STUDY OF THE MECHANISM OF CYCLISATION IN THE PREPARATION OF DIOXAZINES AND DEVELOPMENTS OF SYNTHETICAL METHODS BASED UPON THE RESULTS

A Thesis

Presented for the Degree of

Doctor of Philosophy

by

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University of Leeds.

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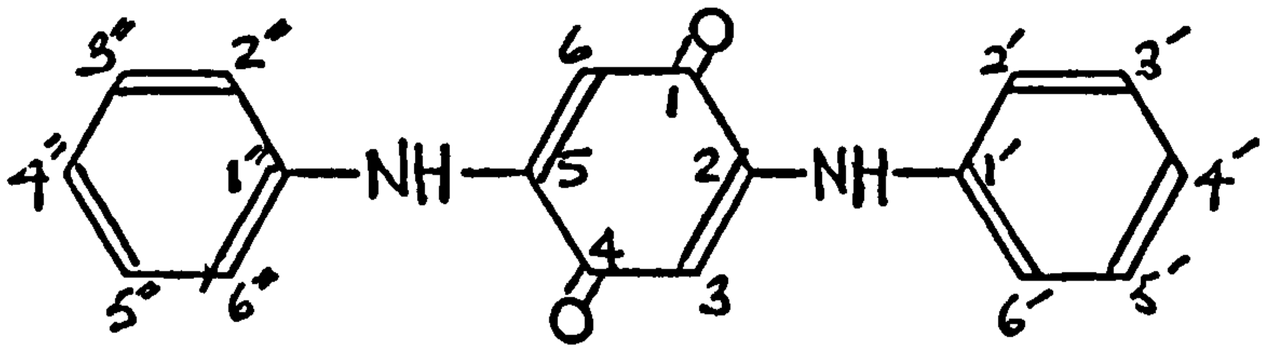
ABBREVIATIONS

Annalen.	Justus Liebig's Annalen der Chemie.
A.R.	Analytical Reagent.
Ber.	Berichte der Deutschen Chemischen Gesellschaft. (Chemische Berichte since 1946).
B.I.O.S.	British Intelligence Objectives Subcommittee, Final Report.
b.p.	Boiling point.
B.P.	British Patent.
Bull.Soc.Chim.Belg.	Bulletin de la société chimique de Belgique.
Chem.Abs.	Chemical Abstracts.
Chem.-Ztg.	Chemiker-Zeitung.
Fort.Chem., Phys., Phys.Chem.	Fortschritte der Chemie, Physik, und Physik Chemie.
Frdl.	Friedländer's Fortschritte der Teerfarbenfabrikation.

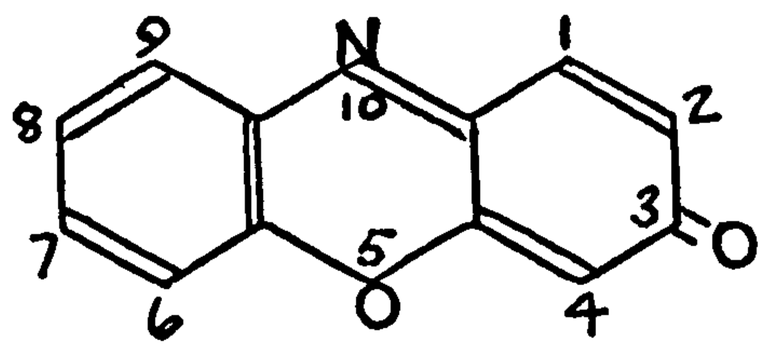
G.P.	German Patent.
Helv.	Helvetica Chimica Acta.
J.Am.C.S.	Journal of the American Chemical Society.
Jaresber.	Jaresbericht über die Fortschritte der Chemie.
J.C.S.	Journal of the Chemical Society.
J.Prakt.Chem.	Journal für praktische Chemie.
Monatsh.	Monatshefte für Chemie, und verwandte Teile anderer Wissenschaften.
m.p.	Melting point.
Proc.Roy.S.	Proceedings of the Royal Society.
Studii si Cercetari Sti., Chim.	Studii si Cercetari Stiintifice Chimie. (Baza de Cercetari Stiintifice, Timisoara, Roumania).
U.S.P.	United States Patent.

NOMENCLATURE

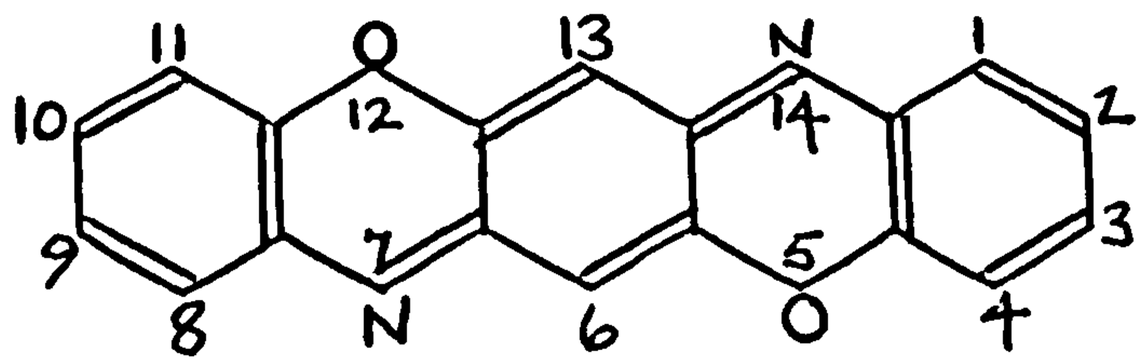
In this thesis, p-benzoquinone derivatives are numbered as below:- 2,5-dianilino-1,4-benzoquinone, all derivatives being referred to the 1,4-benzoquinone nucleus.



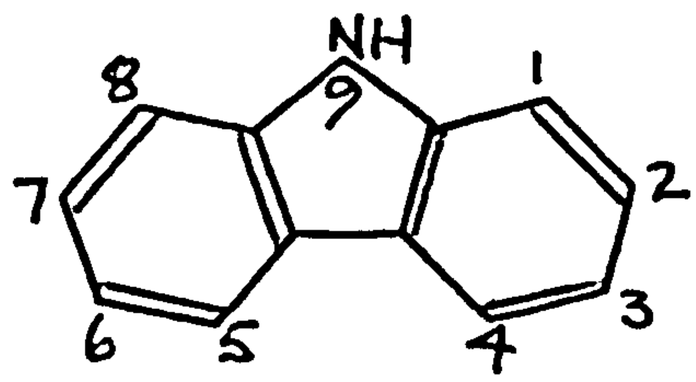
Phenoxazone is numbered on the phenoxazine ring system as chosen in the Ring Index (R.R.I. 3290),* viz:- 3-phenoxazone.



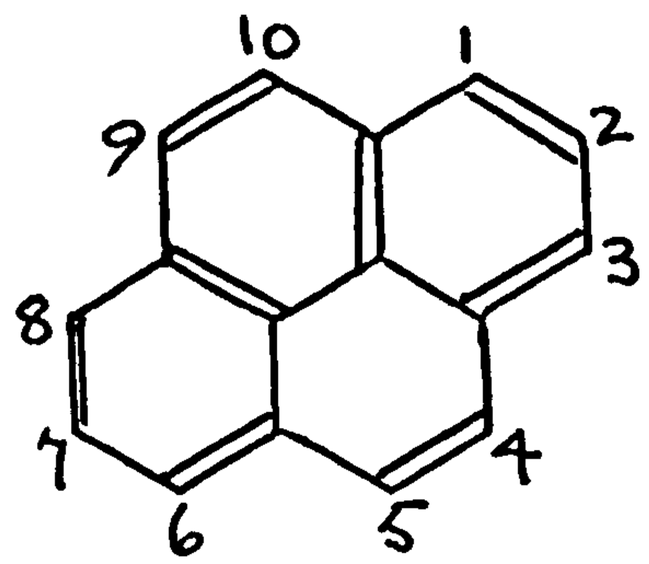
Triphenodioxazine is the nomenclature used for 1,4-benzoxazino [2,3-b] phenoxazine throughout this thesis (R.R.I. 6139) and is numbered on the pentacene system, viz:- 5,12-dioxa-7,14-diazapentacene.



Carbazole (R.R.I. 2927) and associated analogues, are numbered starting with the right hand C-atom next to the heterocylic nitrogen atom.



Pyrene is numbered according to (R.R.I. 5262) using the lowest possible numbering for substituents.



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* Patterson, Cappell and Walker, "The Ring Index", American Chemical Society, Washington D.C., 1959.

SUMMARY

The work was roughly divided into two sections. The first involved the preparation of known tripheno-dioxazine pigments and the purification and examination of their properties which had not been hitherto carried out. Much adaption of existing methods for the preparation of 1-aminopyrene and 3-aminocarbazole was required in order to prepare them pure in large quantities. 3-Amino-9-ethylcarbazole was prepared pure in large quantities, its melting point considerably elevated above that given in the literature. The arylaminoquinones and triphenodioxazines were prepared from the condensation of chloranil with the given amines:- 1-aminopyrene, 3-amino-9-ethylcarbazole, 3-aminocarbazole and 4-amino-diphenylamine; the triphenodioxazines from the latter two not being obtained in a pure state.

The second part of the work involved making 6,13-dichlorotriphenodioxazine, 6-chlorotriphenodioxazine, and triphenodioxazine, by the adoption of existing methods and also attempting new methods of preparation. The preparation and purification of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone, 2,5-dianilino-3-chloro-1,4-benzoquinone,

and 2,5-dianilino-1,4-benzoquinone was carried out and these products were subjected to various thermal experiments. The technique of thin layer chromatography was developed and proved a valuable tool for the identification and quantitative estimation of the products formed during the various described reactions.

INTRODUCTION

PART I

THE LITERATURE OF TRIPHENODIOXAZINE

Triphenodiozazine has been known since 1890 when it was first isolated by Siedel[1]. during his work on the oxidation of o-aminophenol. By boiling an aqueous solution of o-aminophenol hydrochloride for a long time, and passing air through it at the same time, he obtained a red powder of no melting point, which had the empirical formula $C_{18}H_{10}N_2O_2$. From volumetric observations, he found that o-aminophenol was oxidized according to the equation:-

$$3C_6H_4OH.NH_2.HCl + 3O = C_{18}H_{10}N_2O_2 + NH_4Cl + 2HCl + 4H_2O$$

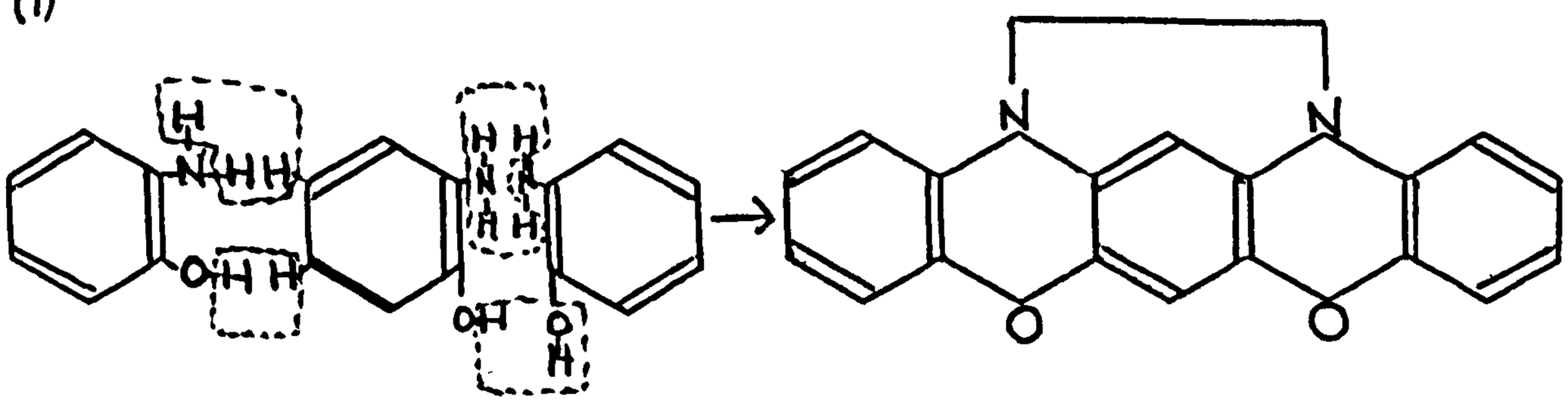
This showed that the unknown compound could contain three benzenoid rings.

The compound was purified by sublimation to give red or violet leaflets. Chlorine had no effect upon it but some substitution did occur with bromine. A mixture of nitric and acetic acids gave a mono nitro-compound in the form of a dark violet powder. Triphenodioxazine

exhibited the characteristics of a weak base forming salts only with strong acids. Concentrated hydrochloric acid gave a crystalline hydrochloride of the empirical composition $C_{18}H_{10}N_2O_2,2HCl$. Phenylhydrazine reduced the compound to a colourless dihydro-derivative, which soon reverted to the coloured parent compound on heating with loss of hydrogen. The dihydro-derivative could be easily acetylated, unlike the parent compound, to a di-N-acetyl derivative, forming colourless plates, m.p. 295°. Concentrated aqueous potassium hydroxide solution decomposed triphenodioxazine to o-aminophenol. Siedel concluded that it must be a heterocyclic compound, similar in nature to the phenoxazines. He first assigned two structures to the compound, both based on a dioxazine ring system.

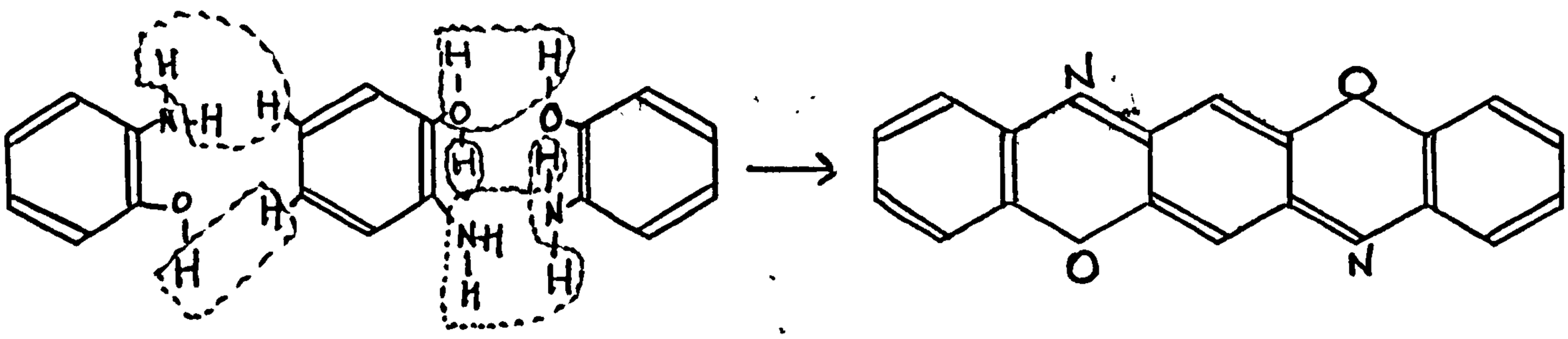
Siedel gave the name of triphenodioxazine to the red compound.

