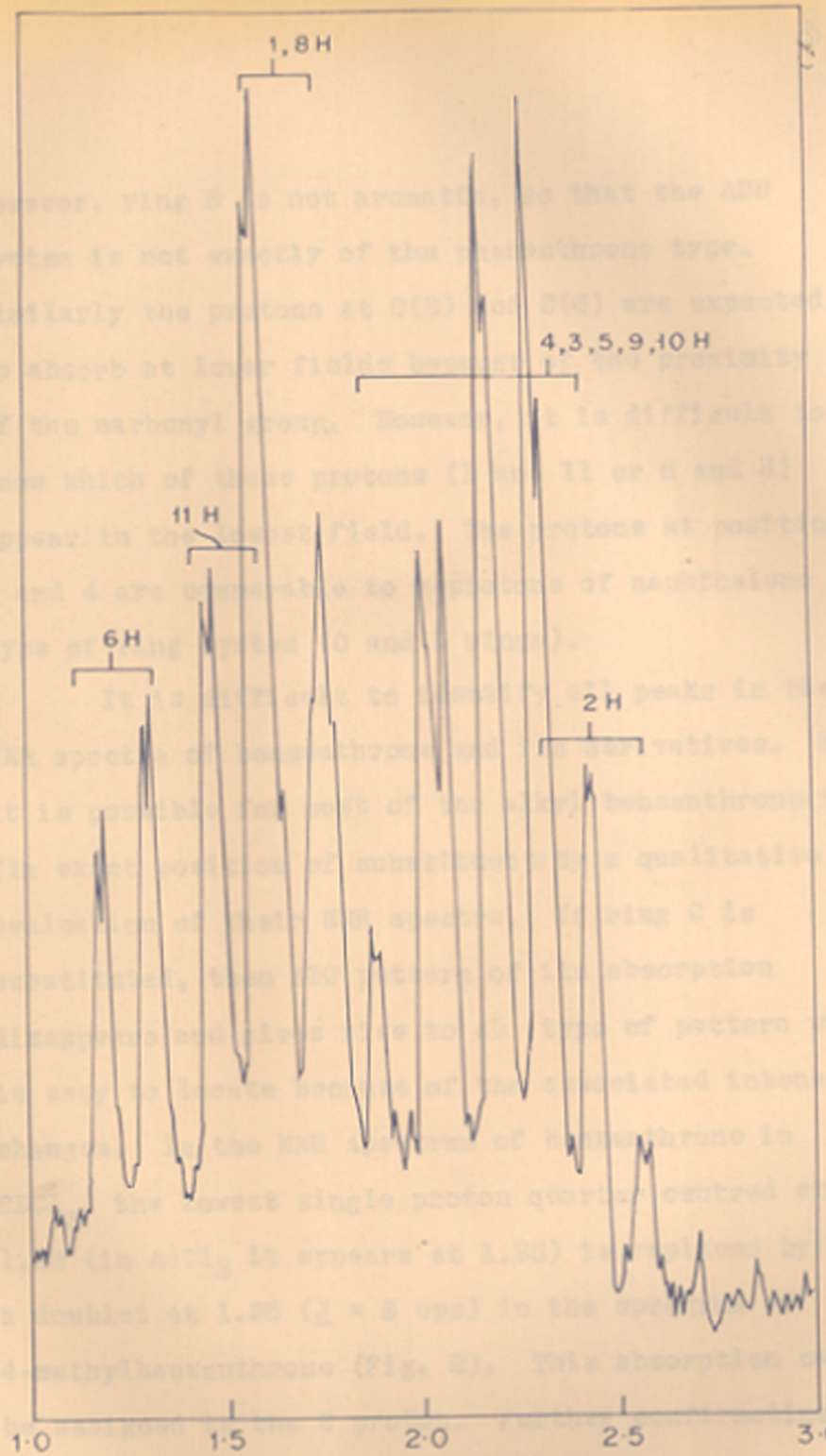


FIG. 1.

NMR SPECTRUM OF BENZANTHRONE IN $AsCl_3$.

However, ring B is not aromatic, so that the ABD system is not exactly of the phenanthrene type. Similarly the protons at C(8) and C(6) are expected to absorb at lower fields because of the proximity of the carbonyl group. However, it is difficult to know which of these protons (1 and 11 or 6 and 8) appear in the lowest field. The protons at positions 3 and 4 are comparable to α-protons of naphthalene type of ring system (C and D rings).

It is difficult to identify all peaks in the NMR spectra of benzanthrone and its derivatives. However, it is possible for most of the alkyl benzanthrones to fix exact position of substituents by a qualitative evaluation of their NMR spectra. If ring C is substituted, then ABC pattern of its absorption disappears and gives rise to AB type of pattern which is easy to locate because of the associated intensity changes. In the NMR spectrum of benzanthrone in $CDCl_3$, the lowest single proton quarter centred at 1.33 (in $AsCl_3$ it appears at 1.23) is replaced by a doublet at 1.35 (J = 8 cps) in the spectrum of 4-methylbenzanthrone (Fig. 2). This absorption can be assigned to the 6 proton. Further confirmation for this assignment was obtained by examining the spectra of 4-ethyl and 4,6-dimethylbenzanthrones.

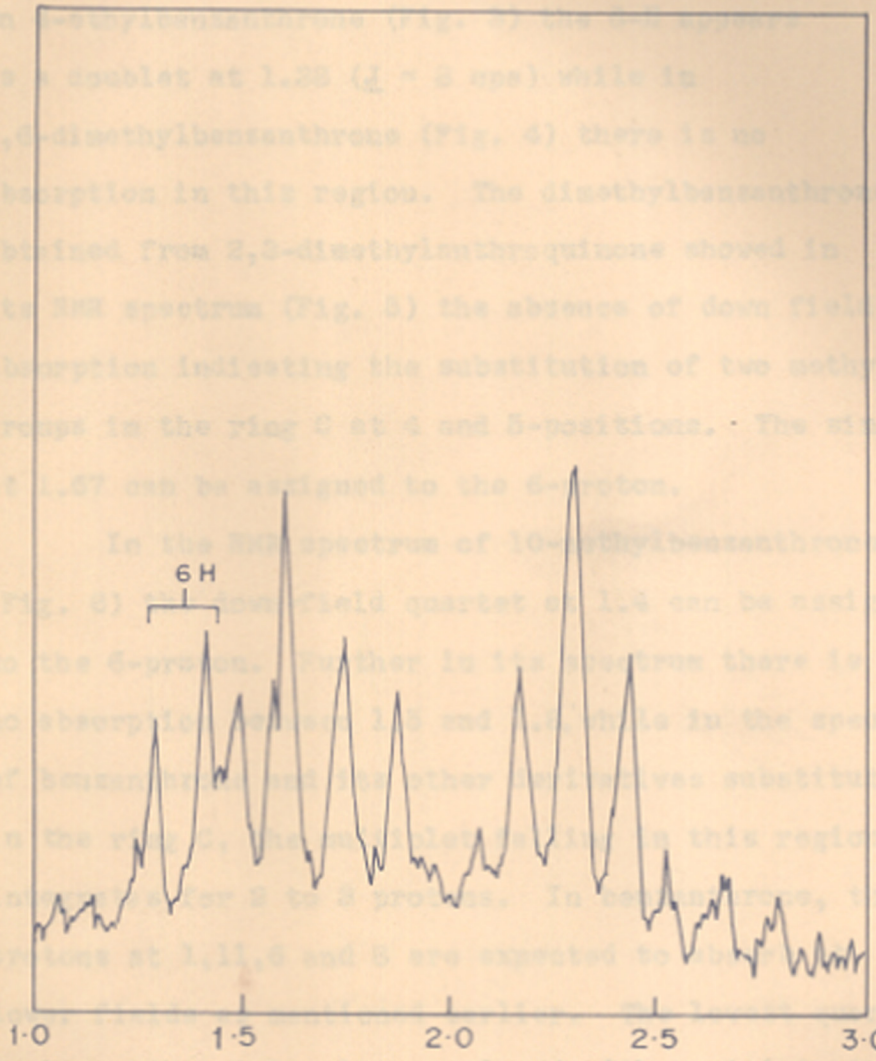


FIG. 2.

NMR SPECTRUM OF 4-METHYLBENZANTHRONE IN $AsCl_3$.

In 4-ethylbenzanthrone (Fig. 3) the 6-H appears as a doublet at 1.38 (J = 8 cps) while in 4,6-dimethylbenzanthrone (Fig. 4) there is no absorption in this region. The dimethylbenzanthrone obtained from 2,3-dimethylanthraquinone showed in its NMR spectrum (Fig. 5) the absence of down field absorption indicating the substitution of two methyl groups in the ring C at 4 and 5-positions. The singlet at 1.67 can be assigned to the 6-proton.

In the NMR spectrum of 10-methylbenzanthrone (Fig. 6) the down-field quartet at 1.4 can be assigned to the 6-proton. Further in its spectrum there is no absorption between 1.5 and 1.8, while in the spectra of benzanthrone and its other derivatives substituted in the ring C, the multiplet falling in this region integrates for 2 to 3 protons. In benzanthrone, the protons at 1,11,6 and 8 are expected to absorb at lower fields as mentioned earlier. The lowest quartet in benzanthrone has been assigned with certainty to the proton at 6-position. The other three protons (1, 11 and 8) are falling in the region between 1.4 to 1.8. The multiplets at 1.5 in benzanthrone and 1.55 in 4,5-dimethylbenzanthrone can be assigned to the 11-proton by examining the NMR spectrum of 10-methylbenzanthrone (Fig. 6) in which this signal appears at 1.9 as a broad signal showing <u>meta</u> coupling.

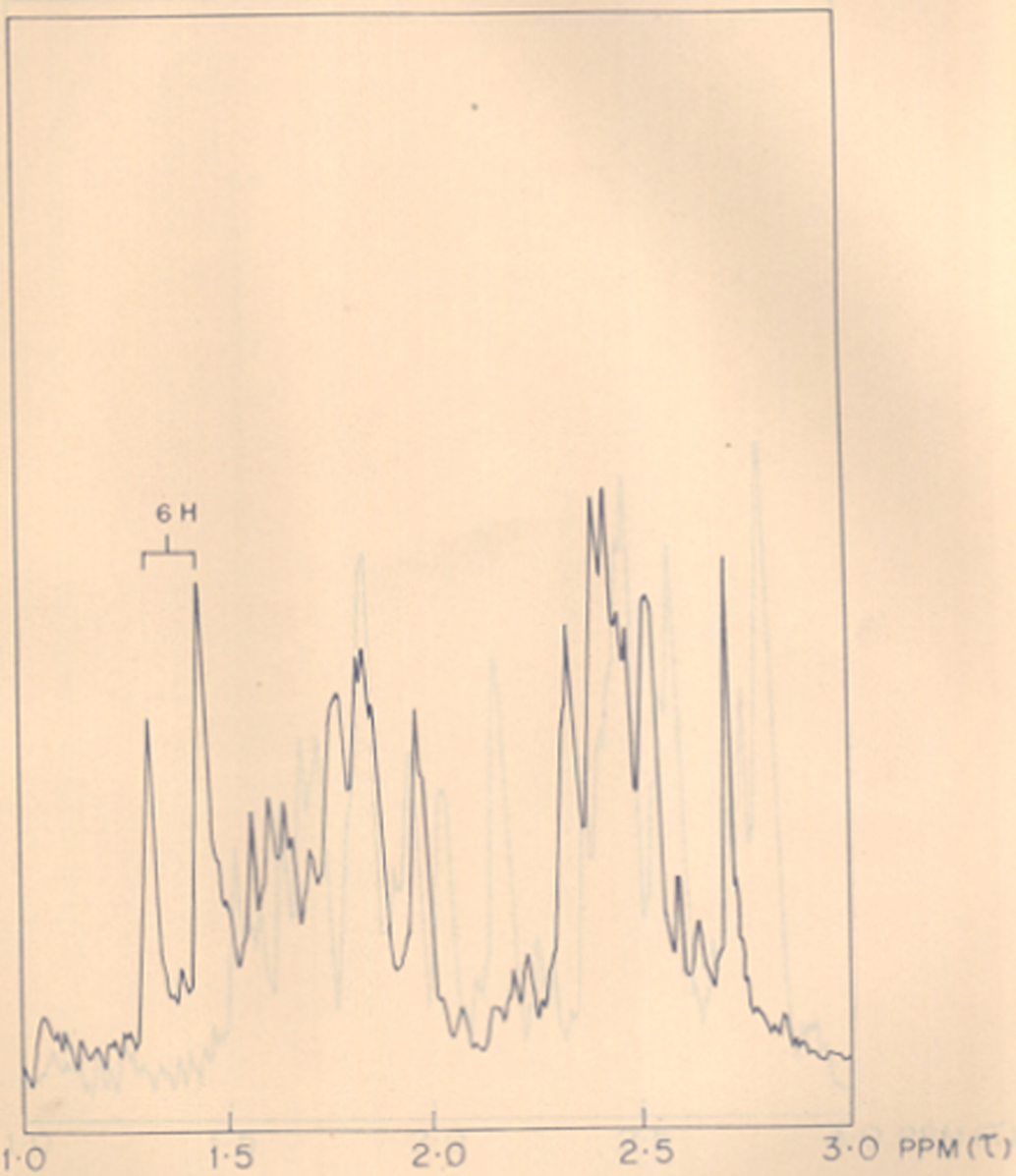


FIG. 3

NMR SPECTRUM OF 4-ETHYLBENZANTHRONE IN $CDCl_3$

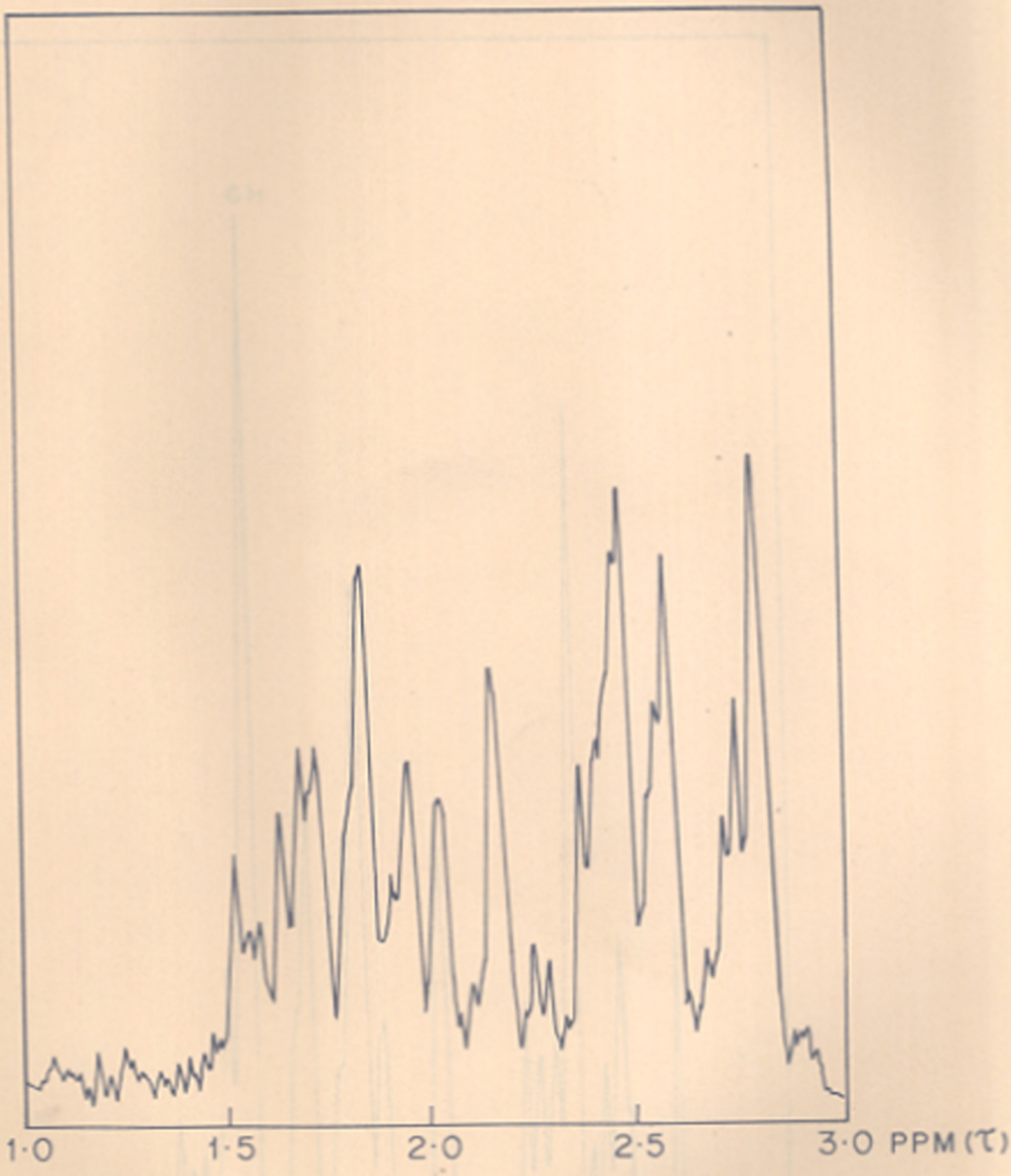


FIG. 4.

NMR SPECTRUM OF 4,6-DIMETHYLBENZANTHRONE IN $CDCl_3$.