(i)



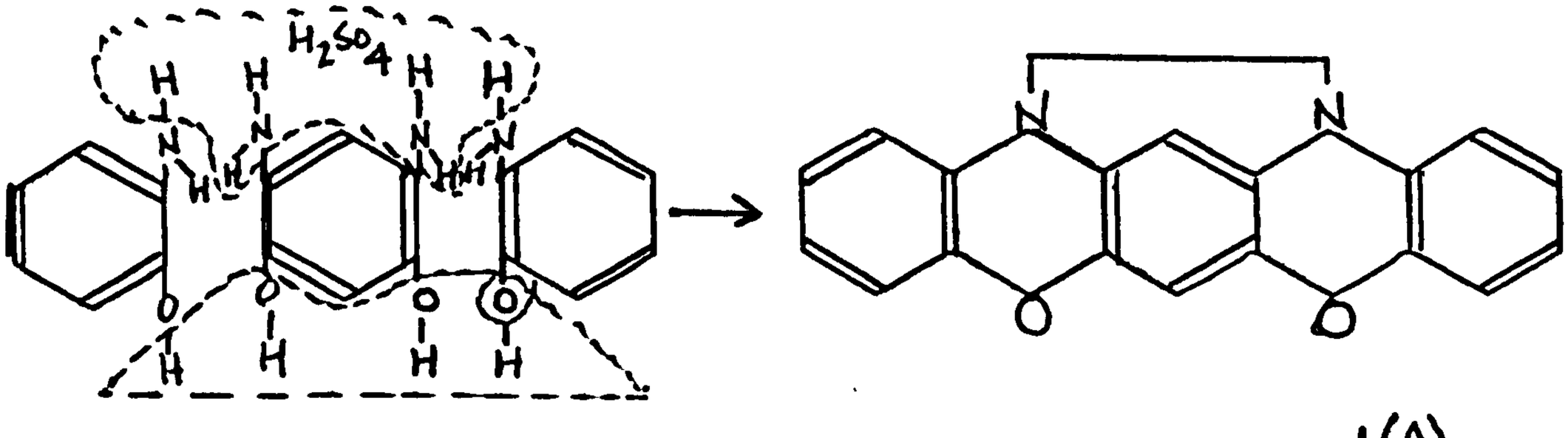
I(A)

(ii)



I(B)

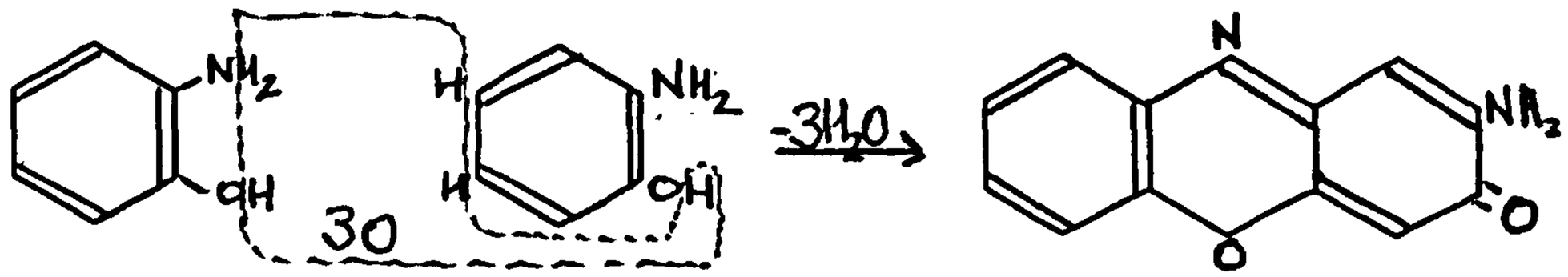
He synthesised it by condensing one mole of water free 4, 6-diaminorescorcinol sulphate with two moles of o-aminophenol. He obtained via the dihydro-derivative, a product identical to the one prepared by oxidation of o-aminophenol and assumed that the condensation could only have occurred by a similar method to (i), namely:-



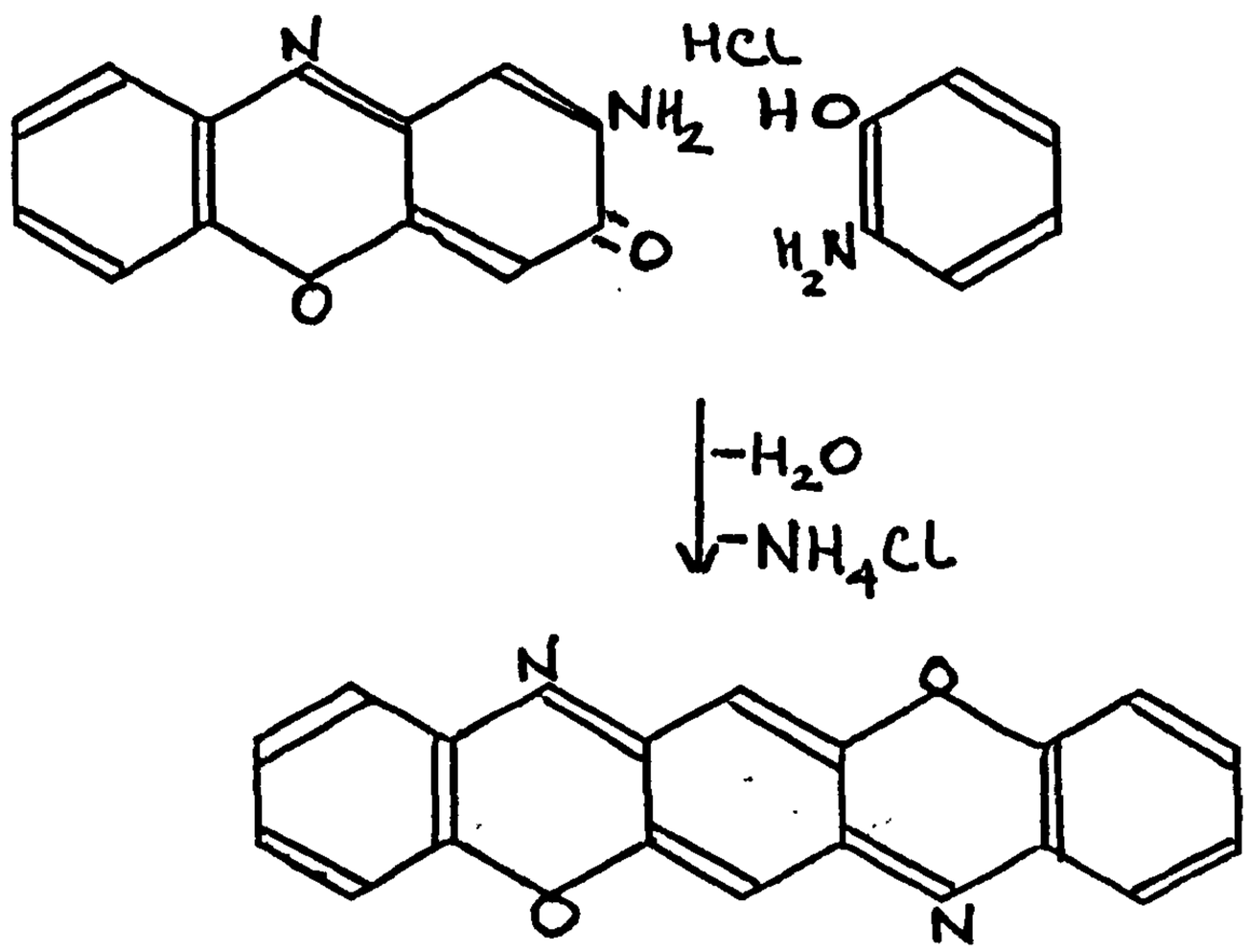
I(A)

Accordingly he chose (I)(A) as indicating the correct structure of triphenodioxazine. Structure (I)(B) was later shown to be correct by Fischer[2]. who oxidized an alcoholic solution of o-aminophenol with mercuric oxide and isolated brown-red crystals of 2-amino-3-phenoxazone, (II), m.p. 250°. By heating

one mole of (II) with one mole o-aminophenol hydrochloride at 180°, triphenodioxazine (I) was formed with elimination of water and ammonia.[3.]



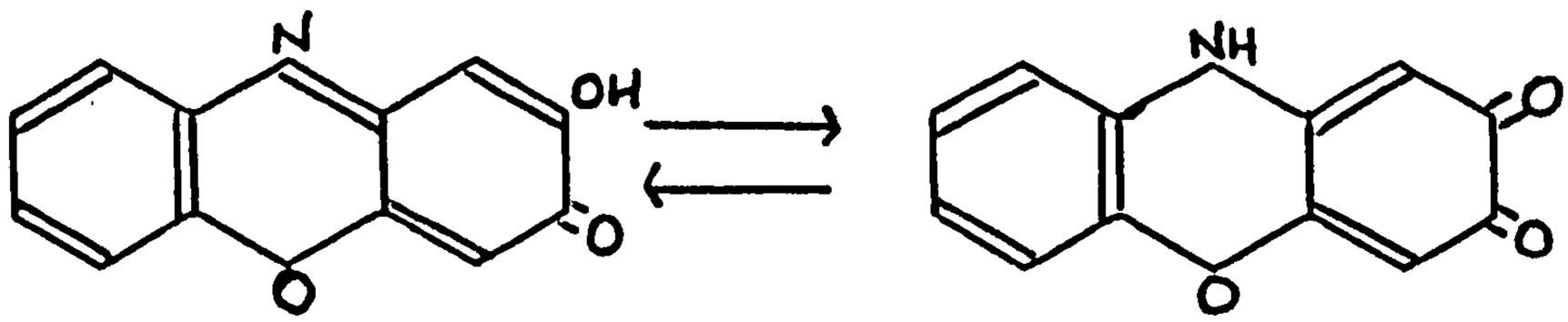
II



I

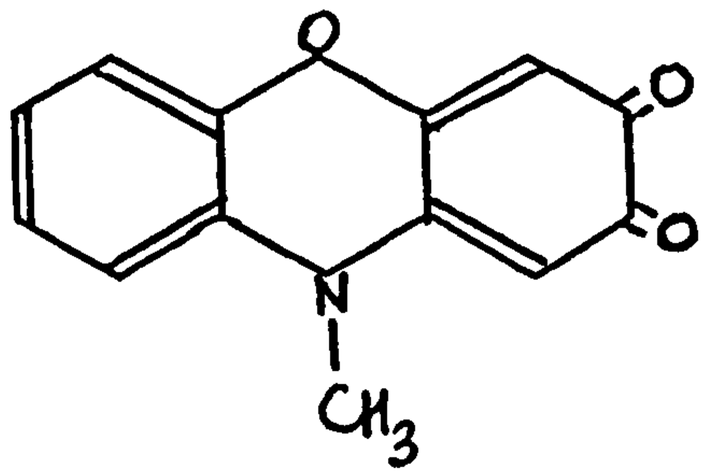
Although structure (I)(A) could conceivably be formed from this synthesis, Fischer chose structure (I)(B) as the correct one, which fits in with present day views on structural organic chemistry, since (I)(A) would be impossibly strained.

Several phenoxazones were already known and Kehrmann[4]. had prepared 1-chloro-2-hydroxy-3-phenoxazone by condensing o-aminophenol with 2,5-dihydroxy-3-chloro-1,4-benzoquinone. He also prepared[5]. 2-hydroxy-3-phenoxazone (III) by condensing 2,5-dihydroxy-1,4-benzoquinone with o-aminophenol. The resultant compound when condensed with o-aminophenol gave triphenodioxazine. The compound was tautomeric with phenoxazine-2,3-quinone (IV).

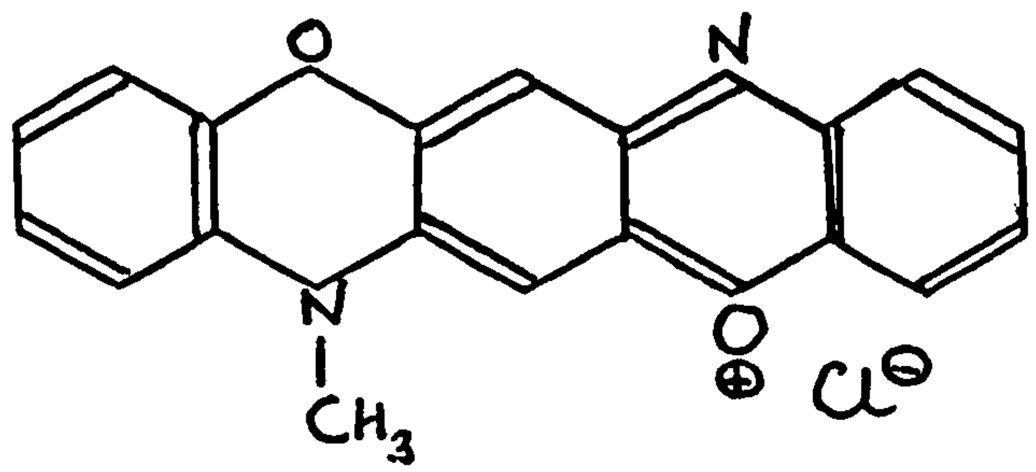


III IV

Kehrmann[17]. synthesised a metho-salt using a derivative of (IV). N-Methylphenoxazine-2,3-quinone (V), which has been prepared earlier by Diepolder[18]. in connection with his work on the oxidation of o-aminocresols, was condensed with o-aminophenol hydrochloride to give a compound which was postulated as 7-methyltriphenodioxazinium chloride (VI).

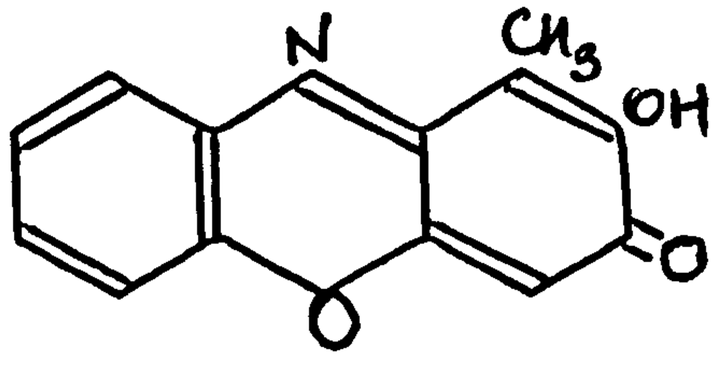


V.