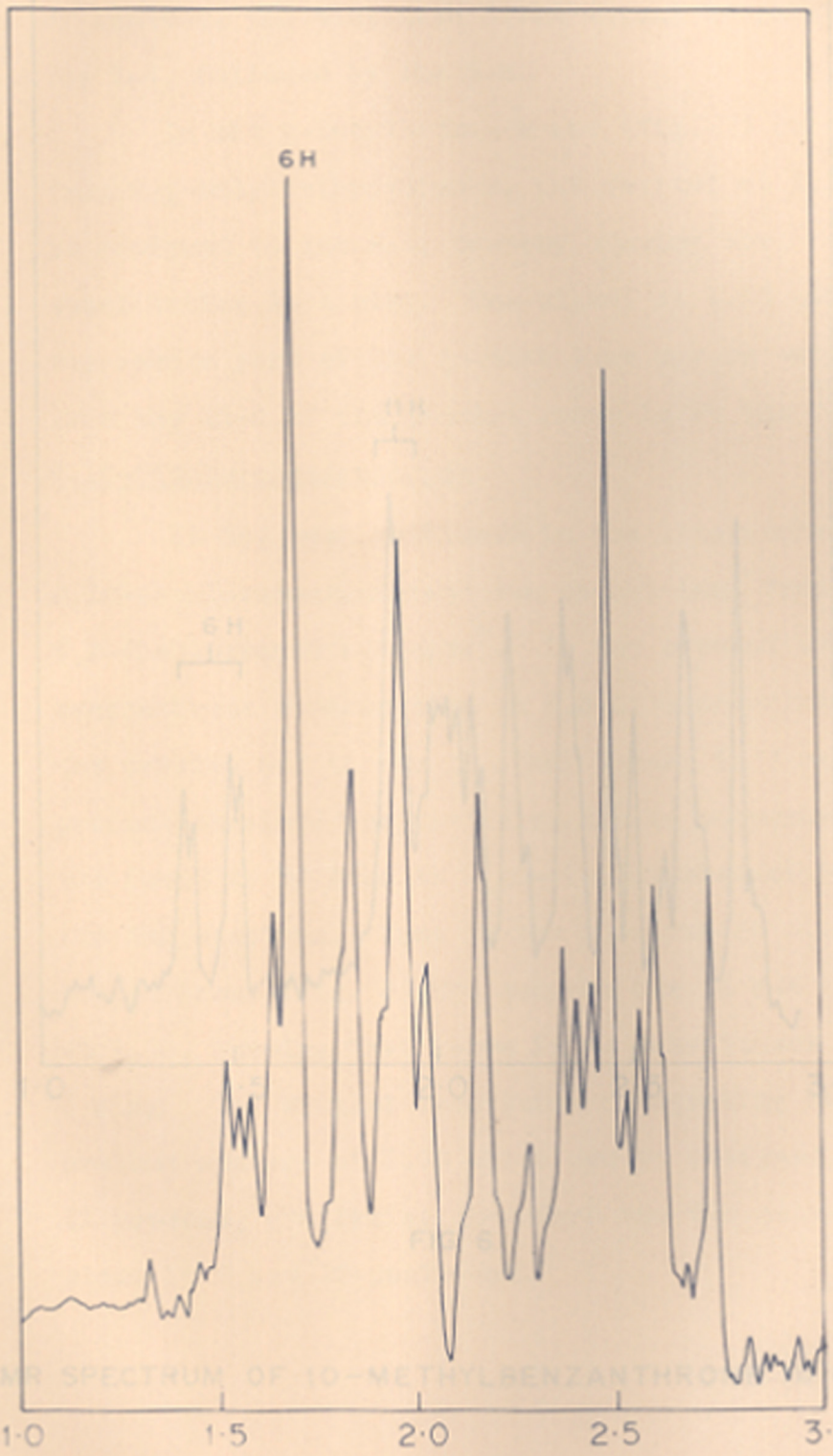


FIG. 5.

NMR SPECTRUM OF 4,5-DIMETHYLBENZANTHRONE IN $CDCl_3$.

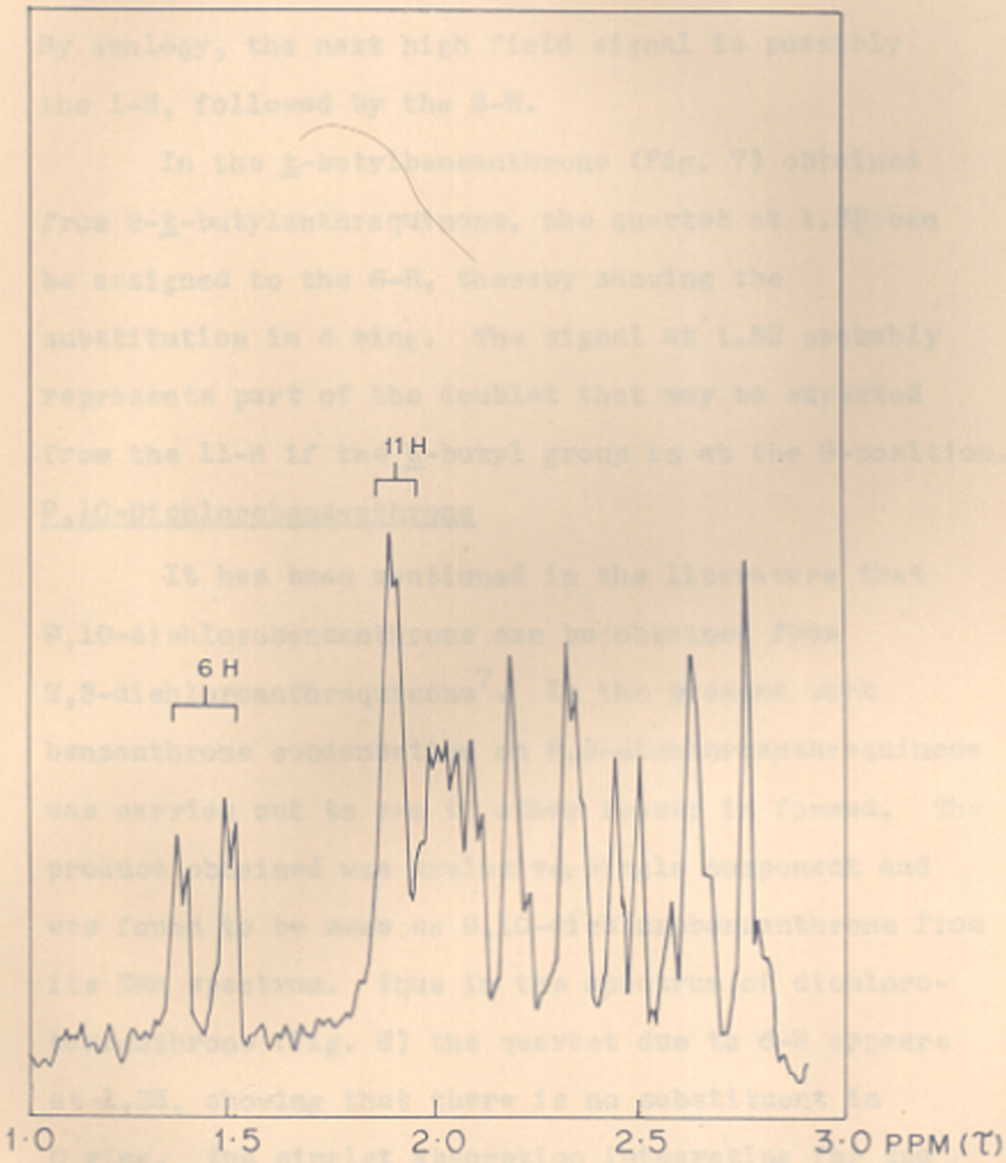


FIG. 6.

NMR SPECTRUM OF 10-METHYLBENZANTHRONE IN $CDCl_3$.

By analogy, the next high field signal is possibly the 1-H, followed by the 8-H.

In the t-butylbenzanthrone (Fig. 7) obtained from 2-t-butylanthraquinone, the quartet at 1.38 can be assigned to the 6-H, thereby showing the substitution in A ring. The signal at 1.52 probably represents part of the doublet that may be expected from the 11-H if the t-butyl group is at the 9-position.

9,10-Dichlorobenzanthrone

It has been mentioned in the literature that 9,10-dichlorobenzanthrone can be obtained from 2,3-dichloroanthraquinone[7]. In the present work benzanthrone condensation on 2,3-dichloroanthraquinone was carried out to see if other isomer is formed. The product obtained was exclusively single component and was found to be same as 9,10-dichlorobenzanthrone from its NMR spectrum. Thus in the spectrum of dichlorobenzanthrone (Fig. 8) the quartet due to 6-H appears at 1.35, showing that there is no substituent in C ring. The singlet absorption integrating for two protons appears at 1.62 which can be assigned to 8 and 11 protons, confirming therefore the two chlorine atoms in 9 and 10-positions.

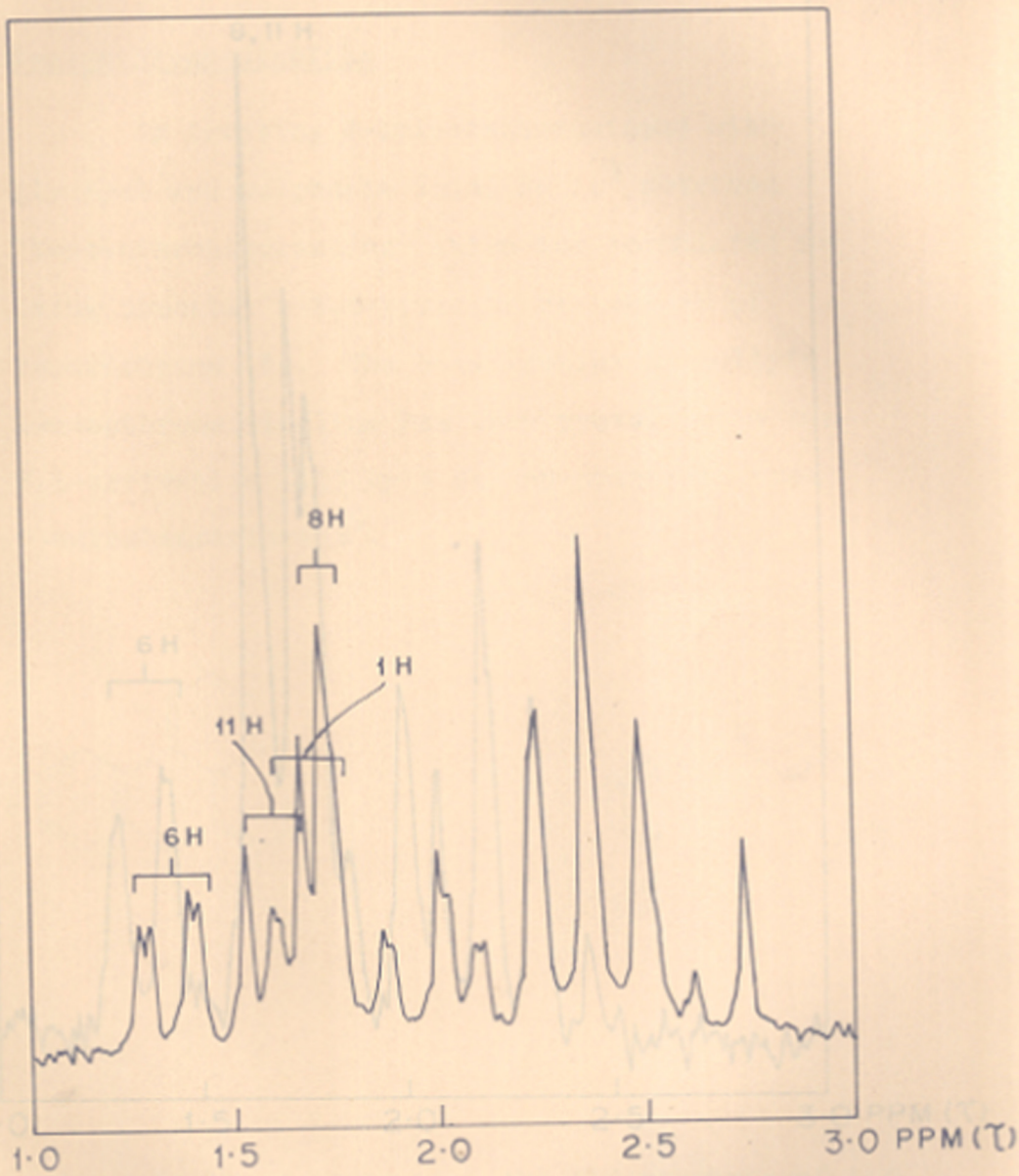


FIG. 7.

NMR SPECTRUM OF 9-t-BUTYLBENZANTHRONE IN $CDCl_3$.

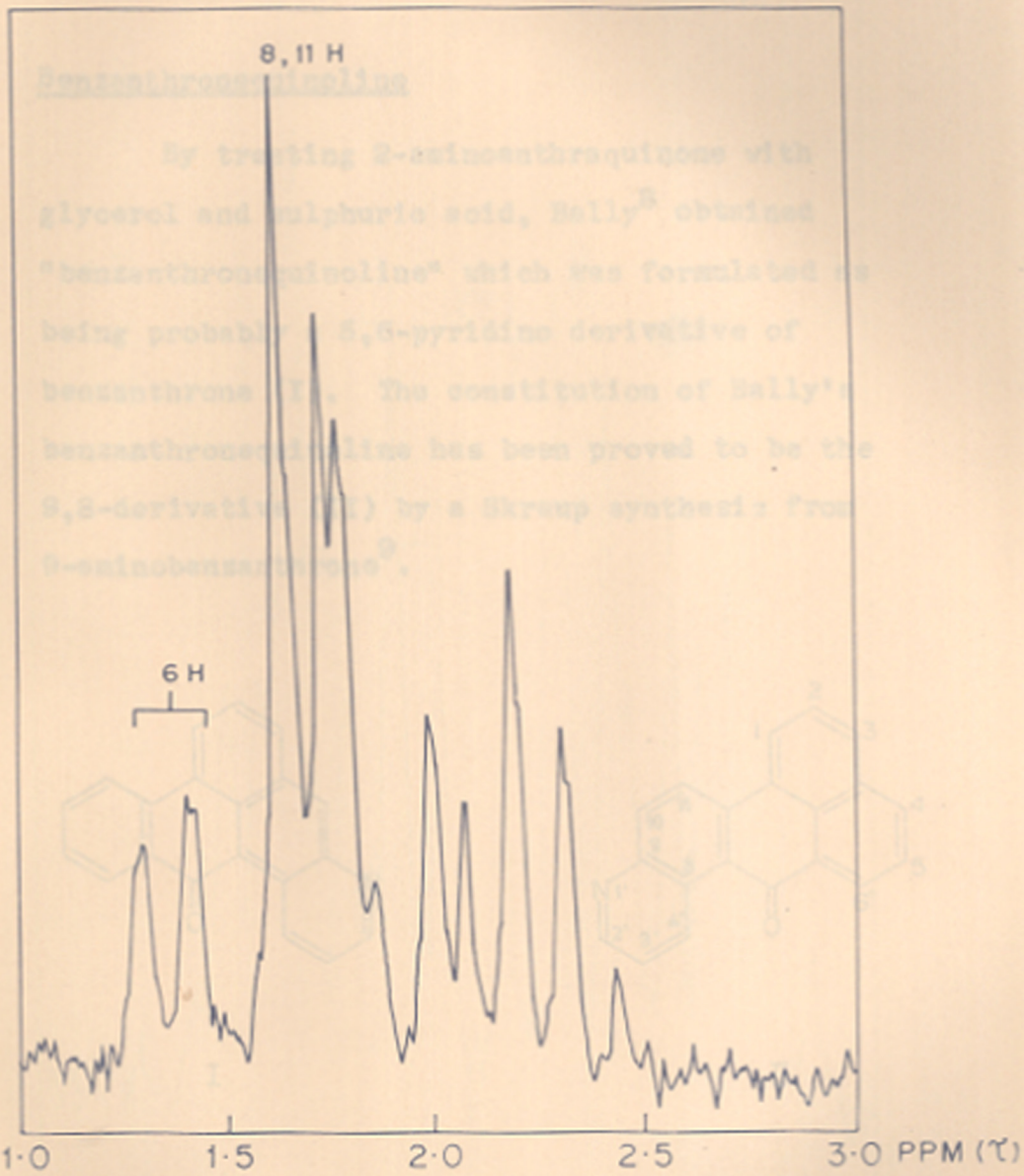
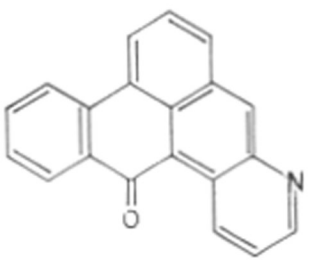


FIG. 8

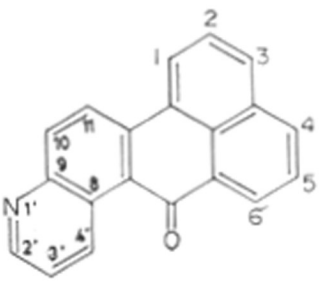
NMR SPECTRUM OF 9,10-DICHLOROBENZANTHRONE IN $AsCl_3$

Benzanthronequinoline

By treating 2-aminoanthraquinone with glycerol and sulphuric acid, Bally[8] obtained "benzanthronequinoline" which was formulated as being probably a 5,6-pyridino derivative of benzanthrone (I). The constitution of Bally's benzanthronequinoline has been proved to be the 9,8-derivative (II) by a Skraup synthesis from 9-aminobenzanthrone[9].



I



II

In the present work the NMR spectrum of the compound, determined in arsenic trichloride, agrees with the structure (II). Thus in the spectrum of benzanthronequinoline (Fig. 9) the quartet at 1.3 which overlaps with the low field of the doublet, can be assigned to the 6-H, showing thereby the

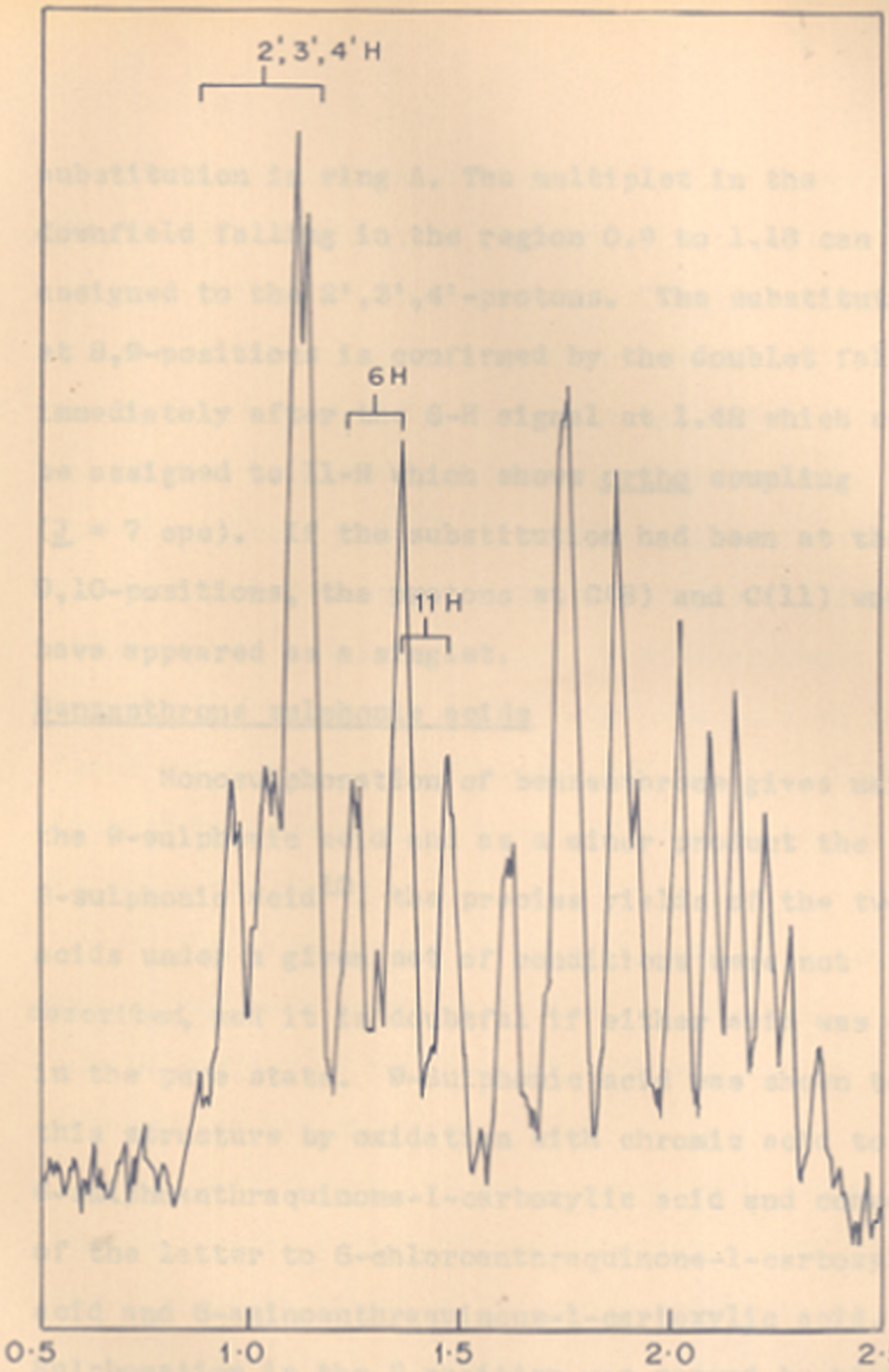


FIG. 9.

NMR SPECTRUM OF BENZANTHRONEQUINOLINE IN $AsCl_3$.

substitution in ring A. The multiplet in the downfield falling in the region 0.9 to 1.18 can be assigned to the 2',3',4'-protons. The substitution at 8,9-positions is confirmed by the doublet falling immediately after the 6-H signal at 1.42 which can be assigned to 11-H which shows ortho coupling (J = 7 cps). If the substitution had been at the 9,10-positions, the protons at C(8) and C(11) would have appeared as a singlet.

Benzanthrone sulphonic acids

Monosulphonation of benzanthrone gives mainly the 9-sulphonic acid and as a minor product the 3-sulphonic acid[10], the precise yields of the two acids under a given set of conditions were not described, and it is doubtful if either acid was obtained in the pure state. 9-Sulphonic acid was shown to have this structure by oxidation with chromic acid to 6-sulphoanthraquinone-1-carboxylic acid and conversion of the latter to 6-chloroanthraquinone-1-carboxylic acid and 6-aminoanthraquinone-1-carboxylic acid. Sulphonation in the 3-position was proved by heating the sulphonyl chloride with xylene when a small quantity of 3-chlorobenzanthrone was obtained. It was suggested that the 3-acid was the primary product which rearranged to the 9-sulphonic acid at high temperature. Sulphonation

in tetrachloroethane with an equivalent amount of chlorosulphonic acid gave chiefly the 3-sulphonic acid[11], which was confirmed by oxidation to anthraquinone-1-carboxylic acid and by conversion to 3-nitrobenzanthrone by the action of nitric acid. On further sulphonation both acids give the 3,9-disulphonic acid[10,11]. Ioffe and Mel'teva[12] claimed that treatment of benzanthrone with 22% oleum for 24 hours at 20° gave 81% α-sulphonic acid and 19% β-isomer, but 96.5% sulphuric acid at 160-70° for 8 hours gave 20% of α- and 80% of β-sulphonic acid. It must be assumed that α and β referred to the 3- and 9-positions.

The orientation of substituents in benzanthrone has so far been detected by tedious chemical methods, and the object of the present work was to use NMR spectra for the purpose.

Benzanthrone was sulphonated with oleum (5% SO_3) under Pritchard and Simonsen's conditions[10]. Paper chromatography of the crude sodium sulphonate using water-methanol-cyclohexanol (15:35:50) as the solvent system showed two spots. Thin layer chromatography on silica gel using the same solvent system also showed two spots with very close R_f values, the development was slow and the separation was

unsatisfactory. The crude sodium salt was then converted into the methyl esters by heating it with dimethyl sulphate at 160-70° for two hours. TLC of the product showed two spots by multiple development with benzene on silica gel. Preparative layer chromatography (PLC) was then carried out. Two esters were isolated in pure form, both analysed for monosulphonic acid esters. Two products characterized as methyl 3- and 9-benzanthronesulphonates by NMR spectra.

Sulphonation of benzanthrone with 96.5% sulphuric acid at 160-170° as described by Ioffe and Mel'teva[12] gave the 3- and 9-sulphonic acids in about 25 and 65% yields, as shown by conversion to the methyl esters and chromatographic analysis.

Benzanthrone on sulphonation with oleum (10% SO_3) gives mainly the 3,9-disulphonic acid, identified by its conversion into its methyl ester and by NMR spectrum.

Chlorosulphonation of benzanthrone, was carried out with chlorosulphonic acid at 90-95°. The sulphonyl chloride obtained when treated with methanol in pyridine gave a poor yield of the methyl ester. However, on treatment with dimethylamine, dimethyl sulphonamide was formed. The product showed three spots

on TLC over silica gel using chloroform as solvent. The two major components were obtained in pure form by carrying out preparative layer chromatography; the major product (65%) was identified as 9-sulphonamide and minor as 3-sulphonamide from their chromatographic behaviour and m.ps. and mixed m.ps. on admixture with sulphonamides obtained from the 3- and 9-sulphonic acids.

The NMR spectra of benzanthrone 3- and 9-sulphonic acid methyl esters obtained in the present study are consistent with their structures. Thus in the spectrum of methyl benzanthrone-9-sulphonate (Fig. 10) the downfield signal at 1.08 is a doublet (J = 2 cps) and can be assigned to the 8-H, which suffers a paramagnetic shift of more than 0.8 ppm due to the sulpho group at 9-position of benzanthrone. In the spectrum of N,N-dimethyl naphthalene-2-sulphonamide, the proton at C(1) shifts about 0.6 ppm downfield. This assignment is confirmed with the appearance of 11-proton as a doublet at 1.43 (J = 8.5 cps) showing ortho coupling. The chemical shift and multiplicity of the 6-H (quartet at 1.23) are unaltered as compared to the spectrum of benzanthrone. Similarly in methyl benzanthrone-3-sulphonate (Fig.11) the adjacent peri-proton (4-H) suffers a downfield

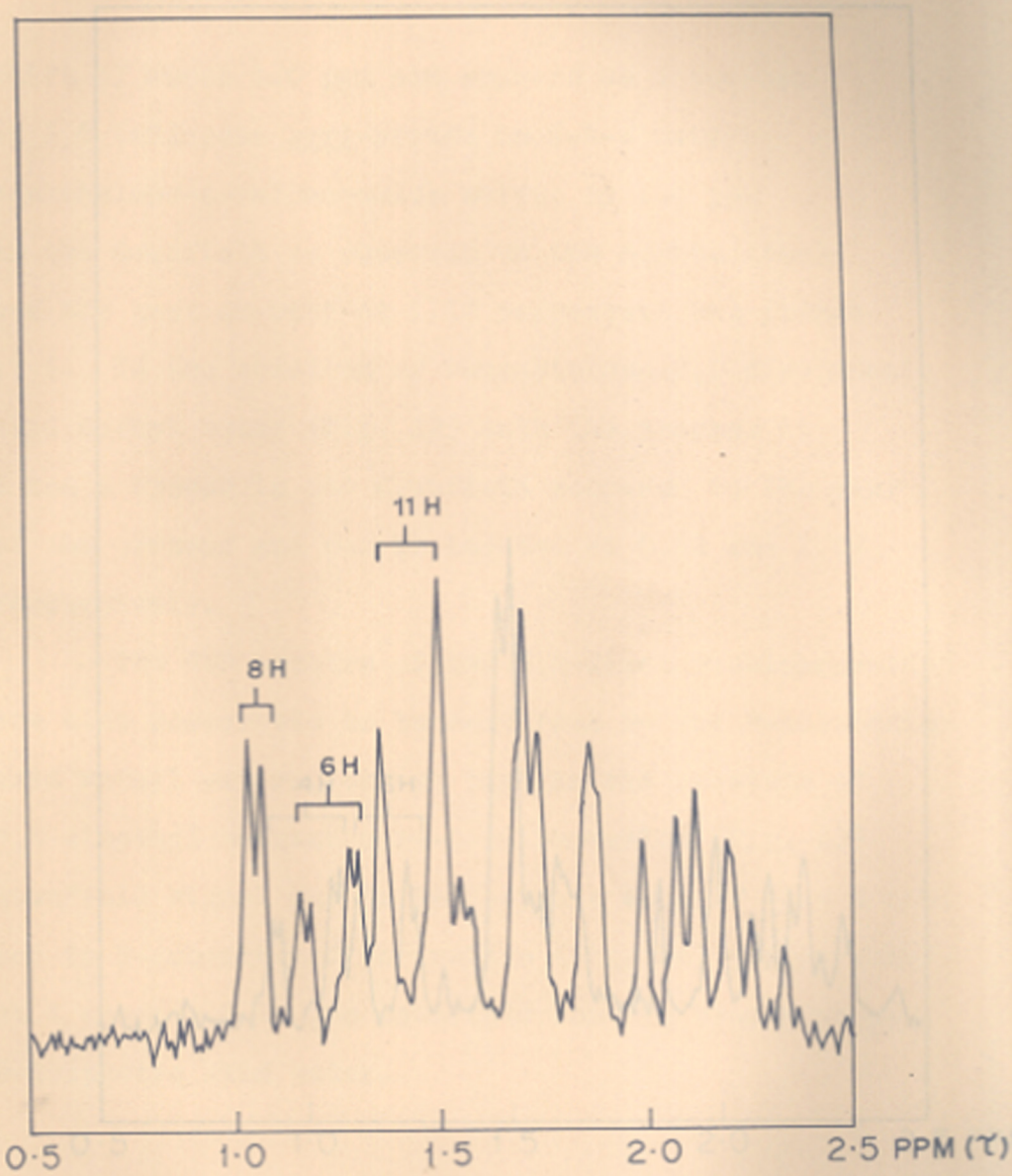


FIG. 10.

NMR SPECTRUM OF METHYL BENZANTHRONE-9-SULPHONATE IN $AsCl_3$.

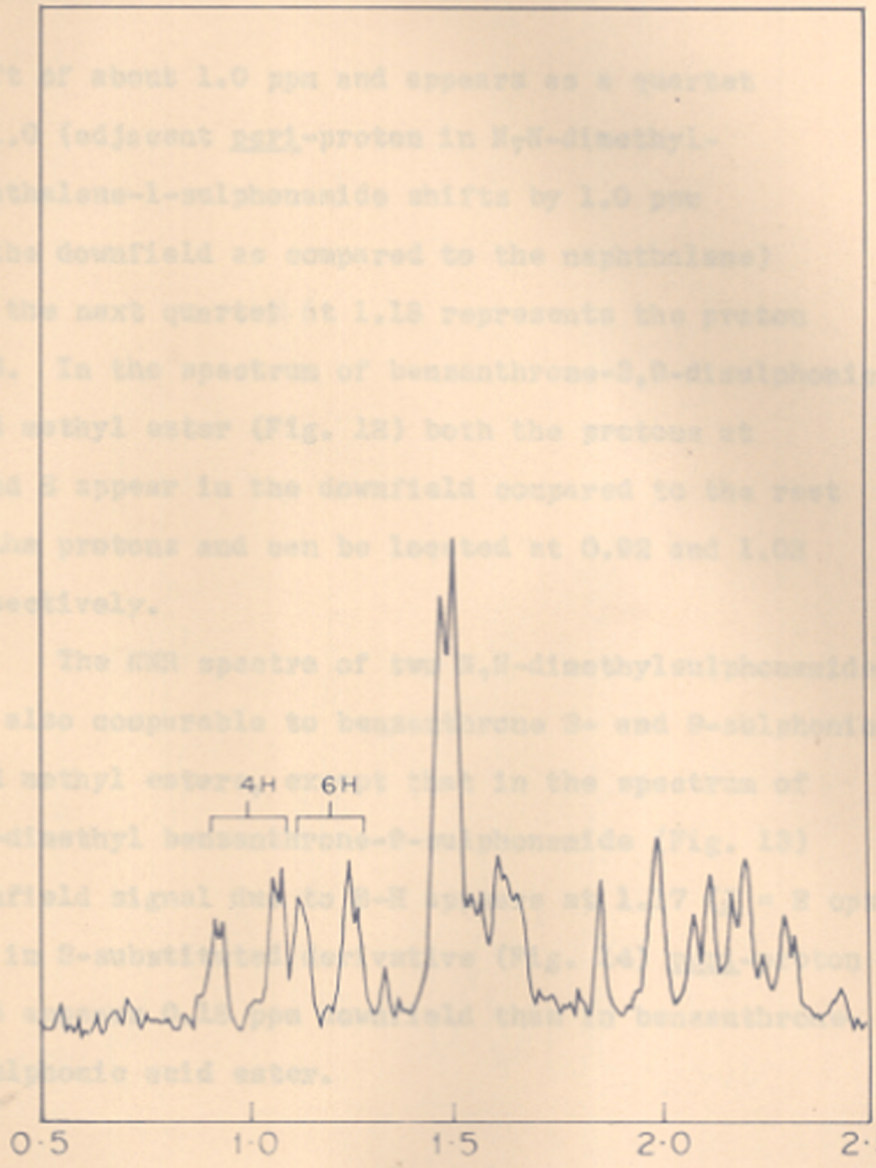


FIG 11.

NMR SPECTRUM OF METHYL BENZANTHRONE-3-SULPHONATE IN $AsCl_3$

shift of about 1.0 ppm and appears as a quartet at 1.0 (adjacent peri-proton in N,N-dimethyl-naphthalene-1-sulphonamide shifts by 1.0 ppm in the downfield as compared to the naphthalene) and the next quartet at 1.18 represents the proton at 6. In the spectrum of benzanthrone-3,9-disulphonic acid methyl ester (Fig. 12) both the protons at 4 and 8 appear in the downfield compared to the rest of the protons and can be located at 0.92 and 1.03 respectively.

The NMR spectra of two N,N-dimethylsulphonamides are also comparable to benzanthrone 3- and 9-sulphonic acid methyl esters, except that in the spectrum of N,N-dimethyl benzanthrone-9-sulphonamide (Fig. 13) downfield signal due to 8-H appears at 1.17 (J = 2 cps) and in 3-substituted derivative (Fig. 14) peri-proton at 4 appears 0.18 ppm downfield than in benzanthrone-3-sulphonic acid ester.

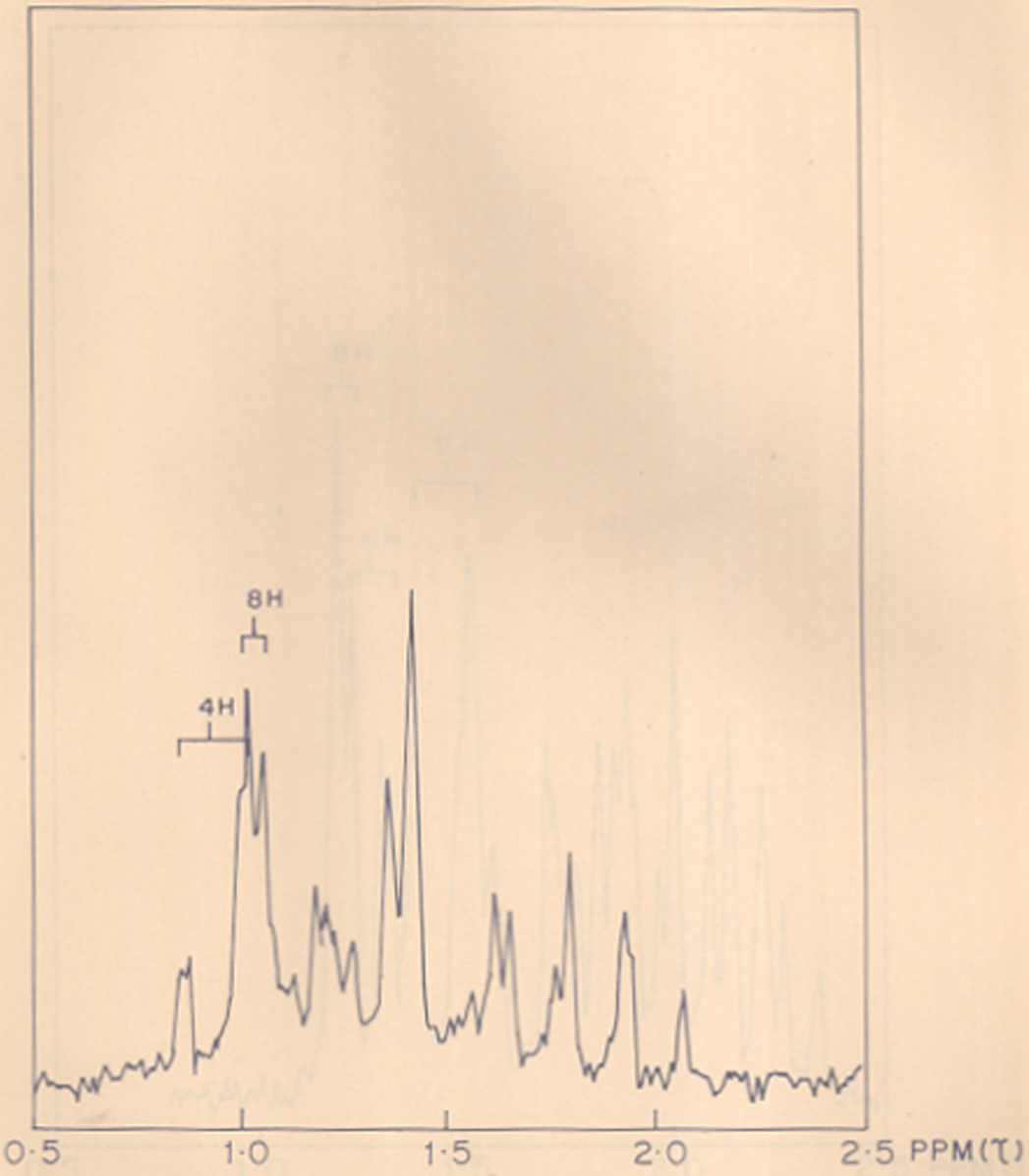


FIG. 12.

NMR SPECTRUM OF METHYL BENZANTHRONE-3,9- DISULPHONATE IN $AsCl_3$.