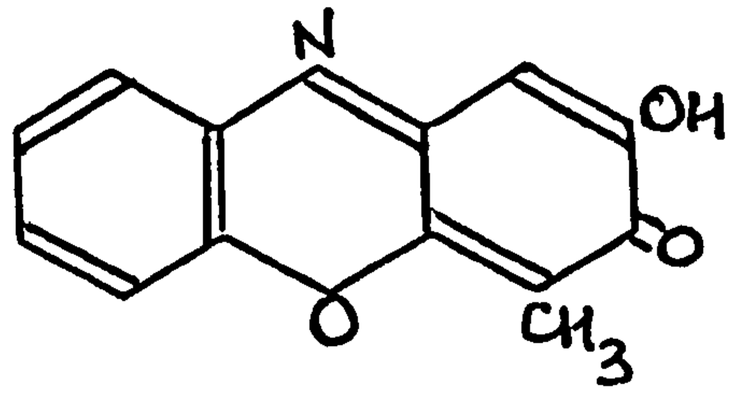


VI

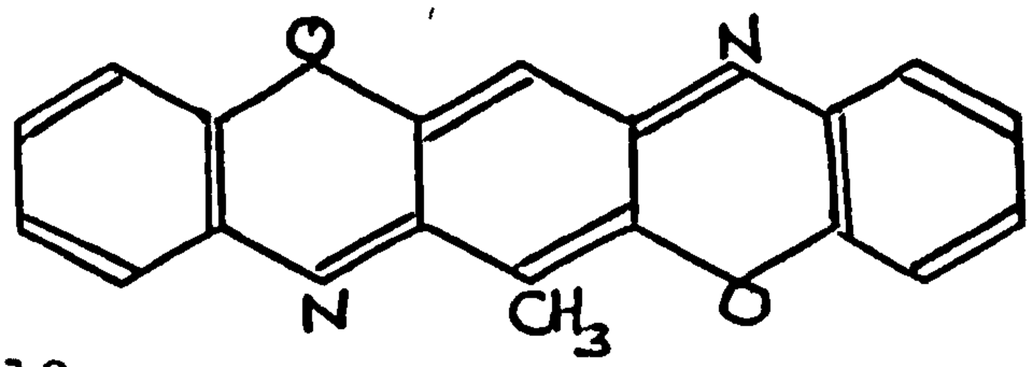
6-Methyltriphenodioxazine (IX) was prepared by Kehrmann[5]. via an intermediate phenoxazone. o-Aminophenol hydrochloride was condensed with 2,5-dihydroxy-1,4-toluquinone in aqueous solution to give a tolu-3-phenoxazone, which was obtained as glistening brown-red prisms, m.p. 215-216°. The tolu-3-phenoxazone could be one of two structures, (VII) or (VIII), either capable of giving the same triphenodioxazine derivative (IX). The tolu-3-phenoxazone was then condensed with o-aminophenol hydrochloride in benzoic acid to give (IX), which gave crystals of no melting point from xylene.



VII

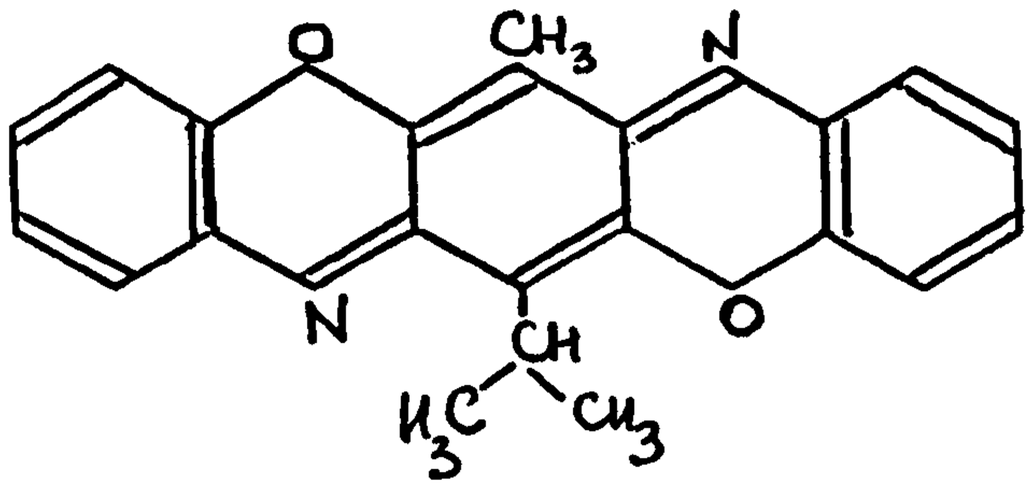


VIII



IX

Kehrmann[19.] also found that 2,5-dihydroxy-3,6-thymo-1,4-quinone would condense directly to 6-isopropyl-13-methyltriphenodioxazine (X) with o-aminophenol hydrochloride in benzoic acid.

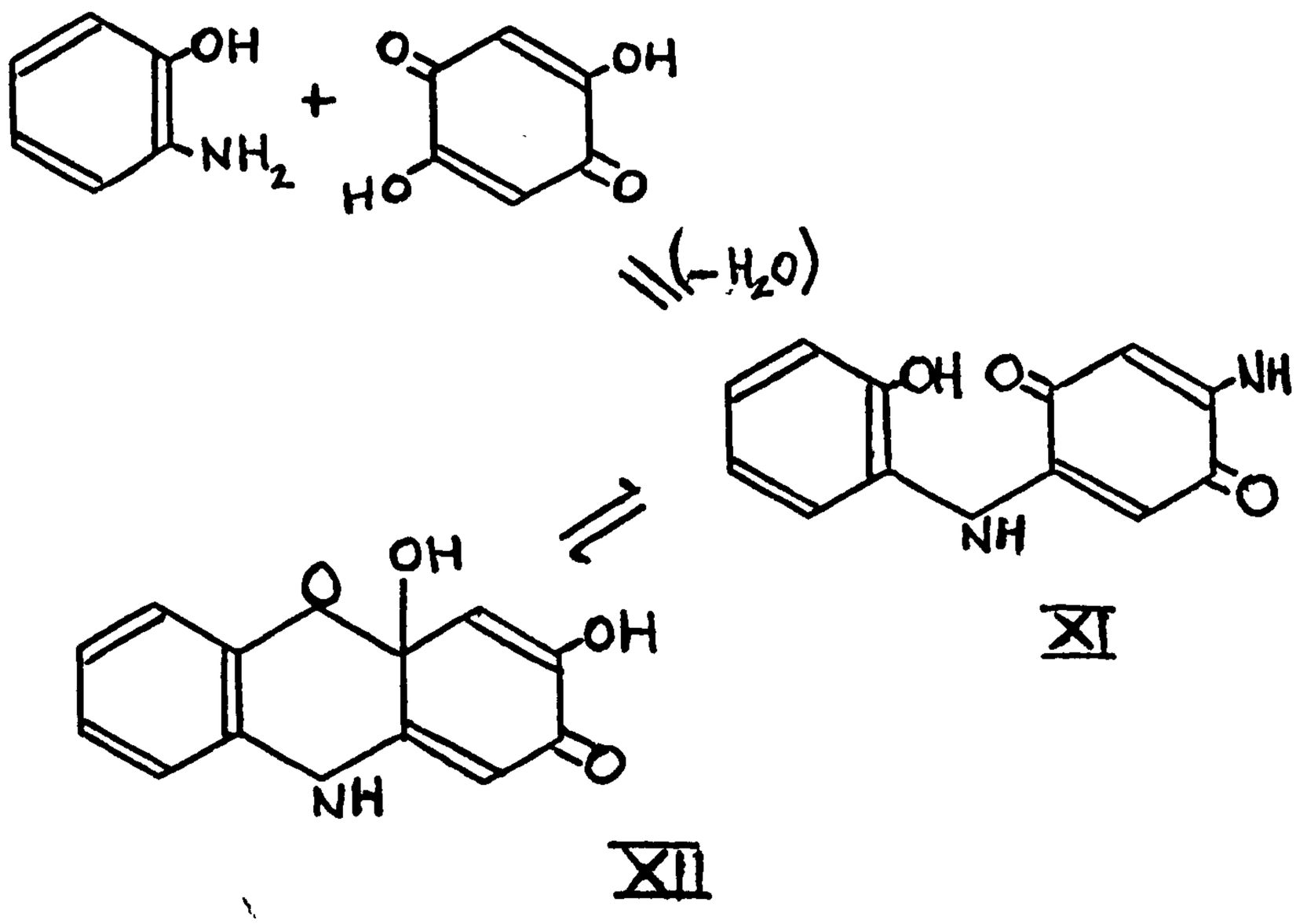


X

The condensation of o-aminophenols with p-quinones to give phenoxazones has recently been investigated in connection with Ommochromes.[6,7,8.] Ommochromes are the phenoxazone colouring matters associated with Ommins, which are the natural pigments in the eyes of many

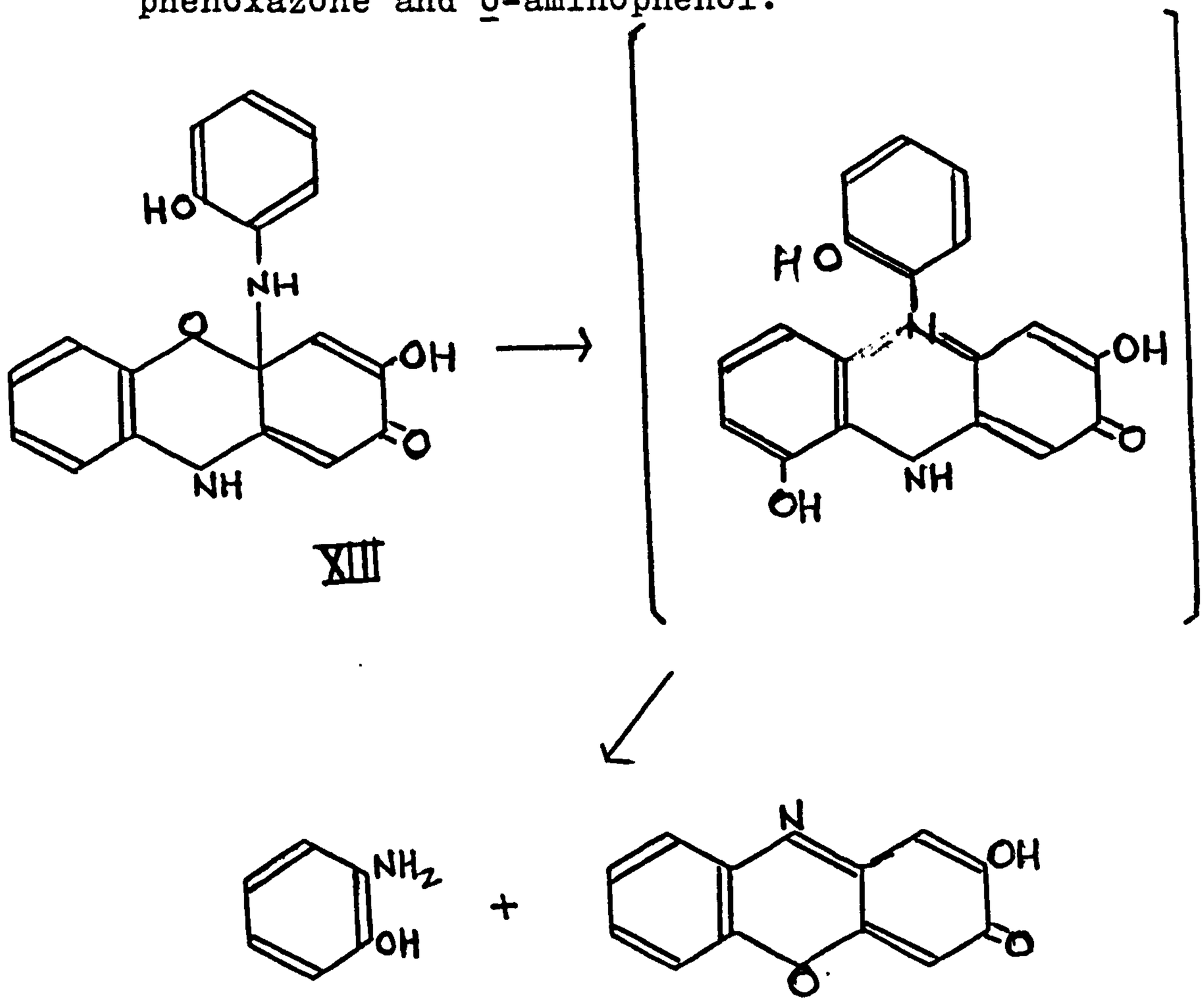
anthropods and cephalods. The reaction went via two stages:-

(i) Condensation between one mole of o-aminophenol and a hydroxy-1,4-quinone, to give an o-hydroxyanilinoquinone (XI). This was in equilibrium with 3,4a-dihydroxy-2-phenoxazinone (XII). Proof of this equilibrium was found from the fact that compounds of the type (XI) have an absorption spectrum maximum around 480 mμ whereas in (XII), a new peak was found between 380-400 mμ.



(ii) (XII) was condensed with a further mole of

o-aminophenol to give an O,N-acetal, (XIII), which immediately broke down to a 3-phenoxazone and o-aminophenol.



XIII

Presumably this series of reactions could be extended to cover the condensation of phenoxazone and o-aminophenol to triphenodioxazine. This mechanism could only give a structure of type (I)(B).

Diepolder[9] obtained (III) by the oxidation of

o-aminophenol hydrochloride with aqueous potassium ferricyanide. The reaction was complicated and followed the given equation:-

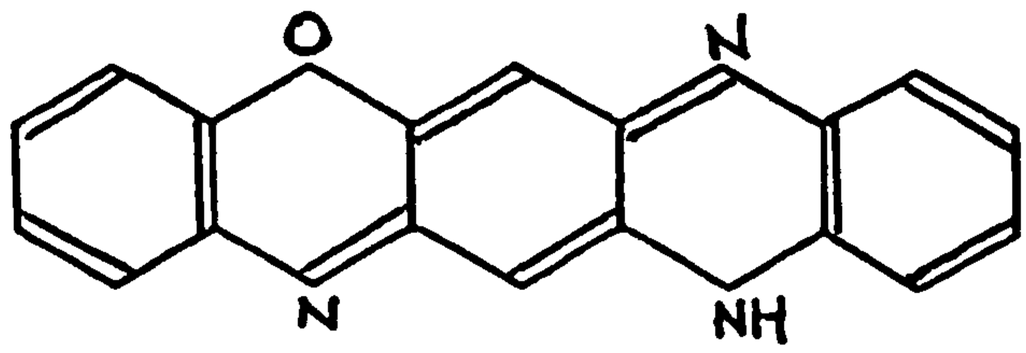
$$2.C_6H_4(OH).NH_2.HCl + 6K_3Fe(CN)_6 + 17HCl + H_2O =$$

$$C_{12}H_6NO_2OH + 6H_4Fe(CN)_6 + 18KCl + NH_4Cl$$

It was noticed that if excess hydrochloric acid was not present, some triphenodioxazine was formed.

2-Hydroxy-3-phenoxazone (III) formed dark red needles from xylene, decomposing at 278°. Sodium hydroxide solution decomposed it into o-aminophenol and 2,5-dihydroxy-1,4-benzoquinone.

Diepolder[10] observed that phenoxazones could be condensed with a variety of amines. For example, one mole of 2-amino-3-phenoxazone with one mole of o-phenylene-diamine hydrochloride gave triphenazineoxazine (XIV).