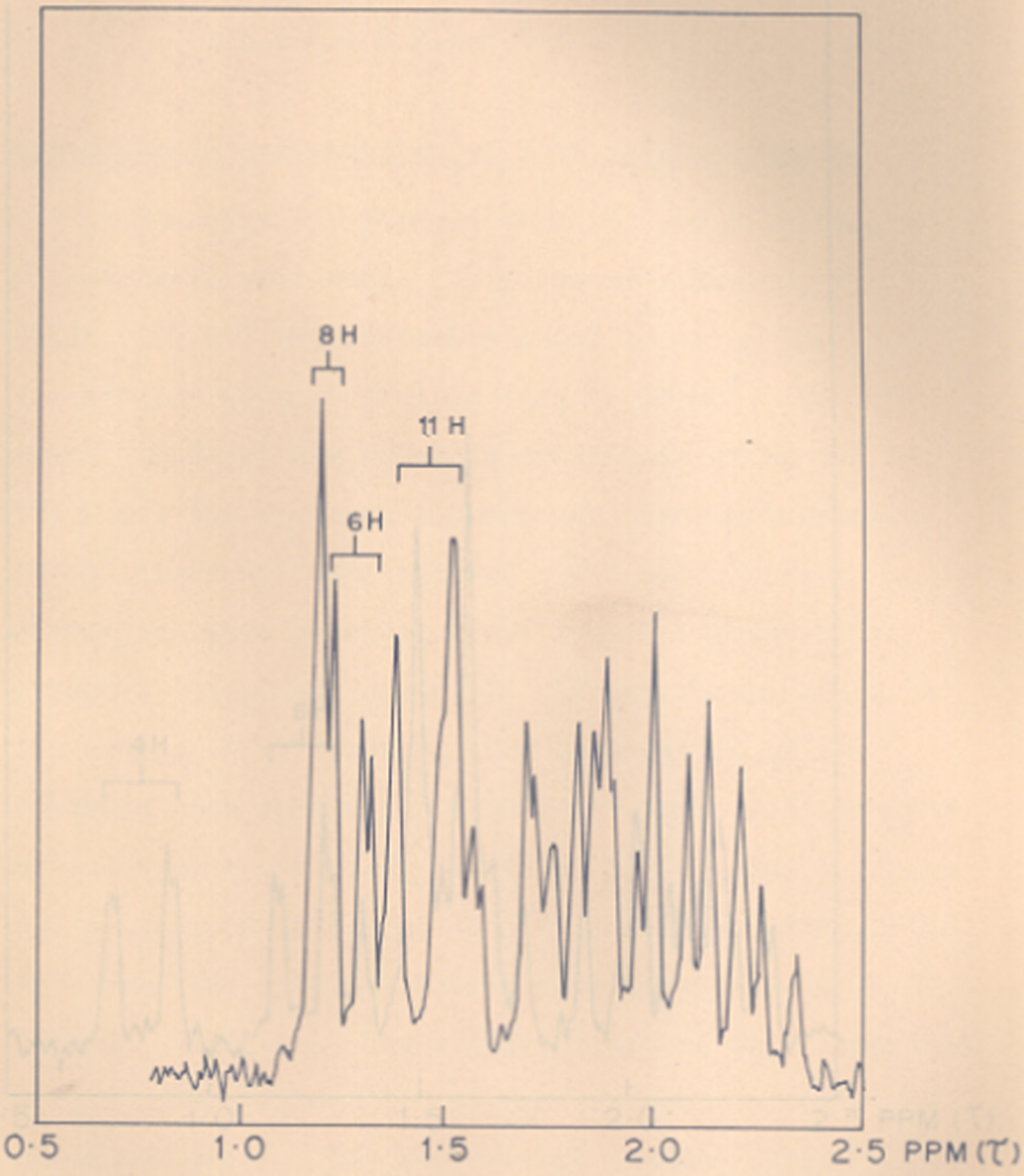


FIG. 13.

NMR SPECTRUM OF N, N-DIMETHYL BENZANTHRONE-9-SULPHONAMIDE IN $AsCl_3$.

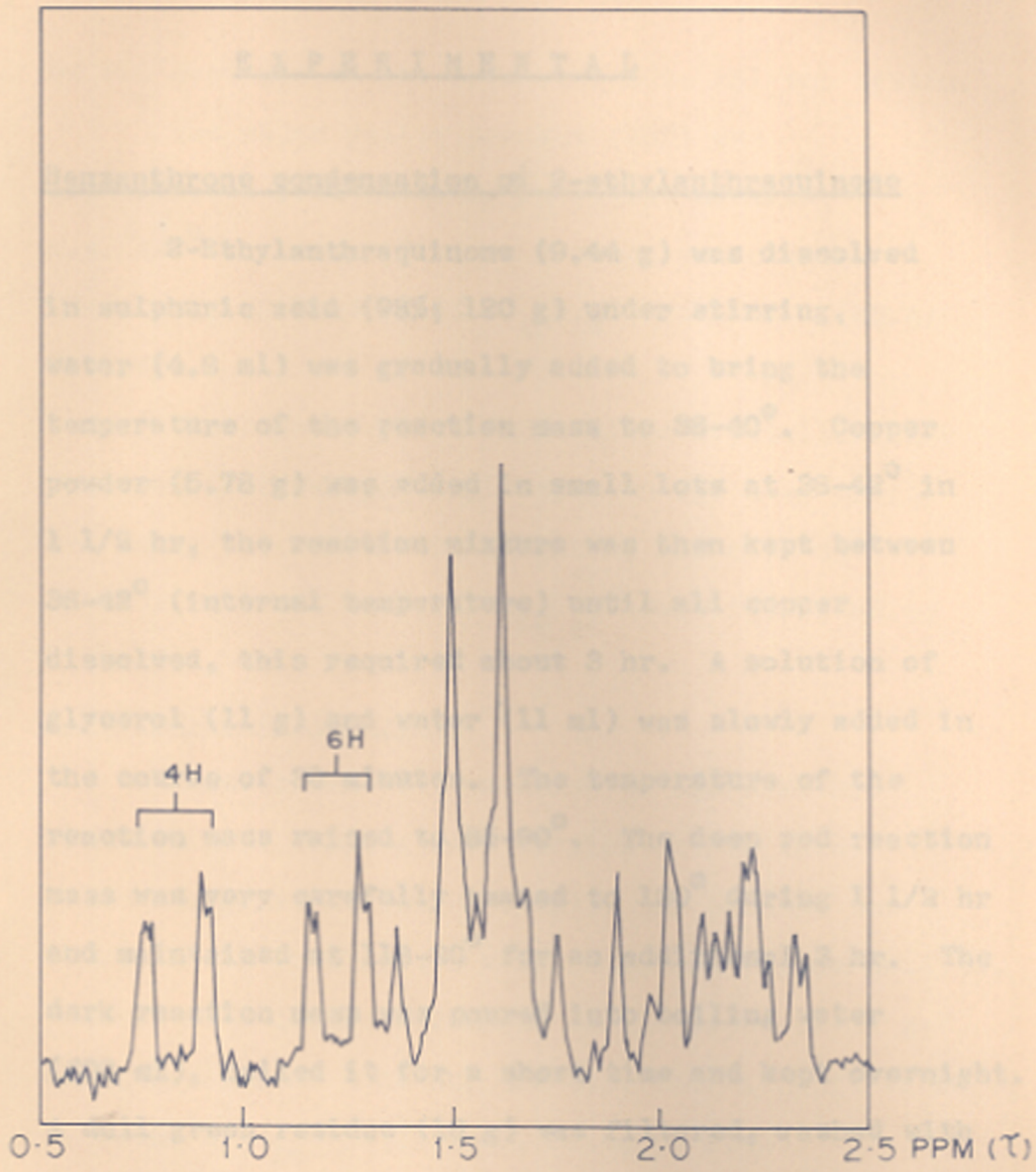


FIG. 14.

NMR SPECTRUM OF N,N-DIMETHYL BENZANTHRONE-3-SULPHONAMIDE IN $AsCl_3$.

EXPERIMENTAL

Benzanthrone condensation of 2-ethylanthraquinone

2-Ethylanthraquinone (9.44 g) was dissolved in sulphuric acid (98%; 120 g) under stirring, water (4.8 ml) was gradually added to bring the temperature of the reaction mass to 38-40°. Copper powder (5.78 g) was added in small lots at 38-42° in 1 1/2 hr, the reaction mixture was then kept between 38-42° (internal temperature) until all copper dissolved, this required about 3 hr. A solution of glycerol (11 g) and water (11 ml) was slowly added in the course of 30 minutes. The temperature of the reaction mass raised to 85-90°. The deep red reaction mass was very carefully heated to 120° during 1 1/2 hr and maintained at 118-20° for an additional 3 hr. The dark reaction mass was poured into boiling water (600 ml), boiled it for a short time and kept overnight. A dull green residue (16 g) was filtered, washed with water and dried. The above crude product after extraction with boiling benzene and concentration gave yellowish brown needles, showed two major spots on TLC over silica gel using benzene-hexane (1:1) as solvent system. Both the products were isolated as single entities by carrying out multiple development

on PLC over silica gel using the same solvent system.

The major yellow product (75%) was crystallized from methanol in yellow needles, m.p. 147° and identified as 4-ethylbenzanthrone (Found: C, 88.5; H, 5.8%. $C_{19}H_{14}O$ requires C, 88.4; H, 5.4%).

The other product (15%) after crystallization from methanol showed single spot on TLC over silica gel using the same solvent system, had m.p. 63° (Found: C, 88.0; H, 5.6%. $C_{19}H_{14}O$ requires C, 88.4; H, 5.4%).

4,5-Dimethylbenzanthrone

Benzanthrone condensation on 2,3-dimethylanthraquinone (2.36 g) was carried out to yield yellowish green residue (2.8 g). The product was crystallized from acetic acid in golden yellow needles, behaved as a single component on TLC over silica gel using benzene as solvent, had m.p. 188° (Found: C, 88.7; H, 5.3%. $C_{19}H_{14}O$ requires C, 88.4; H, 5.4%).

4,6-Dimethylbenzanthrone

4,6-Dimethylbenzanthrone was obtained from 1,3-dimethylbenzanthrone. The crude yellow product was crystallized from acetic acid in yellow needles, m.p. 166° (Lit.[10] m.p. 165°). (Found: C, 88.4; H, 5.6%. $C_{19}H_{14}O$ requires C, 88.4; H, 5.4%).

Sulphonation of benzanthrone with 5% SO_3

A mixture of benzanthrone (3.6 g) and fuming sulphuric acid (5% SO_3; 36 g) was heated in an oil-bath at 145-50° for two hours, cooled partially and poured on ice-water (100 g). Unchanged benzanthrone was removed by filtration and sodium carbonate (100 g) added with stirring at 95°. The solution was made upto 700 ml by adding saturated salt solution, boiled and allowed to cool slowly. The crystalline sodium salt of sulphonic acid (45 g) which separated was collected, washed with saturated salt solution and dried.

The crude mixture was dissolved in dry dimethylformamide, filtered from the salt and the sodium sulphonate was precipitated by adding ether. Filtered the yellow precipitate (3.0 g), washed with ether and dried.

Benzanthrone-sulphonic acid methyl ester

Dried sodium sulphonate free from sodium chloride (1.1 g) was heated for 3 hr. in an oil-bath at 160-70° with dimethyl sulphate (5 ml). From time to time mass was stirred. The mixture after cooling was poured on ice-water. Filtered the greenish yellow residue (1.0 g), washed with water and dried.

The product which was a mixture of at least two components was separated on PLC over silica gel using benzene as developing solvent. After three developments it separated into two clear bands which were collected spearately. The major component (70%) crystallized from benzene in yellow needles, m.p. 216° (Found: C, 66.5; H, 3.6%. $C_{18}H_{12}O_4S$ requires C, 66.7; H, 3.7%).

The other product (about 25%) was crystallized from benzene in bright yellow needles, m.p. 224° (Found: C, 67.0; H, 4.2%. $C_{18}H_{12}O_4S$ requires C, 66.7; H, 3.7%).

N,N-Dimethylsulphonamide derivatives

Dry sodium sulphonate (1 g) was treated with thionyl chloride (20 ml) at room temperature. Dimethylformamide (0.25 ml) was added when the temperature raised to about 40-5°. The mixture was then heated on water-bath for one hour. Excess thionyl chloride was removed under vacuum. The acid chloride thus obtained was treated with dimethylamine (10 ml) at room temperature and kept the mixture on shaker for 12 hr. The residue (0.7 g) separated was filtered, washed with water and dried. It showed three spots on multiple development over silica gel plate using chloroform as solvent. Major two components were

separated on PLC using same solvent. Major product was crystallized from benzene in yellow needles, m.p. 218° and was identified as N,N-dimethyl benzanthrone-9-sulphonamide. The other component crystallized from benzene in yellow needles, m.p. 244° and was identified as 3-sulphonamide derivative.

Sulphonation of benzanthrone with 96.5% sulphuric acid

Benzanthrone (10 g) was heated with sulphuric acid (96.5%; 100g) to 170° and kept between 160-70° for 8 hr. under stirring. Cooled the mixture and poured on ice-water (300 g). Unreacted benzanthrone was removed by filtration and filtrate concentrated to 200 ml, neutralized with sodium carbonate and salted out by adding saturated salt solution. Filtered the sodium salt (135 g), washed with saturated salt solution and dried. The crude product after dissolving in dry dimethylformamide and precipitating with ether separate into yellow product (15.0 g).

The above sodium salt (0.85 g) was converted into methyl ester (0.7 g) by the method described in the previous experiment. The product showed two major spots on TLC over silica gel using acetone-hexane (25:75) as a solvent system. The major product after separation on PLC over silica gel using acetone-hexane

(25:75) as solvent system after three developments, was crystallized from benzene in yellow needles, m.p. 215°, undepressed on admixture with methyl benzanthrone-9-sulphonate.

The other fraction was found identical with 3-sulphonic acid ester.

Sulphonation of benzanthrone with 10% SO_3

The sulphonation of benzanthrone (10 g) with fuming sulphuric acid (10% SO_3; 100 g) was carried out as described in the earlier experiment between 165-70° for two hours.

The dry sodium sulphonate was converted into methyl ester by treatment with dimethyl sulphate. The compound was obtained as single entity after carrying out PLC on silica gel using acetone-benzene (15:85) as solvent system. The compound crystallized from benzene in yellow needles, m.p. 216° (Found: C, 54.9; H, 3.9; S, 15.8%. $C_{19}H_{14}O_7S_2$ requires C, 54.5; H, 3.4; S, 15.3%).

Chlorosulphonation of benzanthrone

To chlorosulphonic acid (24.5 g), benzanthrone (6.9 g) was added during 15 min. under stirring at room temperature. The temperature slowly raised to 95° and maintained between 90-95° for 3 hr. Cooled the mixture and poured on ice. The yellow precipitate

separated was then immediately filtered, washed with ice-cold water free from acid and dried (9.1 g).

Benzanthrone N,N-dimethylsulphonamide

Sulphonyl chloride (1.5 g) obtained in the previous experiment was shaken with dimethylamine (40% solution, 10 ml) for 24 hrs at room temperature. Filtered the yellow residue (0.85 g), washed with water and dried.

The product showed three spots on TLC over silica gel using chloroform as solvent. Two major components were isolated as single entities on PLC using silica gel as an adsorbent and chloroform as solvent.

The major product (65%) crystallized from benzene in yellow needles, m.p. 218-20°, undepressed on admixture with N,N-dimethyl benzanthrone-9-sulphonamide (Found: C, 67.3; H, 4.6; S, 10.0%. $C_{19}H_{15}O_3NS$ requires C, 67.7; H, 4.5; S, 9.5%).

The other product (25%) after crystallization from benzene separated into bright yellow needles, m.p. 246°, undepressed on admixture with N,N-dimethyl benzanthrone-3-sulphonamide. (Found: C, 67.6; H, 4.7; S, 9.8%. $C_{19}H_{15}O_3NS$ requires C, 67.7; H, 4.5; S, 9.5%).

REFERENCES

1. R.H. Martin, Tetrahedron, 20, 897 (1964).
   R.H. Martin, N. Defay, F. Geerts-Evrard and S. Delavarenne, ibid., 20, 1073 (1964).

2. T.J. Batterham, L. Tsai and H. Ziffer, Aust.J.Chem., 18, 1959 (1965).

3. For reviews of benzanthrone derivatives, see K. Venkataraman, The Chemistry of Synthetic Dyes, Academic Press, N.Y., 1952, Vol. 2, p. 958.

   G.M. Badger and J.W. Cook, Chemistry of Carbon Compounds, ed. E.H. Rodd, Elsevier Publ.Co., Vol. IIIB, 1956, 1495.

4. C.J. Sanchorawala, Ph.D.(Tech.) thesis, University of Bombay, 1963.

5. BASF, DRP 200, 335; Ch.Ztbl. (1908II), 655; I.G. Farbenind, DRP 490, 988; Frdl. 16, 1465.

6. L.F. Fieser and L.W. Newton, J.Am.Chem.Soc., 64, 917 (1942).

7. I.G. Farbenind, Ger.Pat. 742, 811; C.A. 40, 3612 (1946); Ch.Ztbl. (1944II), 168.

8. O.Bally, Chem.Ber., 38, 194 (1965); O. Bally and R. Scholl, ibid., 44, 1656 (1911); Graebe, Ann., 201, 333 (1880)

9. P.N. Pandit, B. D. Tilak and K. Venkataraman, Proc.Indian Acad.Sci., 32A, 39 (1950).

10. R.R. Pritchard and J.L. Simonsen, J.Chem.Soc., (1938), 2047.

11. I.S. Ioffe and Z.I. Pavlova, J.Gen.Chem.(USSR), 14, 144 (1944). C.A., 39, 2288 (1945).

12. I.S. Ioffe and N.N. Mel'teva, J.Gen.Chem.(USSR), 9, 1104 (1939); C.A., 33, 8605 (1939).

PART IV

CONSTITUTION OF CIBANONE ORANGE R

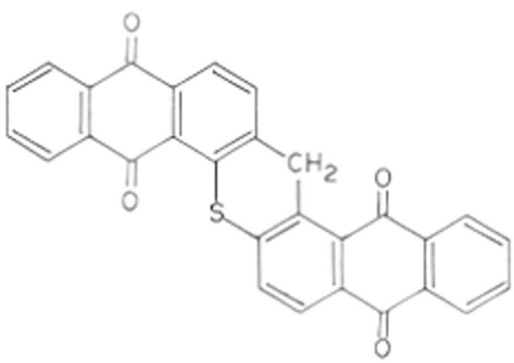
INTRODUCTION

Cibanone Orange R (Ciba, Mayer and Schaarschmidt, 1908)[1] is a sulphurized vat dye obtained by thionation of 2-methylanthraquinone or its halogenated derivatives in which chlorine or bromine is substituted in the 1 or 3- positions or in the methyl group. The intermediates cited in the patents are: 2-methylanthraquinone, 2-chloromethylanthraquinone, 2-dichloromethylanthraquinone, 1-chloro-2-chloromethylanthraquinone, 1-chloro-2-dichloromethylanthraquinone, 3-chloro-2-chloromethylanthraquinone, 3-chloro-2-dichloromethylanthraquinone; a mixture containing 1-chloro-2-chloromethylanthraquinone and 3-chloro-2-chloromethylanthraquinone; a mixture of mono and dichloromethylanthraquinones.