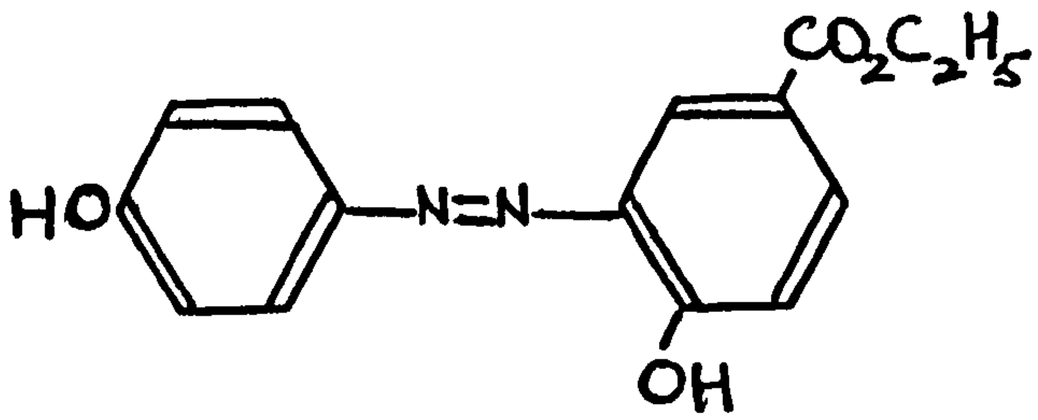


XIV

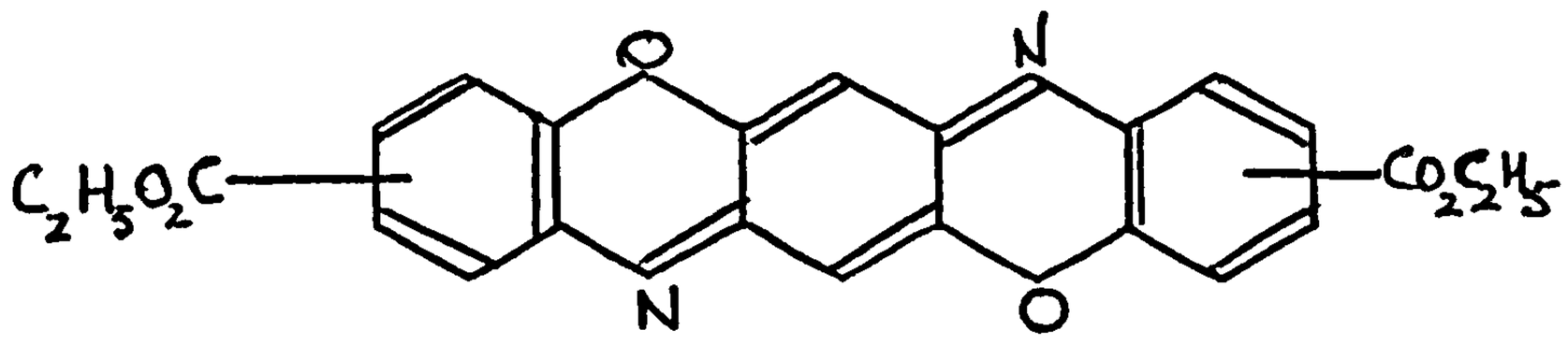
K. Auwers[11] obtained triphenodioxazine derivatives

as by-products in his preparations of new azophenols.

Ethyl 3-amino-4-hydroxy benzoate, m.p. 110-111°, on condensation with nitrosophenol in glacial acetic acid, gave soluble orange-red needles of 3-carbethoxy-4', 6-dihydroxyazobenzene, (XV), m.p. 105-106°, together with an insoluble red powder. This was found to be a dicarbethoxy derivative (XVI) of triphenodioxazine which could be recrystallised in red needles from a high boiling solvent.



XV



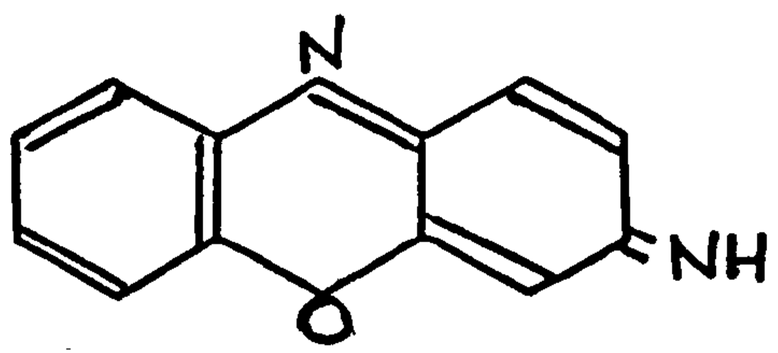
XVI

(XVI) had no melting point and gave a blue colour in concentrated sulphuric acid. Similarly dinitro- and dicyano-derivatives were obtained by the use of 2-amino-4-nitrophenol and 2-amino-4-cyanophenol respectively with nitrosophenol. The soluble azophenol was separated from the triphenodioxazine derivative by filtration of the

reaction medium.

3,10-Dichlorotriphenodioxazine was prepared by K. Auwers.[12.] 5-Chloro-2-aminophenol, prepared by reducing 5-chloro-2-nitrophenol with stannous chloride, was oxidized readily with air to 2-amino-7-chloro-3-phenoxazone. This formed red-violet crystals, m.p. 285°, and on condensing with a further mole of 5-chloro-2-aminophenol, gave 3,10-dichlorotriphenodioxazine. A 3,10-dibromotriphenodioxazine was prepared similarly.

Other methods of preparing triphenodioxazine were studied by Kehrmann. He obtained triphenodioxazine as the main product[13.] by condensing o-aminophenol with 2-hydroxy-1,4-benzoquinone in acetic acid. He[14.] also obtained it, together with small traces of 3-iminooxazine (XVII), by condensing o-aminophenol with 4-acetamino-1,2-benzoquinone in acetic acid in the presence of dilute sulphuric acid.

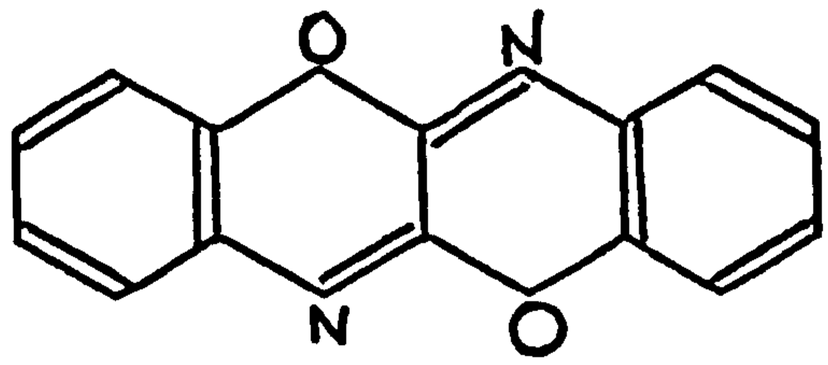


XVII

Willstätter[15.] in his work with azophenols obtained triphenodioxazine together with some o-azophenol, by

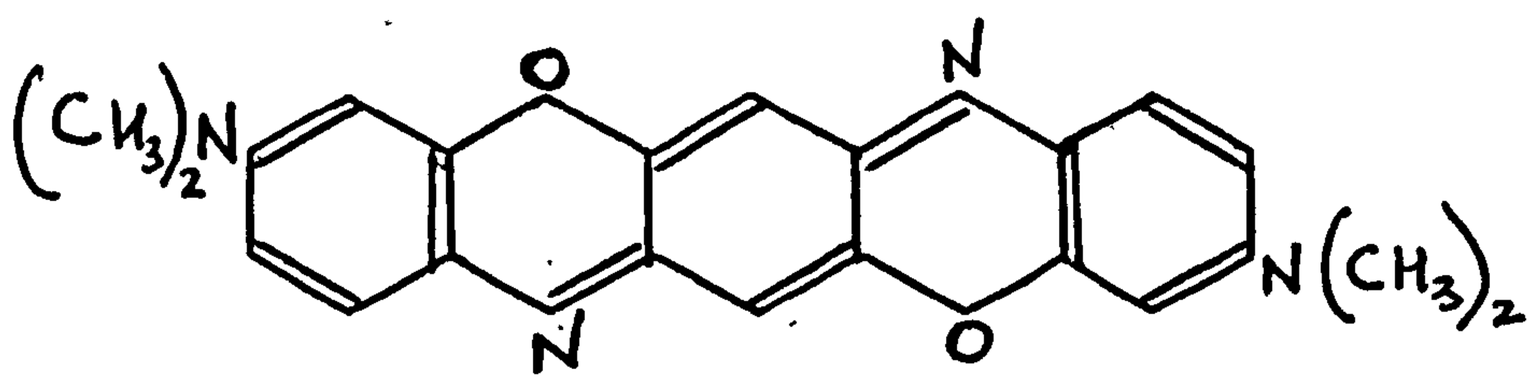
heating o-nitrophenol with potassium hydroxide in the presence of a little water.

Kehrmann[16.] examined the action of oxalic acid on o-aminophenol hydrochloride in phenol at 200°, and obtained a compound which crystallised in colourless leaflets, m.p. 259-260°, from an alcohol-benzene mixture. It gave a greenish yellow colour in concentrated sulphuric acid. It was named diphenodioxazine (XVIII).



XVIII

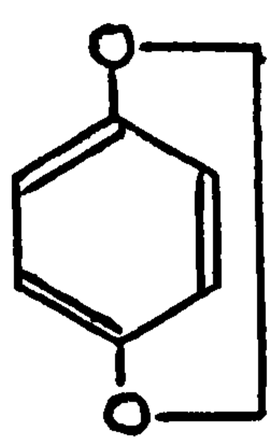
Alkylamino[20.] groups were introduced into the 3,10- positions by condensing 2-amino-5-dimethylaminophenol hydrochloride with 2,5-dihydroxy-1,4-benzoquinone. 3,10-Di(N,N-dimethylamino) triphenodioxazine (XIX) was formed together with 7-N,N-dimethylamino-2-hydroxy-3-phenoxazone and an unknown product.



XIX

PART II

THE LITERATURE OF ARYLAMINO-1,4-QUINONES



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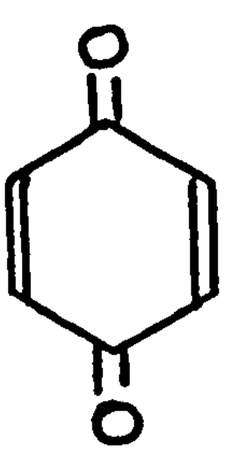
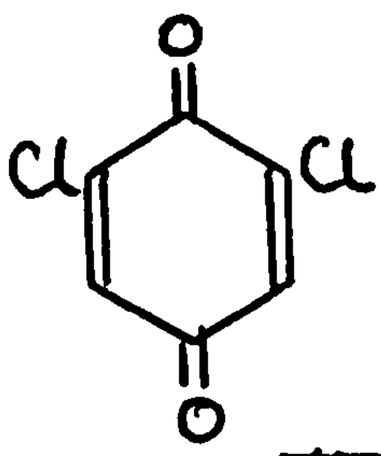
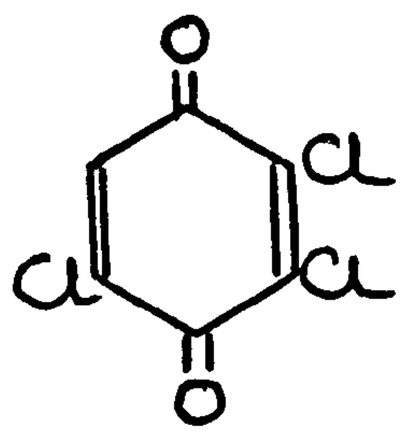


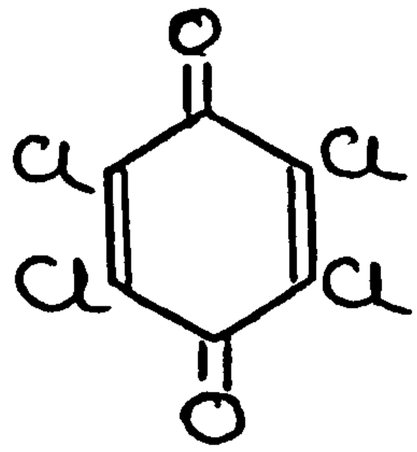
XXI



XXII



XXIII



XXIV

1,4-Benzoquinone has been known from the earliest days of organic chemistry and can be represented by two structures, (XX), (XXI). (XXI) was generally accepted due to its properties as an unsaturated diketone. It forms golden-yellow prisms, m.p. 117°, easily volatile in steam. It is readily obtained by the oxidation of phenol or aniline and is generally produced as the main or by-product of reactions involving the oxidation of aromatic amines.

2,6-Dichloro-1,4-benzoquinone (XXII) was first obtained by Faust[21.] by the oxidation of 2,4,6-trichlorophenol with fuming nitric acid. Weselesky[22.] obtained it in good yield by the quantitative addition of nitrous acid to 2,4,6-trichlorophenol in aqueous ethanolic solution. It forms yellow prisms from ligroin, m.p. 120°.

2,3,5-Trichloro-1,4-benzoquinone (XXIII) was originally obtained by Carstanjen[22A.] by the action of chromyl chloride on benzene. It is generally obtained together with chloranil (XXIV), by the oxidation of phenol-p-sulphonic acid with potassium chlorate solution and fuming nitric acid.[39.] The mixture is suspended in water and a stream of sulphur dioxide passed in. The trichloroquinone goes into solution as the hydroquinone derivative and is separated from the tetrachloro-derivative by filtration. It forms yellow plates from ethanol, m.p. 160-170°.

Chloranil (2,3,5,6-tetrachloro-1,4-benzoquinone,) (XXIV), forms pale yellow leaflets from acetone, m.p. 290°. It was first obtained by Erdmann[23.] as a by-product in the chlorination of Indigo. Sihce then it has been obtained as the end product of the oxidation of a large number of aromatic compounds with hydrochloric acid and

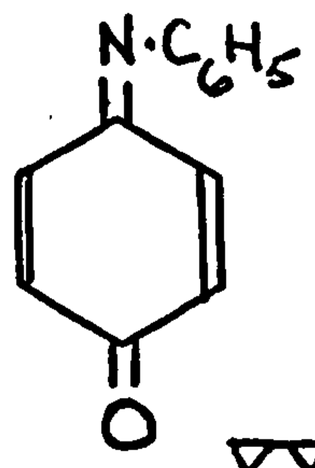
potassium chlorate.[24,25]. It was also formed by the action of an excess of sulphuryl chloride on p-aminophenol at 70° followed by oxidation of the intermediary N,N-dichloro-2,3,5,6-tetrachloro-p-aminophenol. This gave an 80-85 per cent yield of very pure material, free from (XXIII) which generally accompanied technical chloranil. It was also obtained from pentachlorophenol by the action of oleum or chlorosulphonic acid.[27]. Arnold[28]. obtained it in 97 per cent yield by the action of hydrogen peroxide and hydrochloric acid on 1,4-benzoquinone. The most successful technical method is that adopted by I.G. Farbenindustrie A.G.[29]. Phenol or o-chlorophenol is chlorinated without solvent to give mainly 2,4,6-trichlorophenol. The mixture is then oxidized with monohydrate and chlorosulphonic acid. After heating to 90°, chlorine is passed in until a sample gives a melting point of 290°. (XXIII) occurs as an impurity in small amounts.

Reducing agents give the quinol with chloranil and aqueous alkali gives red chloranilic acid (2,5-dihydroxy-3,6-dichloro-1,4-benzoquinone).

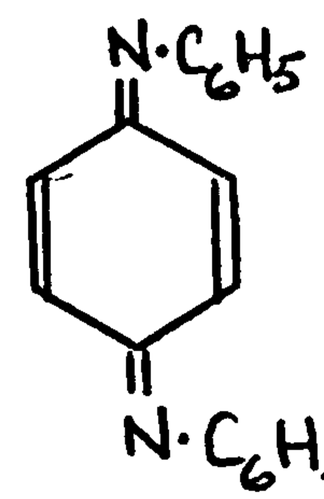
1,4-Benzoquinone anils are not usually formed by the action of amines on 1,4-benzoquinone and derivatives,

because replacement of hydrogen on the ring is usually favoured in the first instance. The simple anils have generally been obtained by oxidation of a suitable amine.

1,4-Benzoquinone monoanil (XXV) was obtained by Willstatter[30]. as red crystals from hexane, m.p. 97°, by the oxidation of aniline with cold aqueous alkaline potassium permanganate.



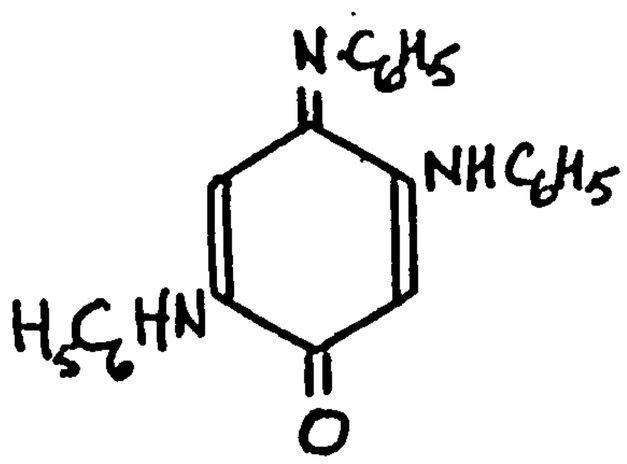
XXV



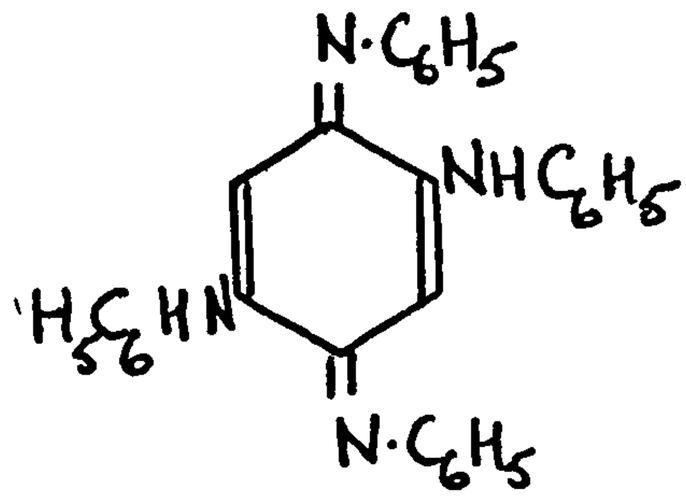
XXVI

1,4-Benozquinone dianil (XXVI) was obtained as long yellowish brown needles, m.p. 176-180°, by warming diphenylamine with aqueous alkaline potassium permanganate solution.[31]. It gave a red-violet colour in concentrated sulphuric acid. On heating with aniline, azophenine (2,5-dianilino-1,4-benzoquinone dianil) (XXVIII) was formed.

2,5-Dianilino-1,4-benzoquinone monoanil (XXVII) was prepared by condensing aniline with 1,4-benzoquinone in acetic acid.[32]. It gave brown-red needles, m.p. 202-205°, with a brown-red colour in concentrated sulphuric acid.



XXVII



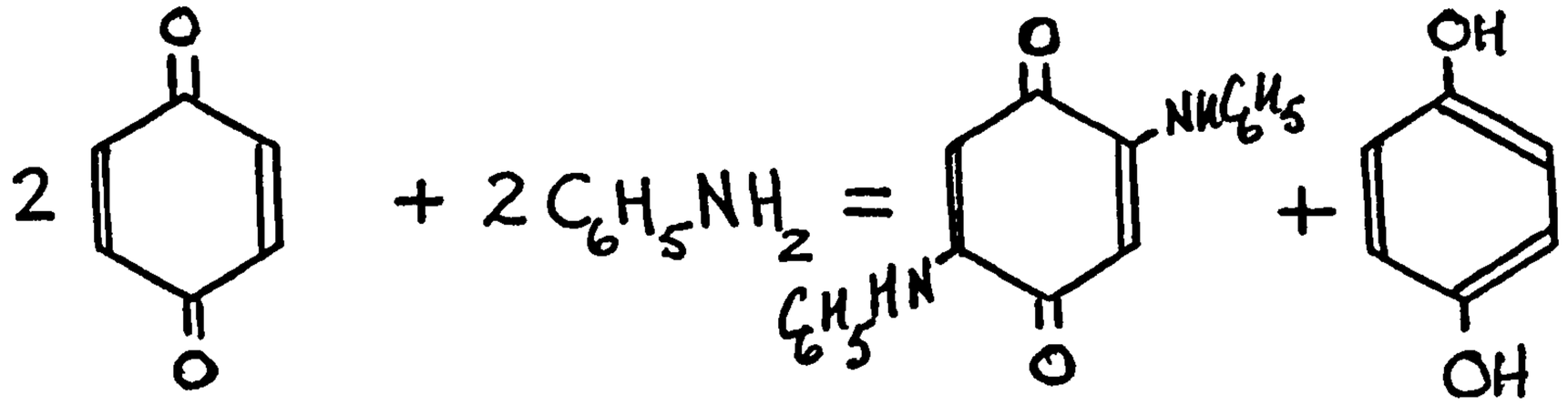
XXVIII

XXXI

Anilino-1,4-benzoquinones

Hoffmann[33, 34.] first investigated the reactions of aniline with chloranil and 1,4-benzoquinone, and postulated them both as diarylaminoquinone derivatives. Zincke[37.] on his work with quinones, noticed that 1,4-benzoquinone was more reactive with amines than other previously studied quinones. Two moles of aniline would react with an ethanolic solution of 1,4-benzoquinone whereas only one mole of aniline would react with 1,4-naphthaquinone to form scarlet needles, m.p. 190 - 191°. This was later found to be 2-anilino-1,4-naphthaquinone. Zincke[38.] investigated the product he obtained from aniline and 1,4-benzoquinone. It gave red-brown needles from acetic acid, m.p. 345°, with a red colour in concentrated sulphuric acid. It gave a complex orange nitroso-product, m.p. 245°, by the action of nitrous acid in the presence

of acetic acid. Knappe and Schultz[39.] confirmed Hoffmann's findings and found 2,5-dianilino-1,4-benzoquinone (XXIX) was formed from aniline and 1,4-benzoquinone. It was not fully understood how the substitution occurred but they suggested this scheme:-



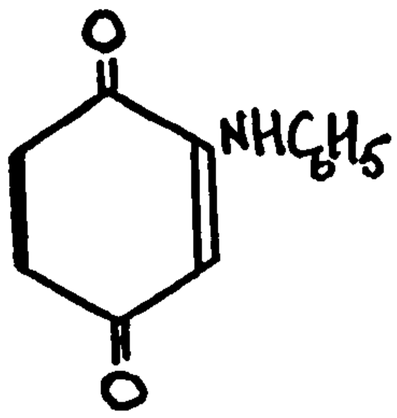
XXIX

H. Suida[45.] considered the mechanism of substitution of aniline into the 1,4-benzoquinone nucleus. He found that a dianilino-derivative was not formed in the first instance but a monoanilino-derivative. The reaction went smoothly via the monoanilino-derivative to the 2,5-dianilino-derivative and then finally to azophenine, (2,5-dianilino-1,4-benzoquinone dianil, (XXXI).)

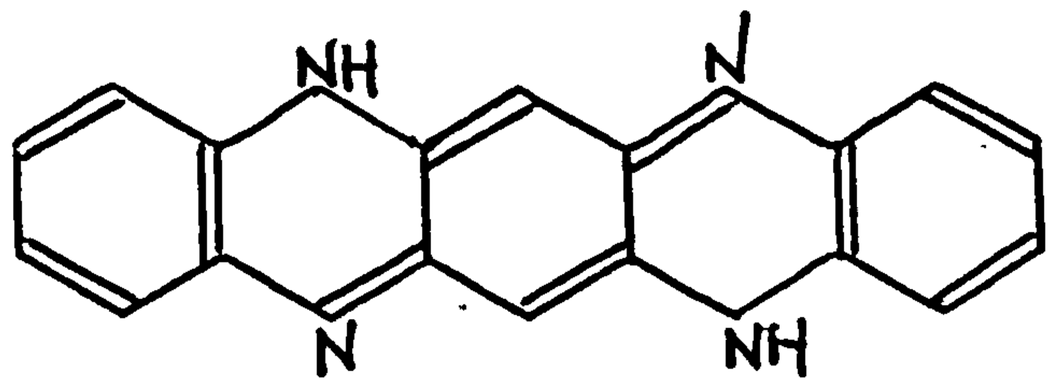
2-Anilino-1,4-benzoquinone (XXX) was obtained as golden-brown needles, m.p. 119-120° from ligroin, by the judicious addition of aniline to an ethanolic solution of 1,4-benzoquinone. It was obtained earlier by Willstätter[46.] who oxidized 2-anilino-1,4-quinol and aniline

respectively with ferric chloride. Further addition of aniline gave 2,5-dianilino-1,4-benzoquinone and finally azophenine.

Azophenine (XXXI) could be prepared directly from 1,4-benzoquinone by melting it with aniline and aniline hydrochloride. Its derivatives could be converted into the nitrogen analogues of triphenodioxazine by oxidation, i.e., fluorindine (XXXII).

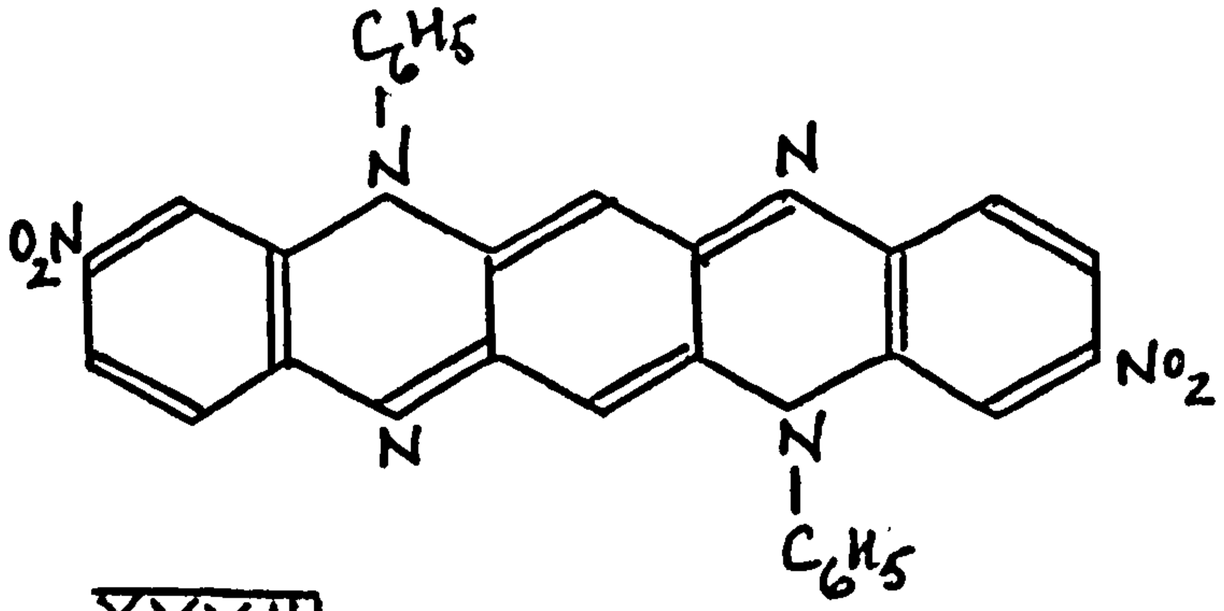


XXX

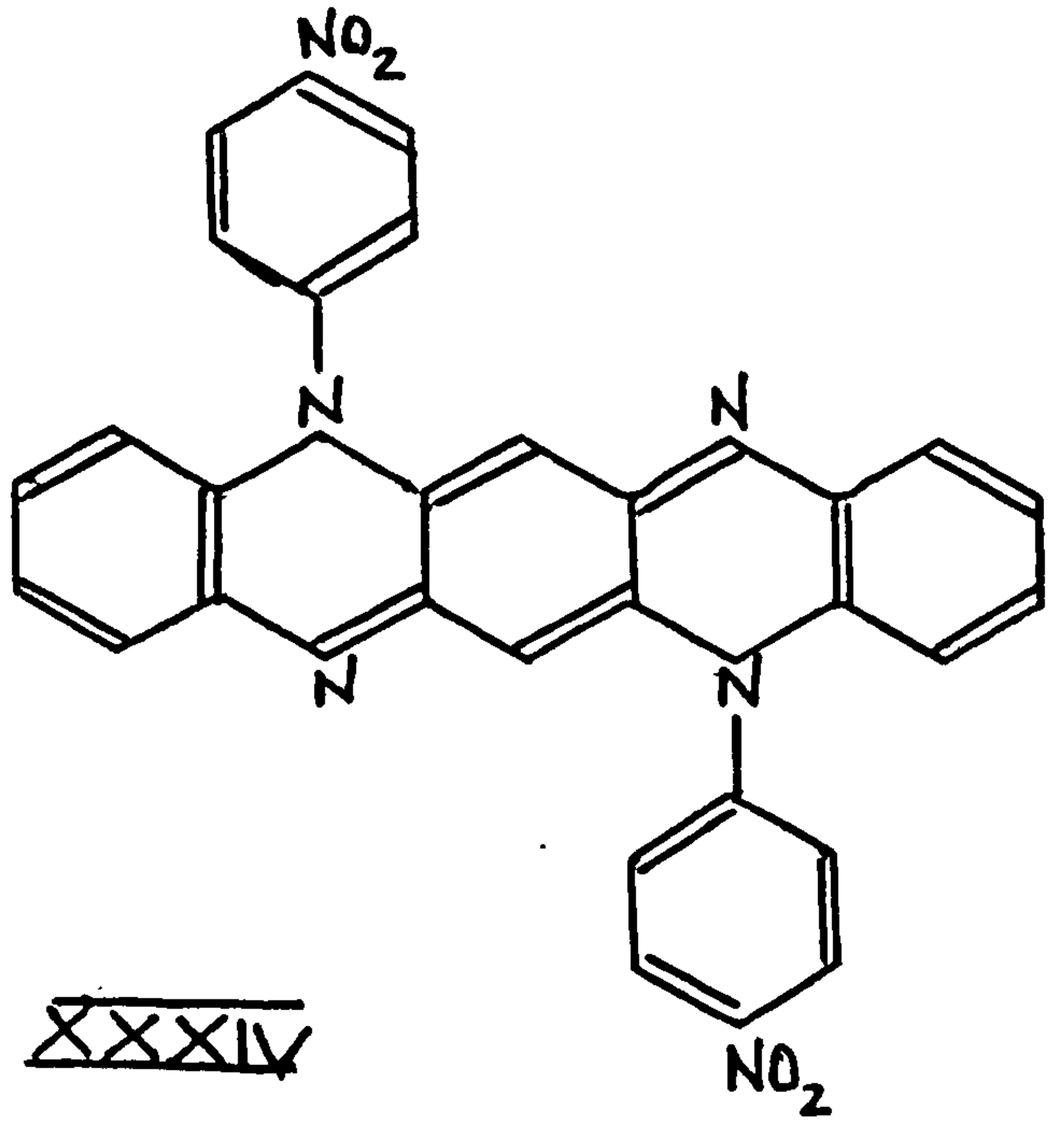


XXXII

The azophenine derivatives[47, 48] were refluxed with an oxidizing agent in a high boiling solvent, to convert them into fluorindines, which were intensely coloured products. 1,4-Benzoquinone dianil with p-nitroaniline in glacial acetic acid at 120°, gave red-brown crystals of 2,5-di(4-nitroanilino)-1,4-benzoquinone dianil. On refluxing this for an hour in nitrobenzene containing some manganese dioxide, dark crystals of the fluorindine were formed. It was suggested that this could be either of two structures, (XXXIII) or (XXXIV).