The thionation procedure consists in heating any one of the intermediates with a large excess (4-5 times by weight) of sulphur at high temperature (between 300-330°). The product dyes bright, attractive shades with excellent fastness to chlorine (5); the light fastness grade is about 6-7. However, the dye has been withdrawn from the commercial range of Cibanone colours because of its tendering action on cellulose when the dyed material is exposed to light.

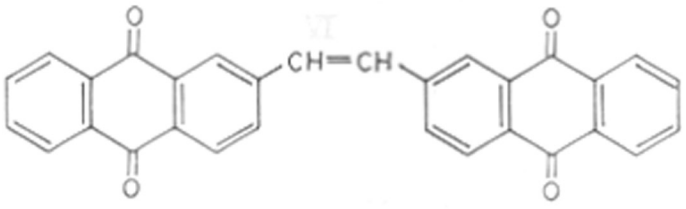
The tendering action is so powerful that even when cotton dyed with a mixture of Cibanone Orange R and Caledon Jade Green, which has excellent light fastness, is exposed to light, the green dye fades rapidly. Cibanone Orange R has therefore been the dye of choice for investigations on the catalytic action of anthraquinonoid vat dyes in the degradation of cellulose by light.

The constitution of Cibanone Orange R was first studied by Fierz-David and Geering[2], but a specific structure for the dye was not formulated. Analytical values obtained by them suggested the empirical formula $(C_{15}H_6O_2S)_x$, and Cibanone Orange R was regarded as being related to Cibanone Yellow R (which is obtained by thionation of any of the intermediates mentioned above at lower temperature) in the same manner as Primuline to dehydrothiotoluidine. Without citing any evidence or reference, Moran and Stonehill[3] assigned the structure (I) to Cibanone Orange R.



I

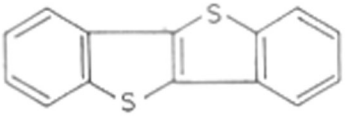
Schaarschmidt and Lewyoff[4] analysed Cibanone Orange R crystallized from nitrobenzene and found that the dye contained one atom of sulphur per molecule of 2-methylanthraquinone. From a study of oxidation-reduction potentials, Atherton and Turner[5] showed that Cibanone Orange R contained two pairs of carbonyl groups and had molecular weight 513, determined by catalytic reduction of the dye, reoxidation of the leuco compound and determination of the hydrogen peroxide formed. Shah[6] re-examined the chemistry of Cibanone Orange R. The elementary analysis of Cibanone Orange R, after purification according to Fierz-David, extraction with acetylene tetrachloride and crystallization from nitrobenzene was in agreement with the empirical formula $C_{15}H_6O_2S$. The acetylene tetrachloride extract gave 10% of Cibanone Yellow R when chromatographed on alumina. So neither Fierz-David and Geering nor Schaarschmidt and Lewyoff were dealing with a homogeneous dye. Distillation of either Cibanone Orange R or anthraflavone (II) with zinc dust, zinc chloride and sodium chloride (Clar reduction) gave



II

2-methylanthracene as one of the products and oxidation of the dye with nitric acid in acetic acid[7] gave anthraquinone-2-carboxylic acid. Structure (I) was, therefore, considered improbable since it should have led to 1-methylanthracene and anthraquinone-1-carboxylic acid together with 2-substituted products. Structure (III), (IV) or (V) was therefore proposed.

The chemistry of Cibanone Orange R was further investigated by Bhavsar[8]. She prepared compounds (III) and (IV) by thionation of 1-bromo-2-bromomethylanthraquinone and 3-bromo-2-bromomethylanthraquinone respectively and compared the products with purified Cibanone Orange R. The constitution of the products (III) and (IV) followed from the analogous formation of dibenzthiophthene (VI) by thionation of o-chloro- or o-bromobenzylbromide[8]. By comparing colour, crystalline nature, colour of the sulphuric acid solution, absorption



VI

spectrum in sulphuric acid, colour of the vat, and the shades obtained on cotton of twice crystallized Cibanone Orange R with compound (III) and (IV), she assigned the structure (III) to the main tinctorial constituent of Cibanone Orange R. She tried to synthesise (IV) by condensation of dibenzthiophthene (VI) with phthalic anhydride in an aluminium chloride- sodium chloride melt, but the product was found to be a mixture of several possible isomers. An unsuccessful attempt was made by her to synthesize (III) and (IV) by the action of phosphorus pentoxide and tetralin on dicarboxy-dianthraquinonyl disulphides. Attempts to elucidate the constitution of Cibanone Orange R by Raney nickel desulphurisation and alkali fusion proved inconclusive.

PRESENT WORK

In the present study the constitution of Cibanone Orange R has been reinvestigated using NMR and mass spectra.

The preliminary purification of the commercial product was carried out according to Fierz-David's exaustive extraction method. The product was further purified by crystallizing thrice from o-dichlorobenzene. The dye so obtained was found to be sparingly soluble in dimethylacetamide, tetramethylurea, and arsenic trichloride, and the NMR spectrum in one of these solvents therefore could not be determined.

The reductive methylation product of Cibanone Orange R was prepared by treating the alkaline vat with dimethyl sulphate at room temperature. The crude product thus obtained showed four spots on silica gel plates when developed with a mixture of acetone-hexane (2:8). The separation of these constituents by preparative layer chromatography was unsuccessful, probably because of reoxidation of the reductive methylation product. However, the major fast-moving compound was obtained by chromatographying the crude mixture over a short column of silica gel, using benzene for development and elution. The major yellow

fraction, after repeated crystallization from benzene, was obtained in chromatographically homogeneous form, m.p. 200-205°. The parent quinone was regenerated by precipitating the reductive methylation product from sulphuric acid. The product so obtained crystallized from nitrobenzene in orange needles.

The reductive acetylation product of Cibanone Orange R was obtained by refluxing a mixture of the dye, acetic anhydride, zinc dust and pyridine. The yellow product crystallized from chloroform in yellow needles, m.p. 300-302°. It behaved as a homogeneous compound when chromatographed on silica gel (TLC; solvent benzene-acetone 9:1).

Cibanone Orange R has not enough solubility in any suitable solvent to obtain the NMR spectrum. However, the reductive methylation and reductive acetylation products are soluble in tetramethylurea and arsenic trichloride respectively. Both the products are also soluble in pyridine. The NMR spectrum of the reductive methylation product in pyridine shows the presence of two singlets of equal intensity at 5.78 and 5.84, assigned to four methoxyl groups. The spectrum in tetramethylurea shows in the downfield region a doublet (J = 1.5 cps) at 1.08, assigned to an

aromatic proton or two equivalent aromatic protons showing meta coupling. This type of signal is not expected from any of the structures suggested earlier for the dye. The other aromatic protons appear in the region between 1.45 and 2.5. Similarly the NMR spectrum of the reductive acetylation product in arsenic trichloride shows the presence of the downfield meta-coupled doublet at 1.47 (J = 1.5 cps). This diamagnetic shift of 0.4 ppm. compared to the similar signal in the reductive methylation product is in accordance with the chemical shifts of the α-protons of the corresponding derivatives of anthrahydroquinone. Thus the α-protons of the reductive methylation product of anthraquinone appear at 1.68, whereas in the reductive acetylation product they appear at 2.07. Taking the coupling constant of 1.5 cps into account, it appears that the downfield signal represents an α-proton of an anthraquinone unit in which the 2-position is substituted and the 3-position is free. None of the structures (III, IV and V) proposed so far for Cibanone Orange R is in accordance with the observed NMR spectra of its derivatives.

The mass spectrum of Cibanone Orange R showed the molecular ion at m/e 504, four mass units more

than the required value for the structures suggested earlier (III, IV and V). Based on the elemental analysis and its molecular weight obtained from the mass spectrum, the molecular formula of the dye has been revised to $C_{30}H_{16}O_4S_2$. This is also in agreement with the mass spectral molecular weight of the reductive methylation product (564) and of the reductive acetylation product (676). The parent dye regenerated from the reductive methylation product also showed the molecular ion at m/e 504.

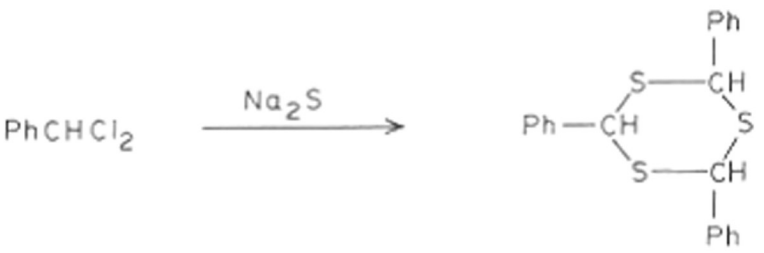
In the mass spectrum of the reductive methylation product, the loss of five methyl radicals successively from the molecular ion was observed (fragments at m/e 549, 534, 519, 504 and 489). The loss of four methyl radicals from four methoxyl groups can be accounted for, but the loss of the fifth 15 fragment cannot be explained as representing a methyl radical, because there is no C-methyl group in the compound as shown by the NMR spectrum in pyridine. This may be possible if there is some drastic rearrangement in the molecule by which a CH group picks up two hydrogen atoms. The fragment at m/e 470 probably corresponds to the loss of H_2S from the fragment at m/e 504.

In the mass spectrum of the reductive acetylation product, the molecular ion was observed at m/e 676 (4.1%), which loses four ketenes $(CH_2=CO)^+$ successively (fragments at m/e 634, 592, 550 and 508). The loss of sulphur from the fragment 508 is shown by an intense peak at m/e 476 (57.1%).

From the data now obtained it is clear that the cyclic structures proposed earlier for Cibanone Orange R have to be revised. The mass spectral and NMR spectral evidence can be reconciled with two structures (VII and VIII).

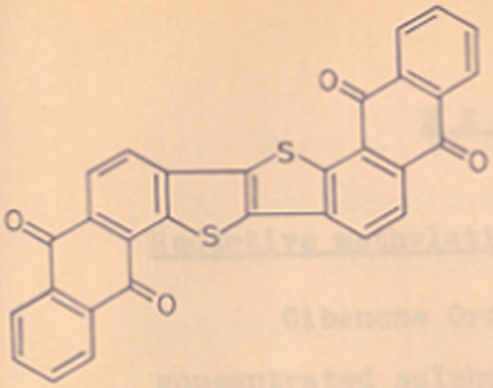
Structure (VIII) can be ruled out in view of the behaviour of Cibanone Orange R as a vat dye and its stability to fission at the S=S bond and desulphurization by a variety of reagents, such as mercuric chloride and mercuric oxide[9], sodium amalgam[10], and hydrazine and potassium hydroxide in boiling diethyleneglycol[11]. Drastic treatment with massive amounts of Raney nickel and aqueous sodium hydroxide at boiling temperature effected desulphurization, but the products have not yet been identified. Structure (VII) finds some support in the conversion of benzal dichloride to

the trimer (IX) by the action of sodium sulphide[12], but further evidence must be obtained before assigning a structure finally to Cibanone Orange R.

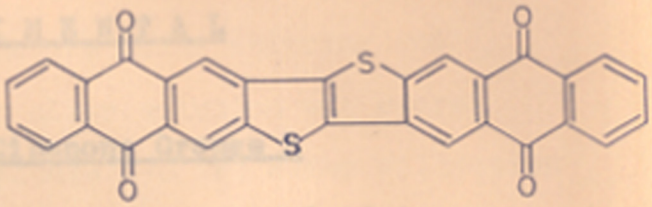


IX

Several compounds containing the 1,3-dithiacyclobutane ring system have been described in the literature[13]. Examples are the desaurins, such as (X) from desoxybenzoin; structure (X), first suggested by Kelber[14], has been confirmed by Yates and Moore on the basis of chemical evidence and IR, UV and NMR spectra[15].



III



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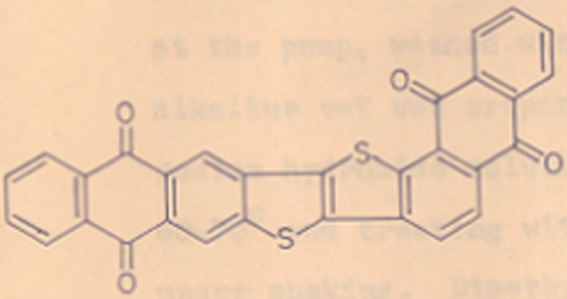
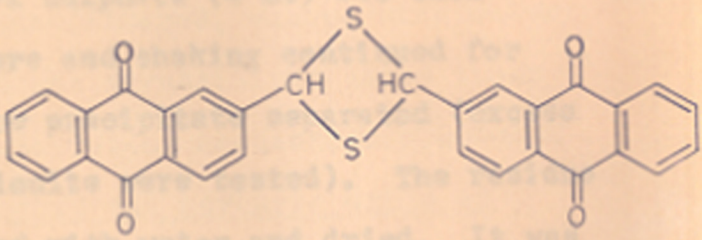
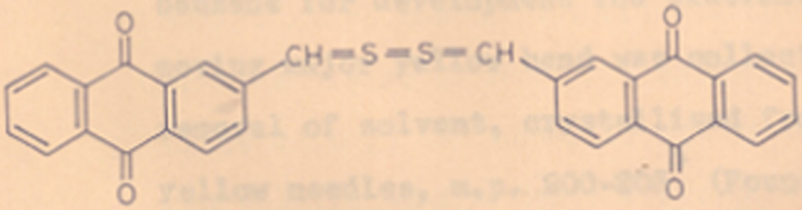


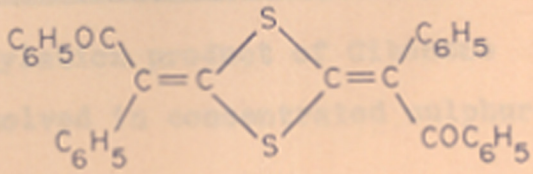
V



VII



VIII



X

EXPERIMENTAL

Reductive methylation of Cibanone Orange R

Cibanone Orange R (1.0 g) was dissolved in concentrated sulphuric acid and precipitated by pouring on ice. The precipitated product filtered at the pump, washed with water free from acid. The alkaline vat was prepared by suspending wet cake in sodium hydroxide solution (5% solution; 20 ml) at 60-70° and treating with sodium dithionite (1.5 g) under shaking. Dimethyl sulphate (4 ml) was then added at room temperature and shaking continued for half an hour when yellow precipitate separated (excess alkali and sodium dithionite were tested). The residue (0.8 g) filtered, washed with water and dried. It was then passed through a short column of silica gel using benzene for development and elution. The faster moving major yellow band was collected which after removal of solvent, crystallised from benzene in yellow needles, m.p. 200-205° (Found: C, 72.4; H, 4.8; S, 11.0%. $C_{34}H_{28}O_4S_2$ requires C, 72.4; H, 5.0; S, 11.3%).

Demethylation of the reductive methylation product

Pure reductive methylation product of Cibanone Orange R (100 mg) was dissolved in concentrated sulphuric

acid (3 ml) at room temperature under stirring and left for ten minutes. The clear solution was poured on ice. The orange precipitate (70 mg) after filtration and washing, crystallised from nitrobenzene in orange needles.

Reductive acetylation of Cibanone Orange R

Cibanone Orange R (1.0 g) was refluxed with acetic anhydride (20 ml) and pyridine (0.5 ml) in presence of zinc dust (4.0 g) for 3 hours. The resultant mixture poured on ice (100 g). The yellow precipitate separated was filtered, washed with water and dried (0.95 g). It was crystallised three times from chloroform in bright yellow needles, m.p.300-302°.

Action of mercuric chloride and mercuric oxide on Cibanone Orange R

Cibanone Orange R (0.45 g) were suspended in methyl ethyl ketone (50 ml) and the solution heated after addition of mercuric chloride (0.6 g), mercuric oxide (1.0 g) and water (2 ml) to 55° under stirring and maintained the temperature between 50-60° for 6 hr. The hot solution was filtered (the filrate was light yellow in colour). The residue gave positive sulphur test and showed similar dyeing properties and colouration in sulphuric acid as Cibanone Orange R.

Action of Na/Hg amalgam on Cibanone Orange R

Cibanone orange R (1.0 g) was suspended in sodium hydroxide solution (2% solution; 75 ml). It was heated to 95° in a slow stream of oxygen free nitrogen. Na/Hg amalgam (2%; 20 g) was added and heating continued for 2 hr. under nitrogen atmosphere. Filtered the residue, washed with water and dried. The product found to be starting material.

Action of hydrazine on Cibanone Orange R in presence of alkali

The mixture of Cibanone Orange R (3 g), ethylene-glycol (50 ml), hydrazine (7 ml) and potassium hydroxide (6 g) were heated to 120° and maintained for two hours. The temperature was then raised to 140° and maintained for one more hour. The resultant mixture diluted with water, filtered the residue, washed with water and dried. The product after crystallisation from o-dichlorobenzene, was found to be identical with Cibanone Orange R.

Raney nickel reduction of Cibanone Orange R

The dye (2.5 g), sodium hydroxide (3 g), Raney nickel (25 g) and water (150 ml) were heated under reflux for 8 hours under stirring. The suspension was then acidified and filtered. The residue was extracted three times with 50 ml portions of boiling

chloroform. Total chloroform extract after removal of the solvent gave an orange coloured residue (1.0 g). It was then chromatographed through alumina column using chloroform for development and elution. Two fractions were isolated. The major yellow component crystallised from chloroform in orange needles, m.p. 290-5°. The second fraction crystallised from chloroform, m.p. 244-6°. Both the products could not be identified.