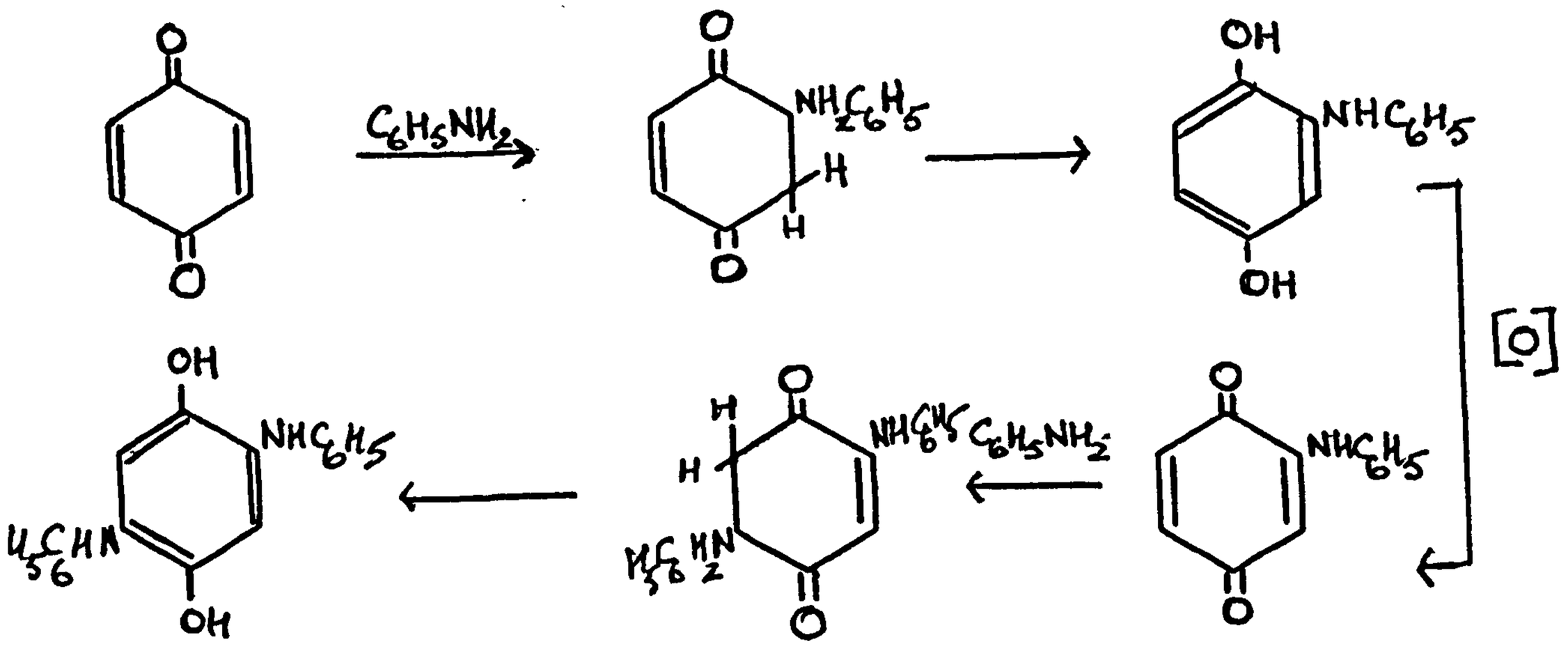


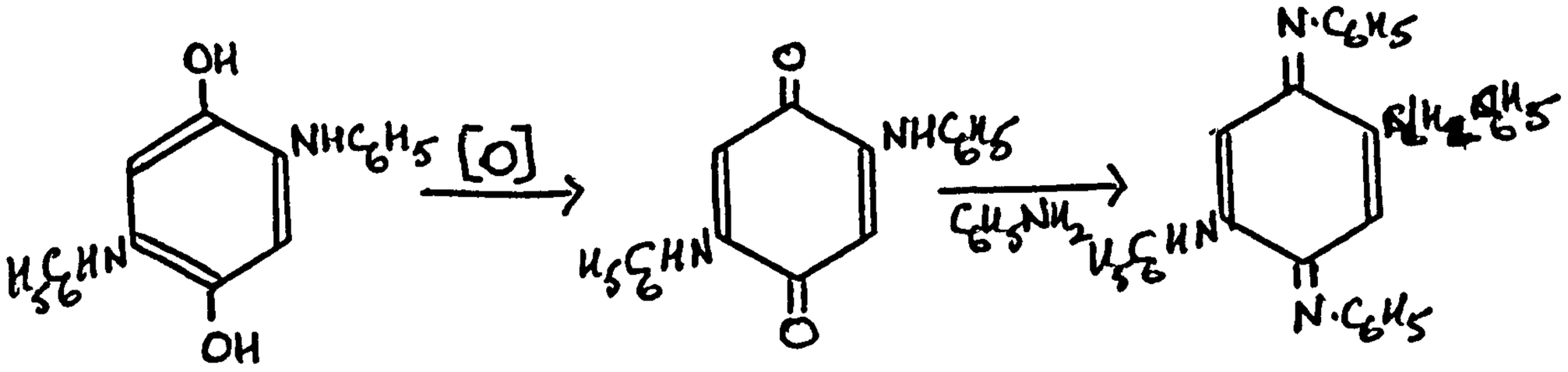
XXXIII



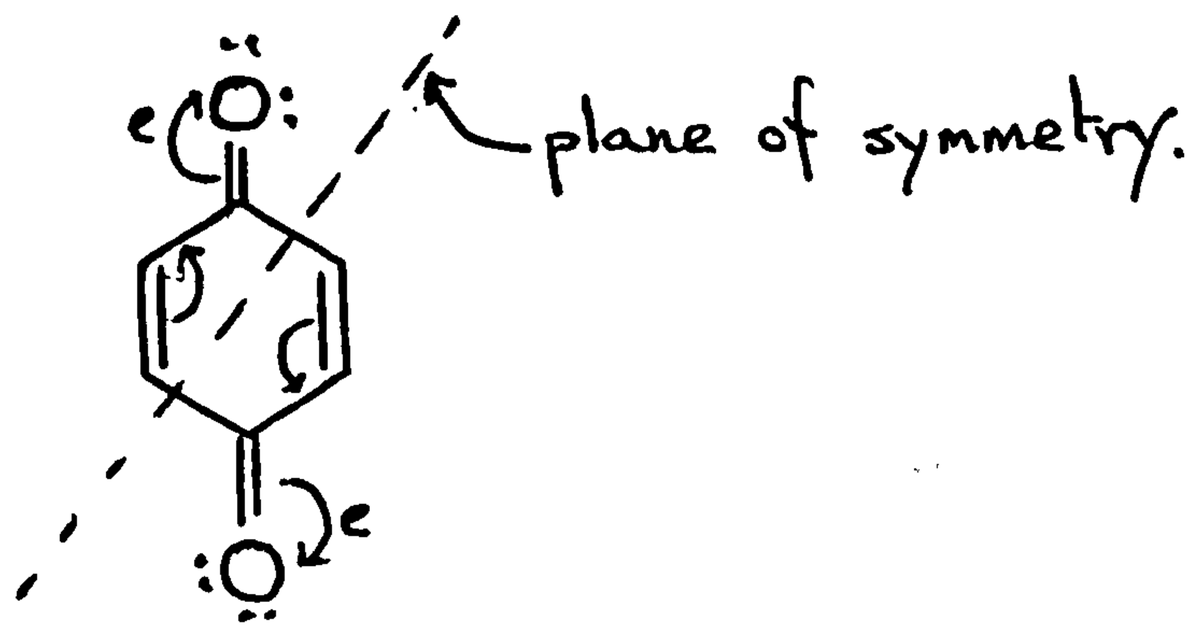
XXXIV

The complete anilation of 1,4-benzoquinone was outlined by Karrer[49]. in the following steps:-

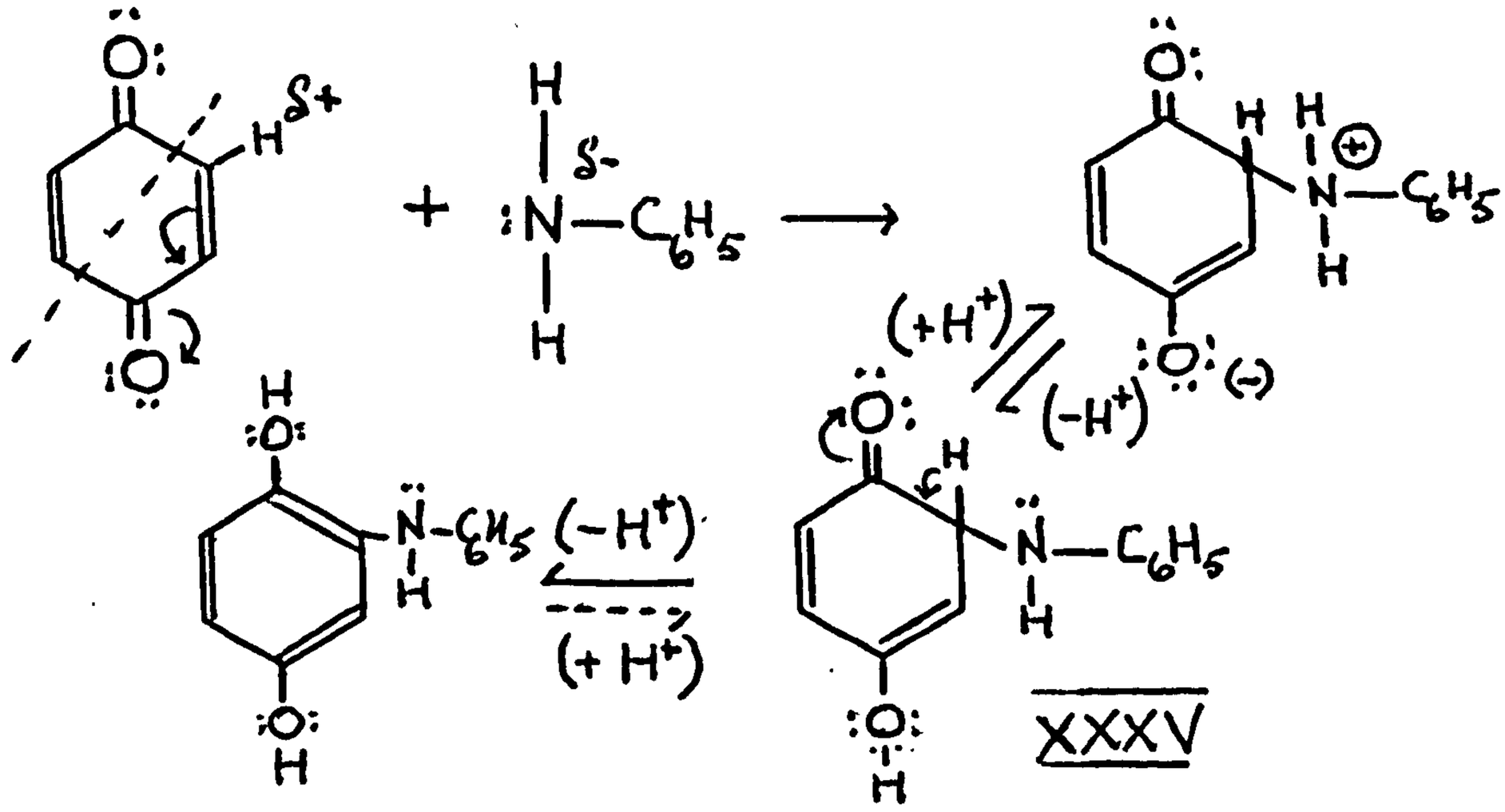




1,4-Benzoquinone acts as an α,β -unsaturated ketone. All the C-atoms are electrophilic in character due to the electron shift towards the O-atoms, via the double bonds.

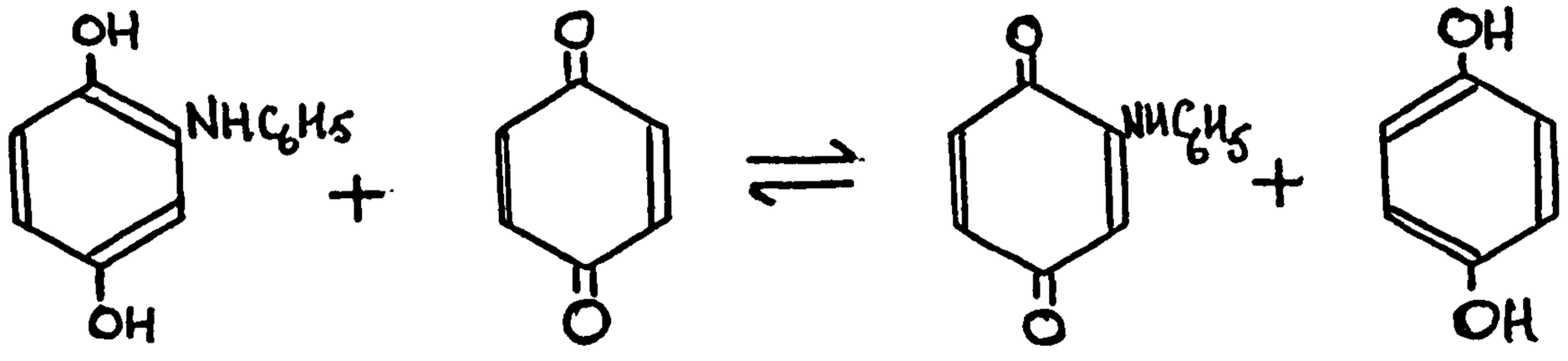


The resultant structure is thus reactive towards nucleophilic reagents, such as aniline, which is in marked contrast to benzene and the phenols, which are nucleophilic in behaviour.



XXXV

One half of the quinone structure acts first with the formation of an addition compound, unlike the one quoted by Karrer, and there is a transference of a proton to form the structure (XXXV). This is in an unstable form of resonance and again there is a transference of a proton to form the stable 2-anilino-1, 4-quinol, which assumes the stable benzenoid structure. In the presence of excess 1,4-benzoquinone, this is in redox equilibrium as shown by the equation.



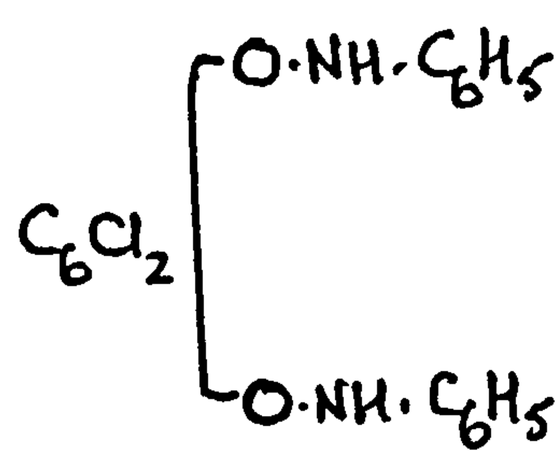
As 1,4-benzoquinone is a stronger oxidizing agent than 2-anilino-1,4-benzoquinone, the equilibrium is

shifted over to the right. Further addition of aniline would take place in a similar way with the formation of 2,5-dianilino-1,4-benzoquinone. Further substitution of ring hydrogen is not observed, presumably due to steric factors, and anil formation takes place.

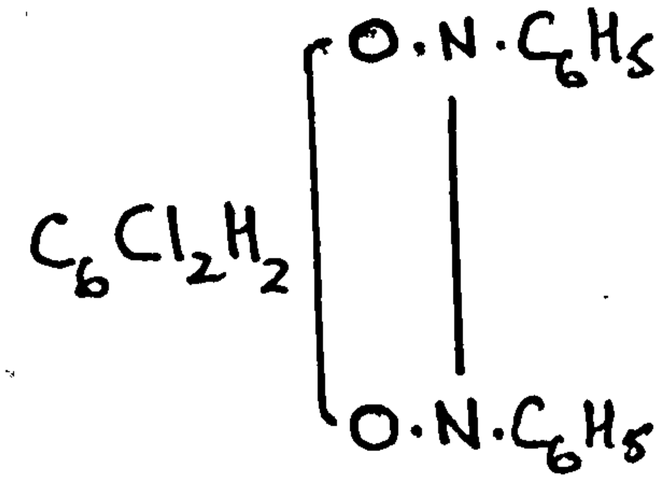
This work was substantiated by Hopff and Schweizer.[50] They found the redox equilibrium was influenced by the arylamino group and also by the pH of the reacting medium. An electron repelling group such as aniline generally reduced the oxidation potential of the substituted quinone, and thereby shifted the equilibrium over to the right. Electron attracting groups would act conversely. Weaker bases than aniline only tended to give mono-substituents. The rate of reaction was decreased by the presence of acidic groups in the amine. This was probably due to the formation of an internal salt or "zwitterion" within the amine itself and thus reducing its basicity. 2,5-Disubstituents always occurred. 2,6-Disubstituents were never found in practice, possibly due to the formation of two transition states, of which the 2,6- was unsymmetrical and thus in an unstable form of resonance. The 2,5- being symmetrical, and in a stable resonance form, was preferred.

Anilino-1,4-benzoquinone chloro-derivatives

By refluxing chloranil with aniline in ethanol, Hoffmann[33, 34.] obtained a dark coloured compound of high melting point, which had the empirical formula, $C_{18}H_{14}O_2N_2Cl_2$. This gave a violet-blue colour in concentrated sulphuric acid, and it was postulated as a diarylamino-chloranil derivative. Hesse[35.] obtained a similar compound by heating aniline with chloranil. This also gave a violet-blue colour in concentrated sulphuric acid and he called it bichloroquinonylpenta-phenylamide. Wichelhaus[36.] obtained a similar product to Hoffmann with chloranil and aniline, but challenged Hoffmann's structure and represented the product a different way.



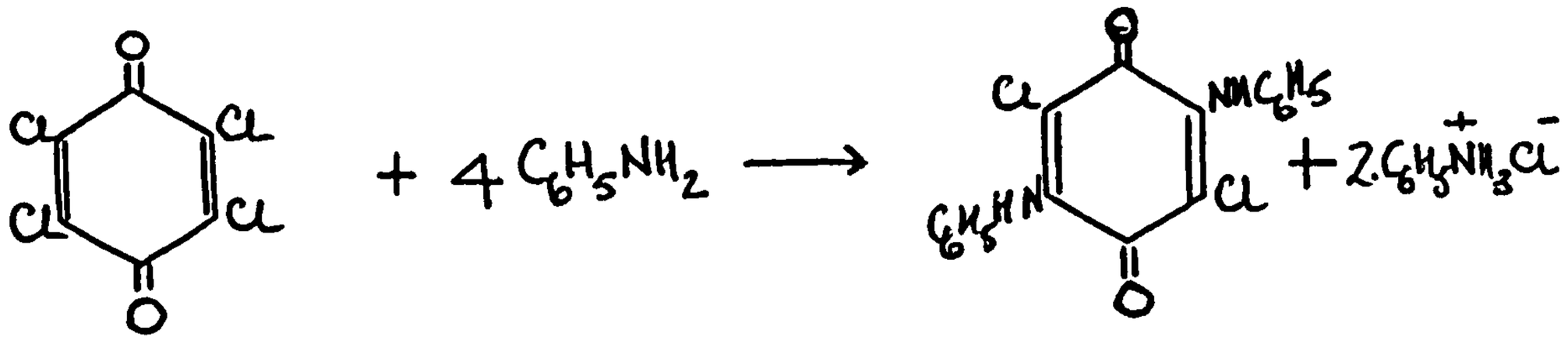
Hoffmann.



Wichelhaus.

Knappe and Schultz[39.] confirmed Hoffmann's findings and found that aniline with chloranil gave 2,5-dianilino-3, 6-dichloro-1,4-benzoquinone (XXXVI). Four moles of aniline were used with chloranil, as two chlorines were

replaced by aniline, and the resultant two moles of hydrogen chloride were absorbed by the excess two moles of aniline, giving aniline hydrochloride.

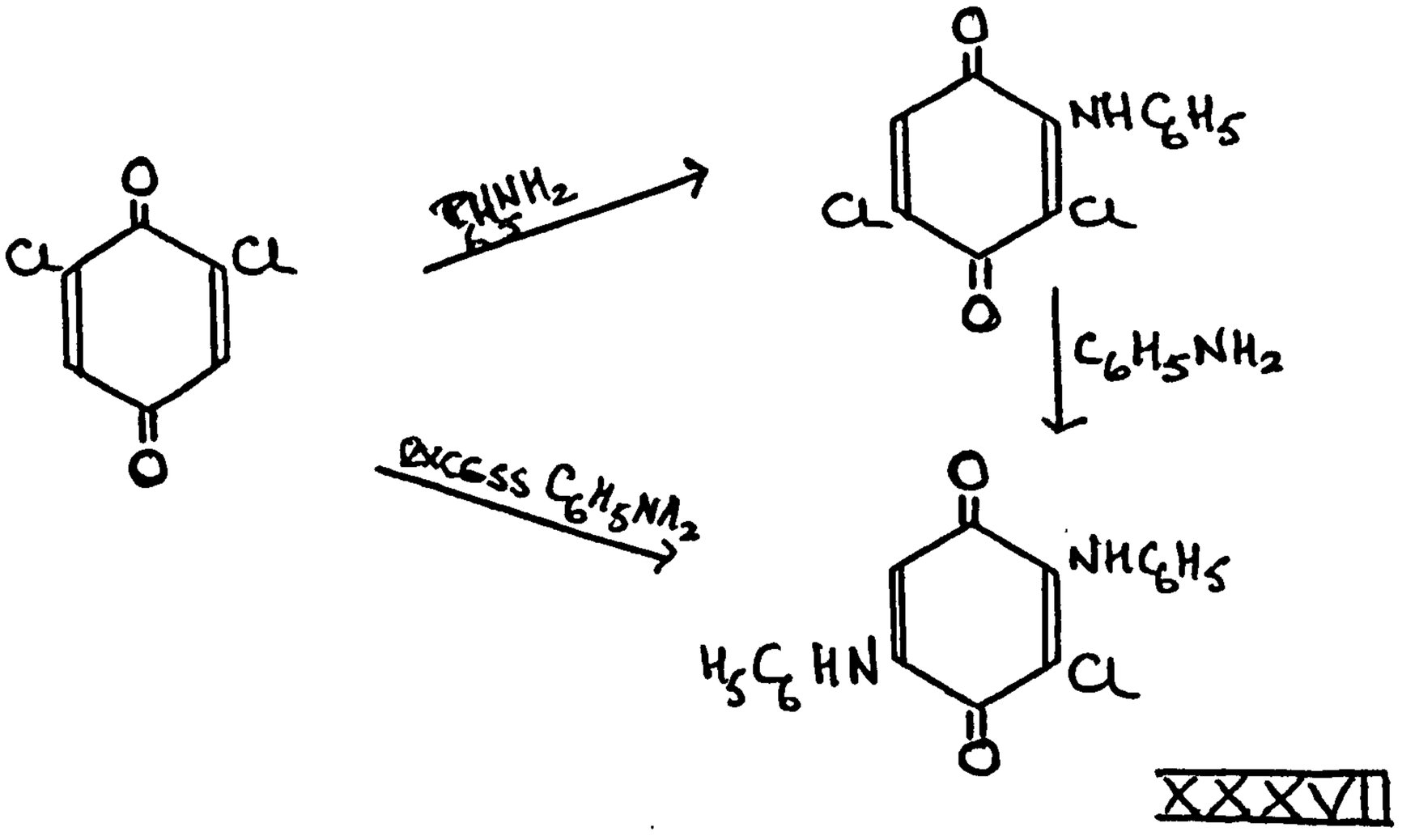


XXXVI

They disproved Wichelhaus's structure for (XXXVI) as 2,5-dianilino-3,6-dichloro-1,4-quinol was formed on reduction with stannous chloride, whereas one would have expected aniline or hydrazobenzene and a dichloroquinone if Wichelhaus's structure were correct. The quinol formed silvery glistening needles from ethanol, rapidly darkening in air back to the quinone. The quinol could be acetylated. (XXXVI) gave a monosulphonic acid derivative with concentrated sulphuric acid, which gave a light brown solution in water.

Concentrated nitric acid gave a brownish red solution but no nitro-compound was isolated from it. (XXXVI) with concentrated potassium hydroxide solution gave aniline.

Niemeyer[40.] examined the reaction of aniline on various chlorinated derivatives of 1,4-benzoquinone. 2,3,5-Trichloro-1,4-benzoquinone gave (XXXVI) with aniline, the H-atom being preferentially replaced to the Cl-atom. This was also observed with 2,6-dichloro-1, 4-benzoquinone and aniline, the end product being 2,5-dianilino-3-chloro-1,4-benzoquinone (XXXVII).



XXXVII

(XXXVII) gave brownish needles from glacial acetic acid, m.p. 262°. Niemeyer noticed that whilst o- and p-nitroanilines only, would react with 1,4-benzoquinone; only m-nitroaniline would react with the chlorinated 1,4-benzoquinones. In general, these were dark green unstable compounds, which could be recrystallised from benzene without decomposition. A few chlorinated quinols would also react similarly. One mole 2-chloro-1,4-quinol

with two moles of aniline, gave 2-chloro-3,6-dianilino-1, 4-quinol in dark glistening plates, m.p. 92°.

Kehrmann[41.] prepared (XXXVII) by condensing aniline with 2,5-dihydroxy-3-chloro-1,4-benzoquinone in acetic acid, the hydroxyl groups being replaced by aniline.

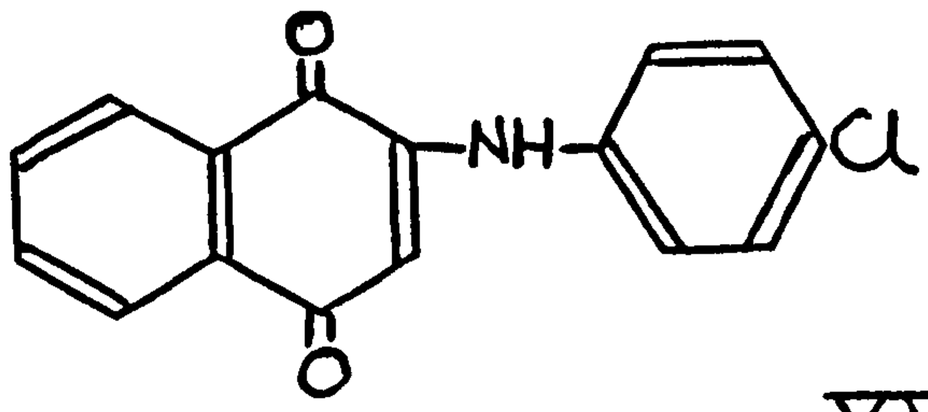
Andresen[42.] obtained (XXXVI) by the action of aniline on 2,3,5-trichloro-1,4-benzoquinone chlorimide.

As well as hydrogen, halogen and hydroxyl groups, bases could replace alkoxy-[37, 43.] and even methyl-1, 4-benzoquinone derivatives.[44.] 2-Methyl-5-methoxy-1, 4-benzoquinone with methylamine gave 2,5-bismethylamino-1, 4-benzoquinone.