REFERENCES

1. Mayer and Schaarschmidt, DRP 209, 231; 209, 233; 211, 967; 213, 506.

2. Fierz-David and Geering, J.Soc.Dyers Col., 51, 50 (1935).

3. J.J. Moran and H.I. Stonehill, J.Chem.Soc., (1957), 765.

4. Schaarschmidt and Lewyoff, J.Prakt.Chem., 113, 48 (1926).

5. Atherton and Turner, J.Soc.Dyers Col. 62, 108 (1946).

6. K.H. Shah, Ph.D.(Tech.) Thesis, University of Bombay, 1949.

7. S.P. Chandavarkar, M.Sc.(Tech.) Thesis, University of Bombay, 1952.

8. Miss M.D. Bhavsar, Ph.D.(Tech.) Thesis, University of Bombay, 1957.

9. G. Drefahl and M. Hubner, J.Prakt.Chem., 23, (1964) 149.

10. H.M. Hurst and J.B. Harborne, Phytochem., 6, 1111 (1967).

11. V. Georgian, R. Harrisson and N. Gubisch, J.Am.Chem.Soc., 81, 5834 (1959).

12. J.H. Wood and R.W. Bost, J.Am.Chem.Soc., 59, 1011 (1937).

13. For a review, see L.L. Muller and J. Hamer, 1,2-Cyclo addition Reactions, Intersc., 1967.

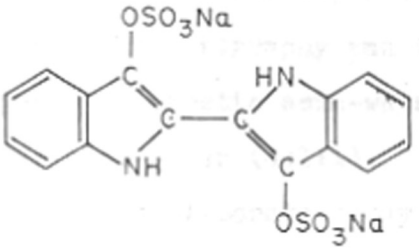
14. C. Kelber, Chem.Ber., 43, 1252 (1910); C. Kelber and A. Schwarz, ibid., 45, 137 (1912).

15. P. Yates and D.R. Moore, J.Am.Chem.Soc., 80, 5577 (1958).

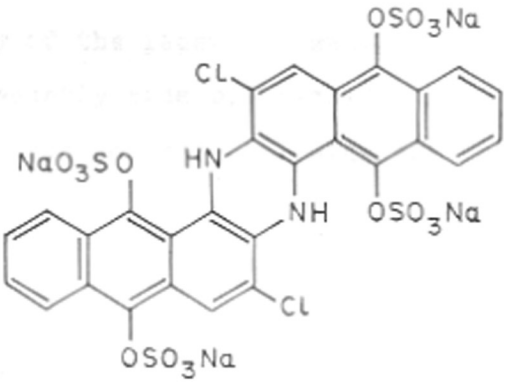
PART V

NMR SPECTRA OF INDIGOSOLS

For the sake of brevity, the trivial word "Indigosol" is used in the present discussion for the sodium salts of sulphuric esters of leuco derivatives of vat dyes[1]. Examples are Indigosol O (I) and Indigosol Blue IBC (V).



I



V

An obvious solution of the problem of separating vat dyes, which are very sparingly soluble in organic solvents, is to use them in the form of indigosols. The procedures used so far are briefly reviewed and an improved technique for the separation of indigosols using TLC is described. The main purpose of the present work, however, is to use indigosols for the determination of

NMR spectra as another approach for investigating structural problems concerning vat dyes.

Ruggli and Stauble[2], who used a column of alumina and calcium carbonate, were the first to carry out the chromatography of indigosols. Kolsek, Mlakar and Perpar separated indigosols by ascending paper chromatography and the solvent systems n-butanol-acetic acid-water (4:1:5) and butanol-pyridine-water (4:1:1).

An elaborate study of the paper chromatography of indigosols has been recently made by Sramek[4]. He used the descending technique and the following solvent systems:

S_1 - ammonia (25%)-methanol-water (1:2:3);

S_2 - pyridine-isoamyl alcohol-ammonia (25%)(1.3:1:1)

S_3 - methanol-acetic acid-water (4:1:1)

With the solvent system S_1, the following relationships were established: " (1) In all instances it is obvious that the chromatographic behaviour of the vat dyes (parent dyes) is analogous, the size of the dye molecule being of decisive influence. Dyes with a simple structure possess the highest R_f value, and this decreases with increasing size of the molecule as a result of increasing dye adsorption. (2) Simpler indigoid, thioindigoid and arylminoquinone dyes have

a higher R_f than the more complex anthraquinone dyes. (3) Thioindigoid dyes have a higher R_f than indolethionaphthene dyes and miscellaneous dyes. (4) Symmetrical indigoid dyes usually have a higher R_f than asymmetrical dyes. (5) Dibenzanthrones have a higher R_f value than isodibenzanthrones. (6) In the case of dyes with the same carbon skeleton, an increase in the number of substituents, e.g. -Cl, -Br, $-CH_3$, $-OCH_3$, causes the R_f value to decrease".

TLC of Indigosols on silica gel plates has been carried out. The silica gel plates were prepared by making a slurry with 2.5% aqueous sodium carbonate. Two solvent systems are used for the separations:

S_4) DMF-water-isopropyl alcohol (1:1:8);

S_5) DMF-ethanol-isoamyl alcohol (1:1:8)

Four indigosols of the indigoid type were examined and they were found to separate with the solvent system (S_5), in which four of the six anthraquinonoid vat dyes examined had very small R_f values. Solvent system (S_4) is found useful for the separation of anthraquinonoid vat dyes.(see Table 1).

NMR spectra of a few Indigosols as their sodium salts have been determined in dimethylacetamide solution, using tetramethylsilane as an internal reference. The commercial Indigosols were dissolved in dry dimethyl-

Table 1

Rf Values of Indigosols

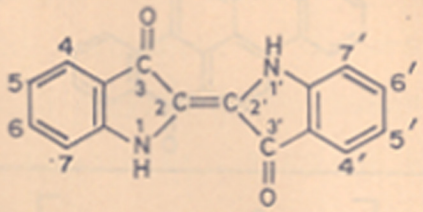
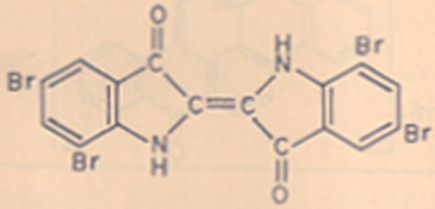
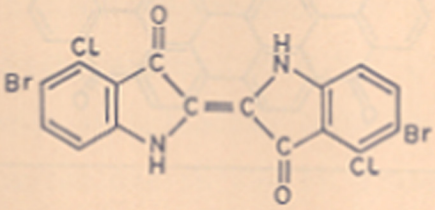
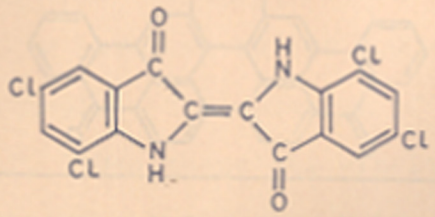
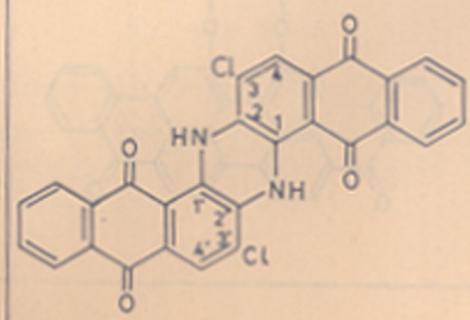
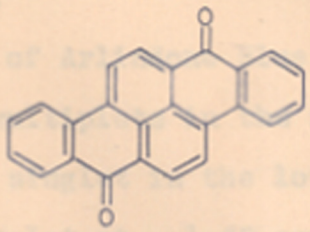
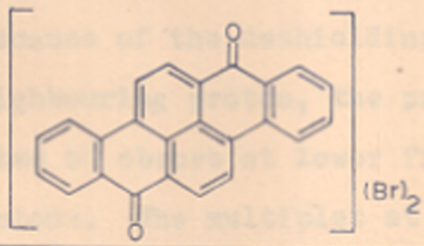
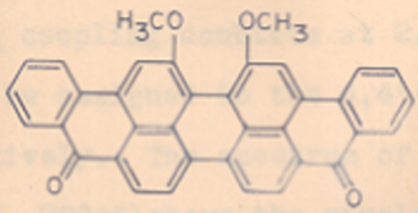
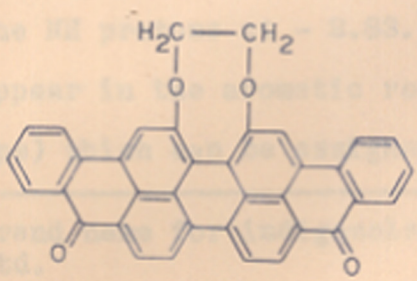
Compound No.	Colour Index No.	Commercial name	Parent dye	Rf values	
				S_4	S_5
I	73002	Arlindone Blue O		—	0·38
II	73066	Arlindone Blue 04B		—	0·61
III	73046	Arlindone Blue 04G		—	0·47
IV	—	L.S.E of Brilliant Indigo B		—	0·57
V	69826	Arlindone Blue IBC		0·36	—

Table 1 (contd.)

Compound No.	Colour Index No.	Commercial name	Parent dye	Rf values	
				S_4	S_5
VI	59101	Arlindone Golden Yellow IGK.		0·75	0·39
VII	59106	Arlindone Golden Yellow IRK		—	0·5
VIII	—	L.S.E. of Indanthren Dark Blue BOA		0·58	—
IX	59826	Arlindone Green IB		0·63	—
X	—	L.S.E. of Indanthren Navy Blue G.		0·65	—

L. S. E. — Leuco Sulphuric Ester

acetamide, filtered and the spectra were determined without any prufication.

The NMR spectrum of Arlindone Blue O (I)* (C.I. 73002) showed two multiplets in the aromatic region and a two-proton singlet in the lower part field (Fig. 1). The singlet at - 1.63 can be assigned to the NH protons. Because of the deshielding effect of sulphate on the neighbouring proton, the protons at 4 and 4' are expected to absorb at lower field than the other aromatic protons. The multiplet at 2.22 can therefore be assigned to the 4,4'-protons. The multiplet centred at 2.83 integrating for six protons represents the remaining protons (5,6,7,5',6',7').

In the spectrum of Arlindone Blue 04 B(II) (C.I. 73066) the singlet due to the NH protons appears at - 2.08. The meta coupling doublets at 2.05 and 2.5 (J = 2 cps) can be assigned to the 4,4'- and 6,6'-protons respectively. The spectrum of Arlindone Blue 04 G (III) (C.I. 73046) shows the singlet absorption due to the NH protons at - 2.83. Two ortho-coupling doublets appear in the aromatic region at 2.55 and 2.67 (J = 8.5 cps) which can be assigned to the

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*Arlindone is the brand name for indigosols manufactured by Messrs Arlabs Ltd.

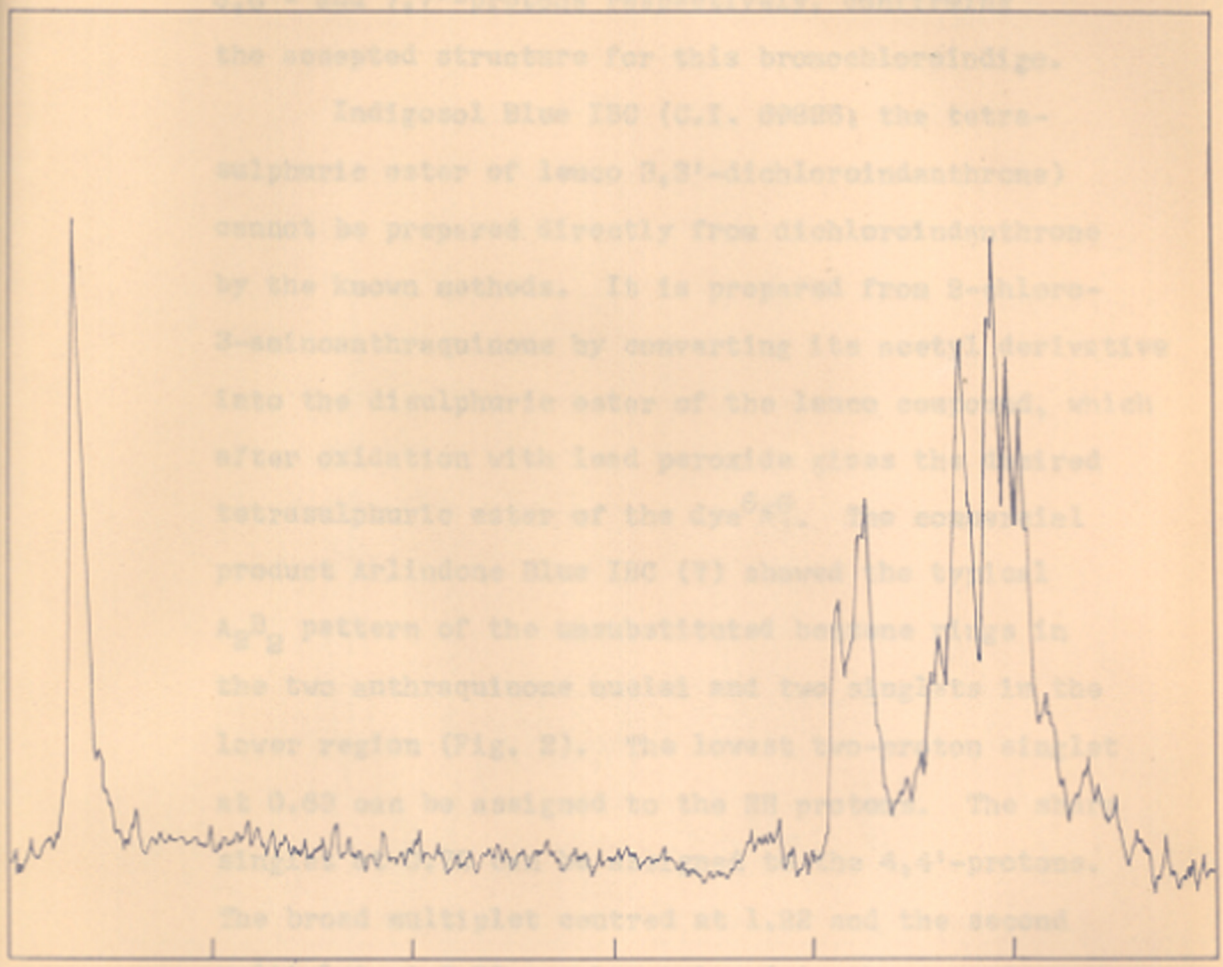


FIG. 1.

NMR SPECTRUM OF ARLINDONE BLUE O

6,6'- and 7,7'-protons respectively, confirming the accepted structure for this bromochloroindigo.

Indigosol Blue IBC (C.I. 69826; the tetrasulphuric ester of leuco 3,3'-dichloroindanthrone) cannot be prepared directly from dichloroindanthrone by the known methods. It is prepared from 2-chloro-3-aminoanthraquinone by converting its acetyl derivative into the disulphuric ester of the leuco compound, which after oxidation with lead peroxide gives the desired tetrasulphuric ester of the dye[5,6]. The commercial product Arlindone Blue IBC (V) showed the typical A_2B_2 pattern of the unsubstituted benzene rings in the two anthraquinone nuclei and two singlets in the lower region (Fig. 2). The lowest two-proton singlet at 0.63 can be assigned to the NH protons. The sharp singlet at 0.72 can be assigned to the 4,4'-protons. The broad multiplet centred at 1.22 and the second multiplet at 2.22 can be assigned to the α- and β-protons of the unsubstituted benzene rings.

The problem of the orientation of two bromine atoms in dibromodibenzopyrenequinone (CI Vat Orange 1; Indanthren Golden Yellow RK; C.I. 59105) was then studied by using the NMR spectra of the Indigosols from dibenzopyrenequinone (VI) and the dibromo derivative (VII).

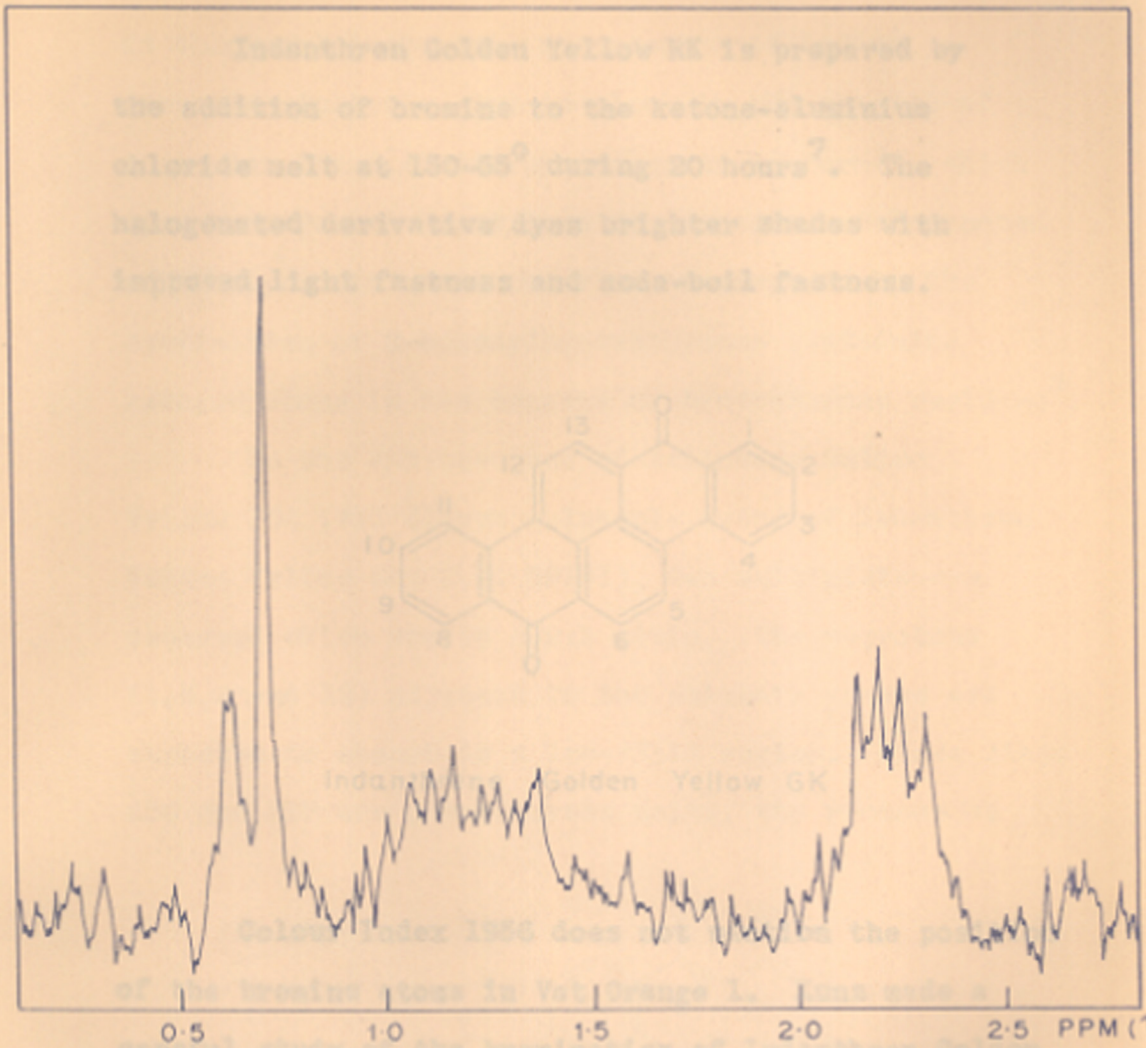
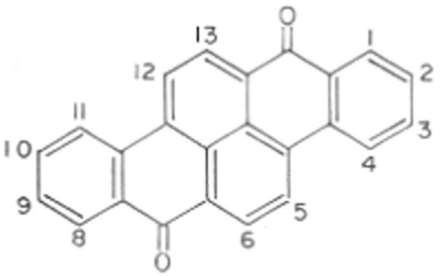


FIG. 2.

NMR SPECTRUM OF ARLINDONE BLUE IBC

Indanthren Golden Yellow RK is prepared by the addition of bromine to the ketone-aluminium chloride melt at 150-55° during 20 hours[7]. The halogenated derivative dyes brighter shades with improved light fastness and soda-boil fastness.

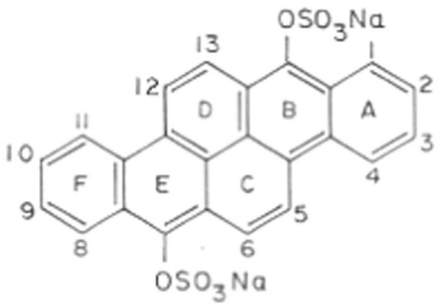


Indanthrene Golden Yellow GK

Colour Index 1956 does not mention the position of the bromine atoms in Vat Orange 1. Kunz made a careful study of the bromination of Indanthren Golden Yellow GK (C.I. 59100), and showed the influence of the conditions of the reaction on the orientation of the bromine atoms which in turn affected the shade and fastness[8]. Halogenation in an organic solvent requires a carrier, such as iodine, and the bromine atoms enter the 2,9-positions, the shades are redder and faster than those from the parent compound. Halogenation

in chlorosulphonic acid in presence of iodine proceeds similarly, but in oleum in the absence of a carrier the 3,10-dibromo compound is formed, which dyes more greenish and less fast shades. Halogenated dibenzopyrenequinones can also be prepared by the cyclisation of 3-benzoylbenzanthrones containing halogen atoms in the benzene or benzanthrone residues[9].

In the NMR spectrum of Arlindone Golden Yellow IGK (VI) (leuco sulphuric ester of Indanthren Golden Yellow GK; C.I. 59101), two multiplets are observed which are in a 2:1 ratio. The α-protons (1,6,8 and 13) adjacent to the sulphate groups are expected to absorb in a low-field region. Since rings ABC and DEF are phenanthrene units, the protons at



VI

4,5 and 11,12 may also be expected to absorb in a lower field than the β-protons of normal anthracene units.

The lower multiplet centred at 0.88 can therefore be assigned to these eight protons (1,4,5,6,8,11,12 and 13). The second multiplet centred at 2.2 represents the remaining β-protons of the system (2,3,9 and 10). The only change seen in the spectrum of the dibromo derivative, Arlindone Golden Yellow IRK (VII) in comparison with that of (VI) is the decrease in the number of protons in the high-field region, which shows that the bromine atoms have entered the 2,9 or 3,10-positions.

EXPERIMENTAL

Leuco sulphuric ester of Brilliant Indigo B

Chlorosulphonic acid (1 ml) was slowly added to DMF (6 ml) between 0 - 5°. Brilliant Indigo B (1.0 g; free from water and alcohol solubles) was introduced to the mixture followed by copper bronze (0.5 g). The temperature allowed to come to 20° and stirred it between 15-20° for 2 hrs. Poured the solution in water (40 ml) containing sodium hydroxide (4 g), filtered to remove copper bronze and unreacted dye. DMF was removed by extraction with benzene and ester was precipitated with saturated salt solution.

Leuco sulphuric esters of Indanthren Dark Blue BOA and Indanthren Navy Blue G were prepared as described in the previous experiment.

REFERENCES

1. K. Venkataraman, The Chemistry of Synthetic Dyes, Academic Press, N.Y. 1952, Vol. II, p.1046.

2. P. Ruggli and M. Stauble, Helv.Chim.Acta., 23, 689 (1940).

3. J. Kolsek, F. Mlakar and M. Perpar, Z.Anal.Chem., 188, 345 (1962).

4. J. Sramek, J.Chrom., 12, 453 (1963).

5. BIOS 960; 1363; FIAT 1313, II.

6. BIOS 1493.

7. BIOS 987.

8. K. Venkataraman, The Chemistry of Synthetic Dyes, Academic Press, N.Y. 1952, Vol. II, p.955.

9. Braun and IG, DRP 742, 811.

PART VI

CONSTITUTION OF INDANTHREN RED F3B

As stated by Venkataraman[1], dye manufacturers, unlike the manufacturers of synthetic drugs are reluctant to reveal the chemical constitution of their products for reasons which are not easy to understand. As part of a general programme of research on synthetic dyes, work has been in progress in this laboratory to determine the structures of new commercial dyes, specially if new structural problems and interesting synthetic reactions are involved. In this connection, the structure of Indanthren Red F3B, which dyes cotton attractice bluish red shades with excellent fastness properties, has been investigated. Colour Index 1956 mentions Indanthren Red F3B (Vat Red 31) and Colour Index Supplement 1963 mentions Caledon Brilliant Red 5B as equivalent to Vat Red 31; but the constitution has not been disclosed.

The present study of Indanthren Red F3B was carried out on a sample kindly supplied by Messrs Chika Ltd., Bombay.

The water-soluble matter from the commercial dye was removed by repeated extraction with boiling water. The product was then crystallized from nitrobenzene in red microscopic needles. A preliminary examination of the dye showed the presence of nitrogen. Sulphur and halogen were absent in the compound. Infra-red spectrum

recorded in nujol showed the characteristic two band absorption of free amino group and the band at 1665 cm^{-1} due to free quinonoid group.

Reductive methylation of the dye was carried out by treating alkaline vat solution with dimethyl sulphate at room temperature under stirring as described in Part I. The product thus obtained after three crystallizations from benzene gave chromatographically homogeneous derivative. Infra-red spectrum of this compound recorded in nujol (Fig. 1) showed no quinone absorption. The free amino group is characterized by a doublet of N-H bands at 3420 cm^{-1} and 3290 cm^{-1}. It is also supported by the band at 1620 cm^{-1} which can be assigned to amino group. The presence of oxadiazole ring[2] has been characterized by the bands at 972 cm^{-1} and 1025 cm^{-1} due to the C-O bond and a sharp band at 1540 cm^{-1} due to the C=N valence vibration. Thus the compound seems to be a 1,3,4-oxadiazole derivative containing an anthraquinone nucleus with free amino group. Analysis for C,H and N of the reductive methylated derivative agrees with the corresponding reductive methylated derivative of bis (aminoanthraquinonyl)-1,3,4-oxadiazole.

The mass spectrum of the above reductive methylated derivative was recorded showed the molecular

ion at m/e 572 which agrees with the reductive methylated derivative of bis (aminoanthraquinonyl)-1, 3,4-oxadiazole.

Comprehensive study of oxadiazole shows that 1,3,4-oxadiazole derivatives can be obtained by cyclising bis-hydrazides of general formula R-CONH·HNCO-R' with various dehydrating agents. The general method of preparing bishydrazide is to react acid chloride with hydrazine to obtain a monohydrazide which after condensing with further molecular proportion of acid chloride gives bishydrazide. Cyclisation is usually obtained by $SOCl_2$, $POCl_3$, p-touenesulphonic acid[3]. The ring closure reaction is preferably carried out at temperatures from 160-75° in an inert organic solvent. With relatively stable substituents R or R' fuming sulphuric acid[4], chlorosulphonic acid[5], and SO_3/DMF[6] may be used. Cyclisation with thionyl chloride in DMF at room temperature is also described[7], but the yield of oxadiazoles obtained are about 45 per cent.

A method of manufacture of 2,5-bis (1-amino-2-anthraquinonyl)-1,3,4-oxadiazole[8] comprises treating N,N'-bis (1-amino-2-anthraquinonyl carbonyl) hydrazine with 4% oleum at 95-100°. The bishydrazide mentioned above is obtained from 1-aminoanthraquinone-2-carbonyl

chloride and hydrazine in nitrobenzene. The method of preparation of the above dye is also described[9,10] which consists in heating 3,4-phthaloylisotoic acid anhydride with hydrazine in nitrobenzene, removing the solvent and treating the product with $SOCl_2$.

A series of new vat dyes having good fastness properties and having one or more 1,3,4-oxadiazole nuclei linked in 2 (or 5)- position to a 2-anthraquinonyl group and in 5 (or 2)- position an alkyl, aryl or substituted aryl groups are described[11]. Thus 2-(p-benzamidophenyl)-5-(1-amino-2-anthraquinonyl) oxadiazole, dyes cotton scarlet shades; 1,4-bis[2-(2-amino-2-anthraquinonyl)-5-oxadiazolyl] butane, dyes scarlet shades from a claret coloured vat. Similarly some more red, yellowish red and scarlet dyes are mentioned. The oxadiazole obtained from diacylhydrazide of 1-amino-4-nitro-2-anthraquinonecarbonyl chloride and hydrazine hydrate, yields on reduction and acylation with benzoyl chloride a product which dyes cotton violet from a claret vat[12].

Halogenated derivatives of 2,5-bis(1-amino-2-anthraquinonyl)-1,3,4-oxadiazole have been described[13], which have in at least one of the anthraquinone radicals in the 4 position a Cl or Br atom, are useful as vat dyes for cotton and pigments for paints and lacquers.

In a paper published in 1958[14] it is mentioned that anthraquinonyloxadiazoles "have recently acquired importance as vat dyestuffs", and two additional patents are cited[15]. Incidentally, Klingsberg[14] made the interesting observation that the reaction of 2-anthraquinonecarbonyl chloride with a large excess of hydrazine gave an apparently intractable product with a high indefinite m.p. and a low nitrogen content; ester hydrazinolysis under normal conditions was also discouraging, although both 1-amino- and 1,4-diaminoanthraquinone-2-carboxylic esters have been reported to react normally with hydrazine[16]. Klingsberg then found that in the absence of an organic solvent ethyl anthraquinone-2-carboxylate was reduced rapidly by aqueous hydrazine hydrate to the deep red hydroquinone, which was converted to the hydrazide and oxidized to the desired anthraquinone-2-carbonyl hydrazide.

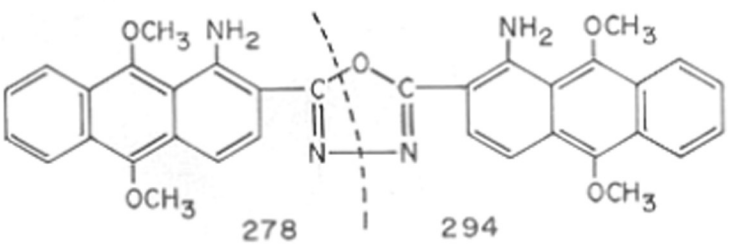
The compound was further thougnt to be 1,3,4-oxadiazole derivative linked in 2- and 5- positions to probably 1-amino-2-anthraquinonyl groups. 2,5-Bis (1-amino-2-anthraquinonyl)-1,3,4-oxadiazole was therefore synthesized from 1-aminoanthraquinone-2-carboxylic acid.

1-Aminoanthraquinone-2-carboxylic acid (I) was

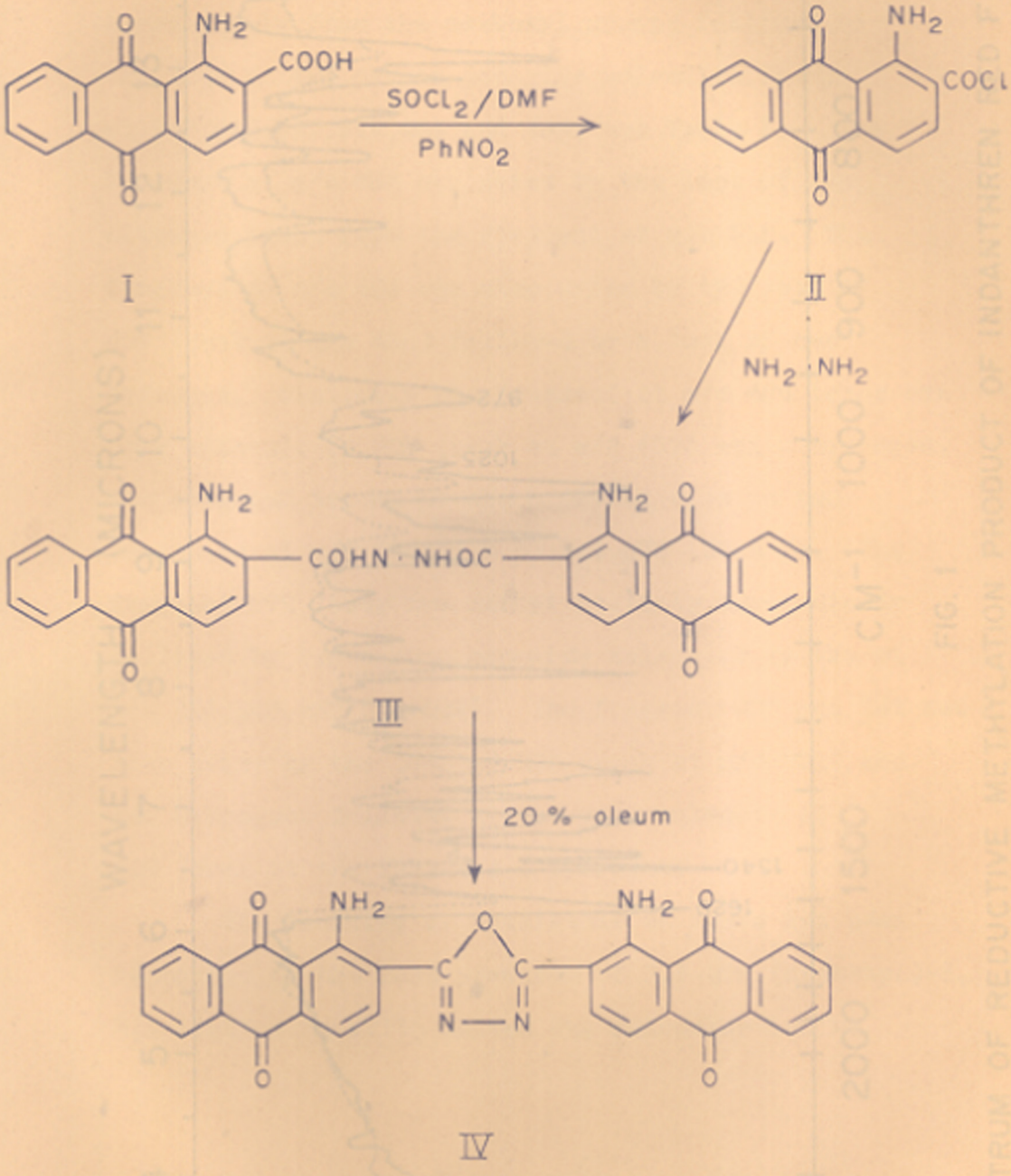
converted into carbonyl chloride by treatment with thionyl chloride in nitrobenzene in presence of catalytic amount of dimethylformamide. Carbonyl chloride (II) was treated with hydrazine hydrate to give bishydrazide (III) which was then cyclised with oleum to give 2,5-disubstituted 1,3,4-oxadiazole (IV).

The product analyses for $C_{30}H_{16}O_5N_4$ which has same dyeing properties as that of the commercial dye.

The synthetic product was reductively methylated which showed same chromatographic behaviour as that of the reductive methylated derivative of commercial product, had m.p. 280-2° undepressed on admixture with the reductive methylated derivative of commercial product. Infrared spectrum was also superposable (Fig.1) which confirms that Indanthren Red F3B has a structure (IV). The mass spectral fragmentation of reductive methylation product (V) also agrees with the proposed structure.



278 294


NH2
COOH
SOCl2/DMF
PhNO2
NH2
COCl
I
II
NH2·NH2
NH2
COHN·NHOC
NH2
III
20 % oleum
NH2
NH2
IV

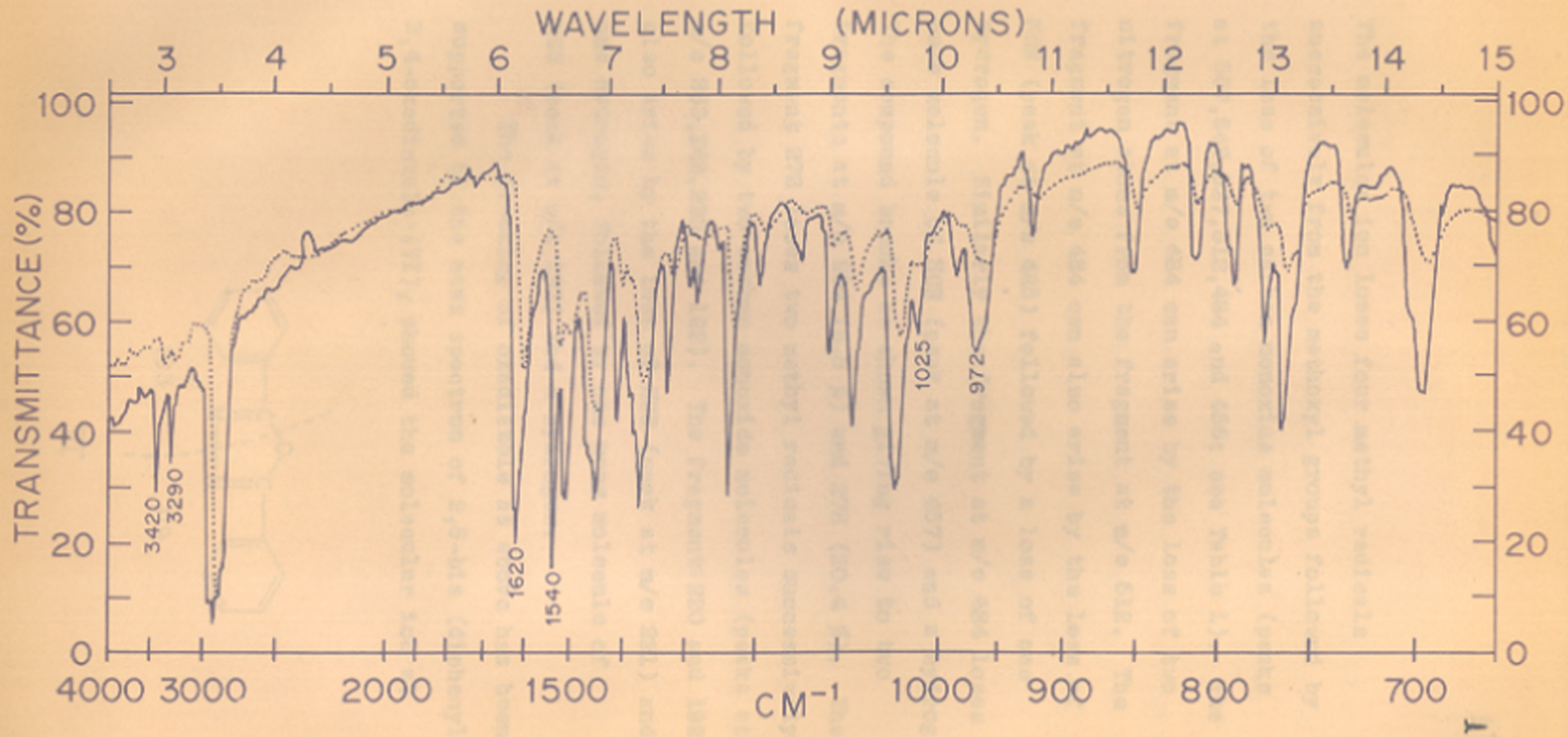


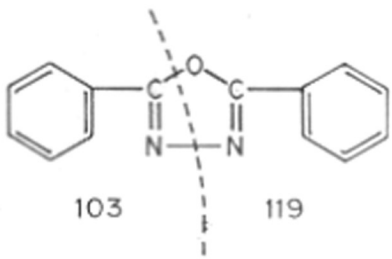
FIG. 1

IR SPECTRUM OF REDUCTIVE METHYLATION PRODUCT OF INDANTHREN RED F3B, ——

IR SPECTRUM OF REDUCTIVE METHYLATION PRODUCT OF IV, ·····

The molecular ion loses four methyl radicals successively from the methoxyl groups followed by the loss of two carbon monoxide molecules (peaks at 557,542,527,512,484 and 456; see Table 1). The fragment at m/e 484 can arise by the loss of two nitrogen atoms from the fragment at m/e 512. The fragment at m/e 484 can also arise by the loss of HCN (peak at m/e 485) followed by a loss of one hydrogen. Similarly the fragment at m/e 484 loses one more molecule of HCN (peak at m/e 457) and a hydrogen. The compound breaks as shown giving rise to two fragments at m/e 294 (6.5 %) and 278 (20.4 %). The fragment 278 loses two methyl radicals successively followed by two carbon monoxide molecules (peaks at m/e 263,248,220 and 192). The fragments 220 and 192 can also arise by the loss of HCN (peak at m/e 221) and one hydrogen, followed by one more molecule of HCN (peak at m/e 193) and a hydrogen.

The breaking of oxadiazole as above has been supported by the mass spectrum of 2,5-bis (diphenyl)-1, 3,4-oxadiazole (VI), showed the molecular ion at



VI

m/e 222. Very insignificant peak at m/e 194 (0.5 %) was observed due to the loss of two nitrogens from the molecular ion. The compound breaks as shown giving rise to the fragment at m/e 103 (7.5 %), the fragment due to the other half is very insignificant. The fragment at m/e 103 loses one nitrogen giving rise to the peak at m/e 89 (10.8 %). The fragment at m/e 77 (13.1 %) was observed due to the breaking of the molecule at C-phenyl bond.

After this work was completed, a paper of Otto Bayer entitled "Die Neuere Entwicklung der Farbenchemie", published in Leverkusen in 1958 apparently for private circulation, in which the structure of Indanthren Red F3B is disclosed became available.

Table 1

m/e	574	573	572	571	570	559
I(%)	7.3	33.5	100	4.6	6.5	5.8
m/e	558	557	544	543	542	541
I(%)	13.5	22.3	5.0	19.2	61.6	13.5
m/e	540	529	528	527	526	514
I(%)	6.9	5.0	18.8	46.2	8.5	2.8
m/e	513	512	511	499	498	497
I(%)	9.2	17.3	6.9	2.3	6.5	6.5
m/e	485	484	457	456	326	325
I(%)	1.0	1.0	0.8	0.8	1.7	7.7
m/e	324	322	321	320	311	310
I(%)	1.7	1.7	1.8	3.2	1.1	4.0
m/e	309	308	307	306	305	304
I(%)	1.2	2.2	2.7	4.4	4.7	2.1
m/e	297	296	295	294	293	292
I(%)	1.7	8.1	4.0	6.5	5.1	6.0
m/e	291	290	286.5	286	281	280
I(%)	7.7	3.8	4.6	10.8	10.8	20.8
m/e	279	278.5	278	277	276	271.5
I(%)	10.8	6.2	20.4	11.5	7.3	10.8
m/e	271	266	265	264	263.5	263
I(%)	32.7	0.9	10.0	39.2	15.4	31.9
m/e	262	261	256.5	256	252	251
I(%)	15.0	6.2	4.5	8.1	5.2	11.2

Table 1 (continued)

m/e	250	249	248	247	246	245
I(%)	50.0	18.5	31.5	7.3	4.3	4.8
m/e	243	242.5	242	239	238	237
I(%)	0.5	0.5	1.2	3.5	7.3	10.0
m/e	236	235	234	223	222	221
I(%)	7.3	11.5	9.6	6.2	6.9	4.6
m/e	220	219	209	208	207	206
I(%)	6.9	3.5	4.0	4.3	5.2	4.5
m/e	205	194	193	192	191	190
I(%)	3.5	1.9	3.8	4.6	3.6	4.6
m/e	181	180	179	178	177	176
I(%)	2.2	4.6	3.1	2.8	4.8	3.1
m/e	166	165	164	163	153	152
I(%)	3.1	6.2	6.9	3.4	4.1	5.0
m/e	151	150	140	139.5	139	138
I(%)	6.9	2.6	2.1	0.9	4.1	3.2

EXPERIMENTAL

Purification of Indanthren Red F3B

The commercial sample was freed from water-soluble impurities by washing it repeatedly with boiling water which was then refluxed with nitrobenzene, filtered hot, concentrated to the small volume and cooled gradually and kept overnight, when separated into red microscopic needles.

Reductive methylation of Indanthren Red F3B

The commercial dye (2.0 g) was suspended in aqueous sodium hydroxide solution (5% solution; 20 ml) at 60-70° and prepared vat by adding sodium hydrosulphite (2.5 g) under shaking. To the well shaken vat at room temperature dimethyl sulphate (12.0 ml) was added and continued shaking for half an hour when bordeaux coloured vat changed to yellowish orange and orange precipitate separated. Excess alkali and sodium hydrosulphite was tested. Filtered the residue, washed with water and dried (1.5 g). Crystallized it thrice from benzene in red brown needles, m.p. 280-82°. The product showed single spot on TLC over silica gel using hexane:acetone (8:2) as a developing solvent.

(Found: C, 71.3; H, 4.9; N, 10.0%. $C_{34}H_{28}O_5N_4$ requires C, 71.3; H, 4.9; N, 9.8%).

Synthesis of 2,5-bis(1-amino-2-anthraquinonyl) -1,3,4-oxadiazole (IV)

a) Preparation of bishydrazide (III)

1-Aminoanthraquinone-2-carboxylic acid (2.67 g; 0.01 mole) was suspended in dry nitrobenzene (150 ml) at room temperature and thionyl chloride (4 ml) and four drops of dimethylformamide were added. The mixture was stirred at 70-80° for 4 hours. Excess thionyl chloride was removed by passing dry air through mixture for one hour between 90-95°. To the resulting solution was then added hydrazine hydrate (0.3 ml of 85% solution; 0.005 mole) and stirred the mixture between 70-80° for two hours, brought to reflux in another two hours and maintained at reflux for two more hours; cooled the reaction mixture to room temperature and filtered the red residue and dried (2.0 g; 75.5 per cent of theory). The compound was crystallized from nitrobenzene in red needles, did not melt upto 350°C (Found: C, 68.0; H, 3.4%. $C_{30}H_{18}O_6N_4$ requires C, 67.9; H, 3.4%).

b) Ring closure of (III) with oleum to oxadiazole IV

Compound (III) (1.5 g) was dissolved in oleum (20%; 35 ml) at room temperature under stirring

and continued stirring for four hours at room temperature. Poured the mixture on crushed ice (600 g), filtered the red residue, washed with water free from acid and dried (1.3 g; 86%). Crystallized the product from nitrobenzene in red needles. (Found: C, 69.8; H, 3.2%. $C_{30}H_{16}O_5N_4$ requires C, 70.3; H, 3.1%).

Reductive methylation of IV

Reductive methylation of (IV) (1.0 g) was carried out as mentioned in earlier experiment. The product after crystallization from benzene, had m.p. 282°, undepressed on admixture with the reductive methylated derivative of commercial Indanthren Red F3B.

REFERENCES

1. K. Venkataraman, J.Ind.Chem.Soc., 38, 452 (1961).
2. A. Hetzheim and K. Mockel, cited in Advances in Heterocyclic Chemistry, edited by A.R. Katritzky and A.J. Boulton (Academic Press), 1966, Vol.7, p. 218.
3. du Pont, USP 2, 511, 018; C.A. 46, 270 (1952).
4. ICI, B.P. 705, 929; C.A. 48, 10353 (1954).
5. Ciba, Ger.Pat. 1,134, 782; C.A. 58, 4675 (1963).
6. E. Baltazzi and A.J. Wysocki, Chem.Ind.(London), 1080 (1963),
7. J.C. Thurman, Chem.Ind.(London), 752 (1964).
8. ICI, B.P. 705, 928; C.A. 48, 10352 (1954).
9. BASF, B.P. 731,008; C.A. 50, 8741 (1956).
10. BASF, Ger.Pat. 955, 174; C.A. 53, 4753 (1959).
11. Bayer, USP, 2, 616, 891; C.A. 47, 3575 (1953).
12. Bayer, Ger.Pat. 825, 111; C.A. 49, 630 (1955).
13. du Pont, USP 2, 650, 926; C.A. 48, 1014 (1954).
14. E. Klingsberg, J.Am.Chem.Soc. 80, 5786 (1958).
15. USP 2,749, 352; 2, 759, 948.
16. P.V. Laakso, R. Robinson and H.P. Vandrewala, Tetrahedron, 1, 103 (1957).

SUMMARY

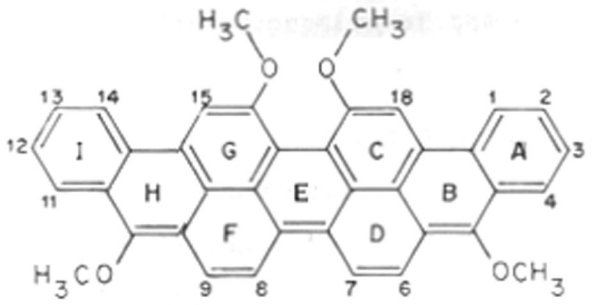
Part I - NMR spectra of reductive methylation products of violanthrone derivatives

Because of the poor solubility of vat dyes in organic solvents, purification by crystallization or chromatography is difficult. A convenient method of purification of violanthrone derivatives through their reductive methylation products has been carried out.

In the elucidation of the structures of polycyclic quinones such as vat dyes, the use of NMR spectroscopy is limited by their poor solubility in organic solvents. However, it has been found that many violanthrone derivatives have, as their reductive methylation products, adequate solubility in tetramethylurea. The reductive methylation products, from which the parent quinones are easily regenerated, are also useful for chromatographic analysis using solvents such as benzene. By this technique, it has been possible for instance to show that bromination of 16,17-dimethoxyviolanthrone gives the 3,12-dibromo-derivative.

Chemical shifts of the aromatic protons of a series of 5,10,16,17-tetrasubstituted violanthrenes have been determined and discussed. In the spectrum

of 5,10,16,17-tetramethoxyviolanthrene (VII), the singlet two-proton absorption at 1.27 was readily



VII

assigned to the $C_{(15)}$ and $C_{(18)}$ protons. Since the ring system DEF is a phenanthrene type of unit the $C_{(7)}$ and $C_{(8)}$ protons may be expected to absorb at lower field than the $C_{(6)}$ and $C_{(9)}$ protons, and the pair of doublets (J = 9 cps) at 1.08 and 1.62 can be assigned to the former and latter respectively. The assignments for the three multiplet absorptions representing the four spin systems of the terminal rings A and I follow from the same considerations, since ABC and GHI are phenanthrene type units. The multiplet representing the $C_{(4)}$ and $C_{(11)}$ protons, which appears to have the same shape as the one representing as the $C_{(1)}$ and

and $C_{(14)}$ protons, is barely resolved on the right side of the singlet absorption of the $C_{(15)}$ and $C_{(18)}$ protons; and on the other side it overlaps with the low-field part of the doublet due to $C_{(6)}$ and $C_{(9)}$ protons. The absorption of the $C_{(2)}$, $C_{(3)}$, $C_{(12)}$ and $C_{(13)}$ protons, which do not come under special influences, are at the highest field (2.15).

The only change seen in the spectrum of the reductive methylation product of dibromo-16,17-dimethoxy-violanthrone (C.I. 59830; vat green 2) as compared to that of (VII) is that the two-proton multiplet at lower field has been changed into a doublet (J = 9 cps) and that the four-proton multiplet at the highest field is replaced by a two-proton quartet (J = 9 cps; 2 cps). In other features the two spectra are identical. Since the signals for the protons at $C_{(1)}$ and $C_{(14)}$ show ortho coupling (J = 9 cps) and there is a decrease in the number of protons in the high-field band, it is clear that the bromine substituents are at 3- and 12-positions.

Appreciable changes in chemical shift are observed for the $C_{(15)}$ and $C_{(18)}$ protons when the methoxyl groups in the 16- and 17-positions are replaced by the closely related ethylene-dioxy, butylenedioxy and methyl groups.

As reductive methylation product of violanthrone had not enough solubility in solvents suitable for NMR spectrum, reductive ethylation, reductive acetylation, reductive pivalylation derivatives were prepared. These derivatives also were not soluble enough for recording spectra.

Part II - Electron impact studies of some violanthrene derivatives

The mass spectra of 16,17-dimethoxyviolanthrone and a few 5,10,16-17-tetrasubstituted derivatives have been analysed. The spectrum of 5,10,16,17-tetramethoxyviolanthrene (III) shows a fragment corresponding to half the molecule. By comparing the spectrum with the spectra of the unsymmetrical compounds, 5,10,16-trimethoxyviolanthrene (V) and 5,10-dimethoxy-16-methylviolanthrene (VI), it has been shown that the above fragment is partly due to a doubly charged ion and partly to the singly charged ion formed by symmetrical cleavage.

A comparative study of 5,10-dimethoxyviolanthrenes shows that from the molecular ion two methyl radicals are lost successively. 5,10-Dimethoxy-16-methylviolanthrene and 5,10-dimethoxy-16,17-dimethylviolanthrene lose three and four methyl radicals; but no loss of a third methyl was observed in the case of the trimethoxy and tetramethoxy compounds (V and III). It has been confirmed

that the methyl radicals are preferentially lost from the 5- and 10-positions.

The monomeric nature of 16,17-ethylenedioxyviolanthrone has been established from the mass spectrum of its reductive methylation product. The mass spectra of 2-methoxybenzanthrone, 3,3'- and 4,4'-bibenzanthronyls have been determined and their fragmentation modes have been discussed.

Part III - NMR spectra of some benzanthrone derivatives

The NMR spectrum of benzanthrone, which does not appear to have been recorded so far, has been determined and attempts are made to analyse it with the help of some of its alkyl substituted derivatives. By comparison of the spectra of substituted benzanthrones and benzanthrone, the orientation of the substituents has been determined. Thus dimethylbenzanthrone obtained by the benzanthrone condensation on 2,3-dimethylanthraquinone is 4,5-dimethylbenzanthrone. The benzanthrone obtained from 2-t-butylanthraquinone is 9-t-butylbenzanthrone.

The action of oleum and chlorosulphonic acid on benzanthrone has been studied. The products were isolated as methyl sulphonates and N,N-dimethylsulphonamides and characterized as the 3 and 9-sulphonic

acid derivatives from their NMR spectra.

Part IV - Constitution of Cibanone Orange R

None of the structures (III, IV and V) proposed earlier for Cibanone Orange R is in accordance with the observed NMR and mass spectra of the reductive methylation and reductive acetylation products. Structures (VII) and (VIII) were therefore considered for the dye . Structure (VIII) was ruled out from its behaviour as a vat dye and its stability to fission at the S=S bond and desulphurization by a variety of reagents. Structure (VII) finds some support in the conversion of benzaldichloride to the trimer (IX) by the action of sodium sulphide, but further evidence must be obtained before assigning a structure finally to Cibanone Orange R.

Part V - NMR spectra of Indigosols

TLC behaviour on silica gel of a few indigosols of the indigoid and anthraquinonoid types has been studied. The NMR spectra of a few indigosols have been determined and analysed as a method of investigating structural problems concerning vat dyes.

Part VI - Constitution of Indanthren Red F3B

The constitution of Indanthren Red F3B (C.I. Vat Red 31) has been investigated. The IR spectrum of the purified dye showed the presence of free amino and quinone groups. The IR spectrum of its reductive methylation product showed the characteristic bands of the oxadiazole ring system (C-O and C=N bands). The mass spectrum of the reductive methylation product has shown that the dye is 2,5-bis(1-amino-2-anthraquinonyl)-1,3,4-oxadiazole which has been confirmed by synthesis.

REF: Page No: 169 of the Ph.D.Thesis submitted by Mr.T.G. Manjrekar, to the Univ. of Bombay for the Ph.D.Degree.

Title: Structural Problems concerning certain Vat Dyes and their Intermediates: Application of NMR and Mass Spectroscopy.

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A C K N O W L E D G M E N T

I wish to express my sincere thanks to Professor K. Venkataraman, National Chemical Laboratory, Poona, for suggesting the problem and for his guidance during the entire course of the investigation.

I thank Drs. A.V. Rama Rao, P.M. Nair and K.G. Das for their interest and helpful discussions.

My thanks are also due to Dr. V.S. Pansare and his colleagues for microanalyses and to Messrs I.S. Mulla and G. Samuel for recording NMR spectra.

Grateful acknowledgment is made to Messrs Arlabs Ltd. for the supply of some indigosols required for the present work.

The award of a fellowship by the Council of Scientific and Industrial Research, New Delhi, is acknowledged.

Finally, I thank the Director, National Chemical Laboratory, Poona, for permission to work in the NCL and to submit a thesis for the Ph.D.

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Candidate

Poona
17th June 1968