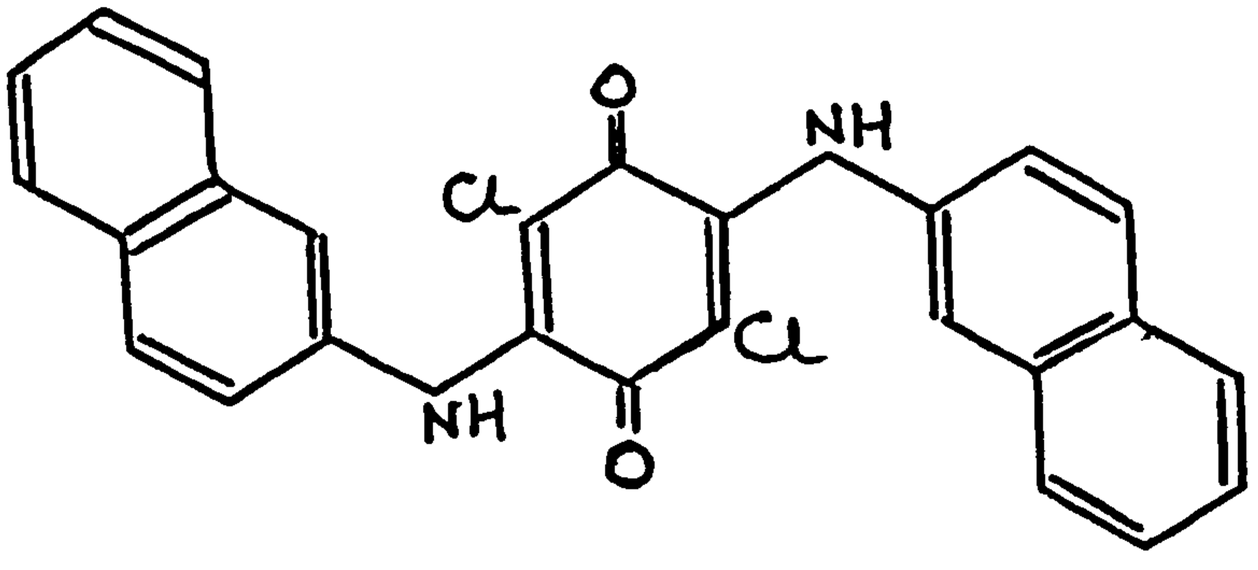
PART III

THE PATENT LITERATURE LEADING TO THE DEVELOPMENT OF TRIPHENODIOXAZINE DYES.

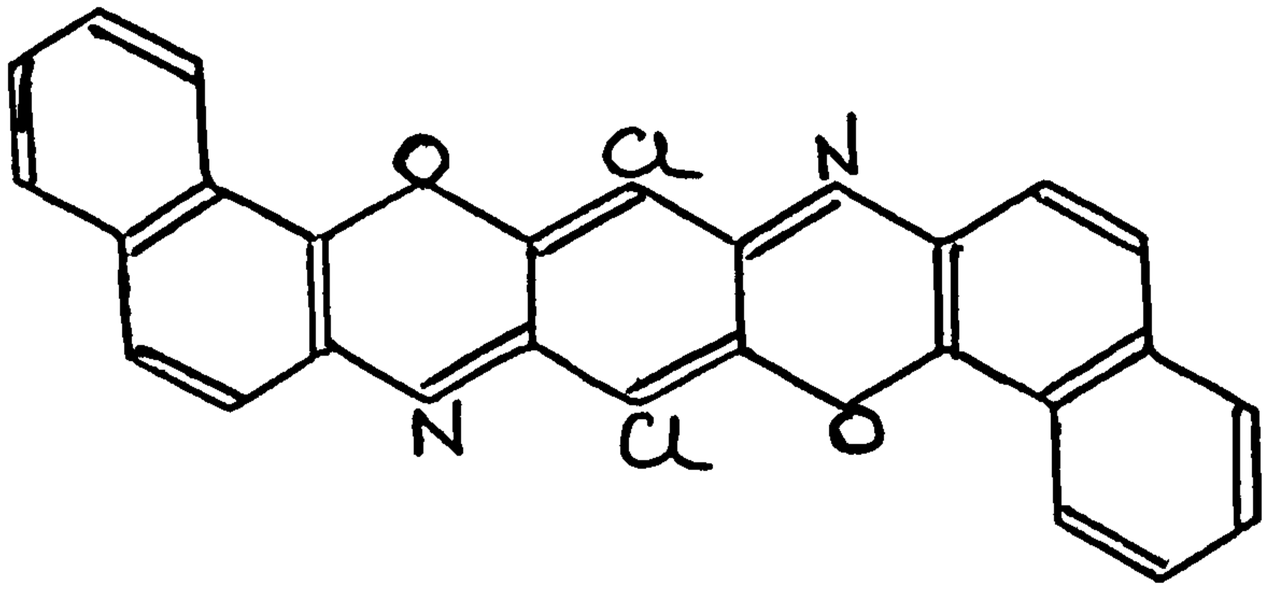
In 1910, the firm of Meister, Lucius, and Brüning,[51] introduced a series of 1,4-quinone derivatives as vat dyes for wool. 2,5-Dianilino-1,4-benzoquinone (XXIX) was used to give a yellow-brown shade on wool when applied from an alkaline vat, and was sold as Helindon Yellow. The vat could be sulphated in the reduced state and could thus be applied as the leuco ester. Better affinity was thought possible by using higher molecular weight compounds. Helindon Brown, or 2,5-di(2-naphthylamino)-3,6-dichloro-1,4-benzoquinone (XXXVIII) was prepared by condensing 2-naphthylamine with chloranil, and gave a brown shade on wool from an alkaline vat. 1,4-Naphthaquinone derivatives were used to widen the range of shades. 2-Anilino-1,4-naphthaquinone gave a yellowish red shade on wool, whilst the p-chloroanilino derivative (XXXIX) gave a bright red shade.



XXXIX



XXXVIII



XL

In 1912[52.] the same firm noticed that if compounds such as Helindon Brown were refluxed with nitrobenzene for five hours, greenish grey needles of no fixed melting point were formed. This was assumed to be 3,4,10,11-dibenzo-6,13-dichlorotriphenodioxazine (XL) even though analyses results agreed with a formula of $C_{26}H_{15}N_2O_2Cl$ compared to $C_{26}H_{12}N_2O_2Cl_2$. The needles dissolved in concentrated sulphuric acid to give a deep blue colour and gave a violet colour with an orange fluorescence in xylene. The same reaction was carried out on the unchlorinated derivative of Helindon Brown but cyclisation required more stringent conditions, i.e. refluxing in nitrobenzene for eighteen hours.

It was generally accepted that the final products were triphenodioxazine derivatives and that the cyclisation was more easily effected by the addition of catalysts such as aluminium, ferric, or zinc chlorides. The product from the cyclisation of Helindon Brown was obtained in two hours by the addition of a little ferric chloride to the reaction mixture. It was thought that these catalysts promoted oxidation.

Various amines[53.] were condensed with chloranil and cyclised to triphenodioxazines by using high boiling solvents and catalysts. A series of derivatives were prepared using aniline, o-anisidine, o-phenetidine, and p-toluidine. The uncyclised arylaminoquinone was removed from the product by treatment with alkaline dithionite solution. A range of brown to red products were formed but none were found to be of any technical importance.

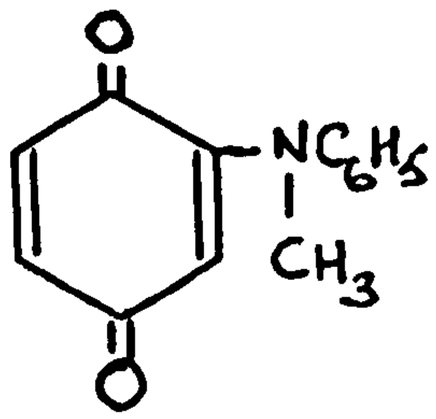
Water soluble triphenodioxazines[54.] were prepared by using arylamino sulphonic acids. Both 2-naphthylamine-5- and -8-sulphonic acids were condensed respectively with chloranil in sulphuric acid. The temperature was raised to 150° and cyclisation appeared to take place with the formation of dark violet powders. These were isolated as the sodium salts and gave red-violet shades on wool.

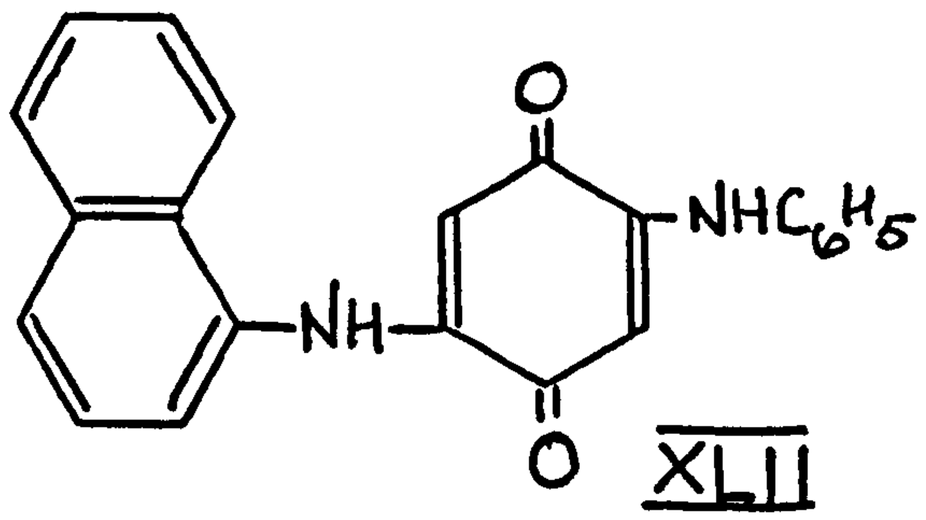
Sulphurisation[55.] of arylaminoquinones was carried out in order to prepare sulphur vat dyes. 2,5-Dianilino-3, 6-dichloro-1,4-benzoquinone (XXXVI) was sulphurised by heating with sodium sulphide and gave a dull brownish olive shade on wool from a weak sodium sulphide vat. These arylamino-quinones could be sulphurised under a variety of conditions using agents such as sodium sulphide, sodium hydrosulphide, and sodium thiosulphate.

These conditions[56.] of condensation of amines with chloranil were improved by the addition of acid-binding agents such as sodium acetate, and magnesium oxide.

W. and H. Suida[57.] prepared unsymmetrical arylamino quinones by varying the types of amine used. Secondary amines generally only gave a monoarylamino-derivative. N-methylaniline in fifty per cent aqueous acetic acid gave 2-(N-methylanilino)-1,4-benzoquinone (XLI) with 1,4-benzoquinone. 2-Anilino-1,4-benzoquinone (XXX) with 1-naphthylamine gave 2-anilino-5-(1-naphthylamino)-1,4-benzoquinone (XLII) in orange-yellow crystals, m.p. 278-280°; greenish yellow colour in concentrated sulphuric acid.

XLI

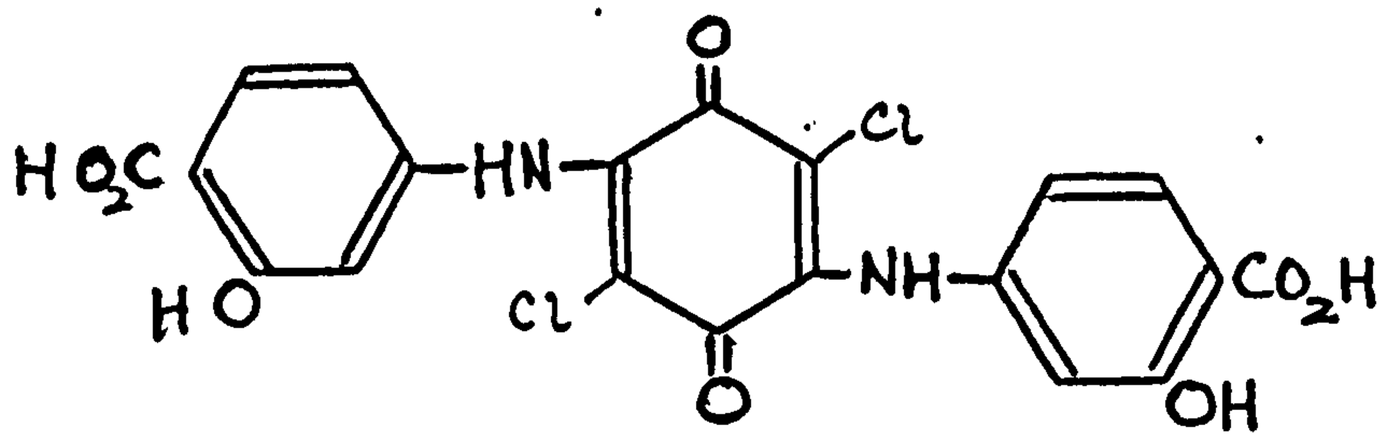




XLII

These compounds could be sulphonated to produce acid dyes or conversely, sulphonic acid intermediates could be used. Chloranil, on condensation with p-aminodiphenylamine-o-sulphonic acid in fifty per cent aqueous acetic acid and in the presence of sodium acetate, gave a grey-blue powder of the monoarylaminoquinone. The next Cl-atom was then replaced with sodium sulphanilate in an aqueous medium, made alkaline with sodium carbonate, to afford a dark powder ([redacted]). This product was soluble in water and gave dark brown shades on chromed wool.

Durand and Hugenin[58]. prepared a series of mordant arylaminoquinones by the use of aminosalicylic acid derivatives. One mole of chloranil on condensation with two moles of p-aminosalicylic acid gave (XLIV).



XLIV

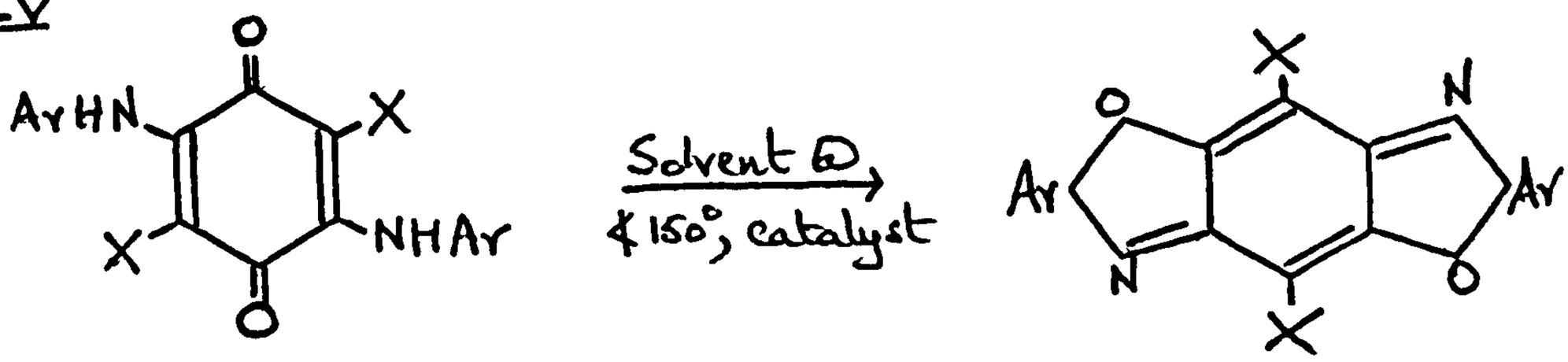
This was further treated with ninety-eight per cent sulphuric acid at 100-105^{0} for three and a half hours

and on dilution and neutralisation with sodium carbonate, it gave a red-violet powder, soluble in water. This gave blue-violet shades on chromed wool.

Further 1,4-quinone derivatives were produced by the use of nitrodiphenylamino sulphonic acids[59], as specially selected nitro-aromatic amines were more reactive than unnitrated products.

In 1931, I.G. Farbenindustrie A.G.[60] published a series of patents for the preparation of triphenodioxazine pigments. They claimed that an arylaminoquinone of the type (XLV) could be cyclised to a triphenodioxazine (XLVI) by refluxing in a high boiling solvent containing an oxidation catalyst.

XLV

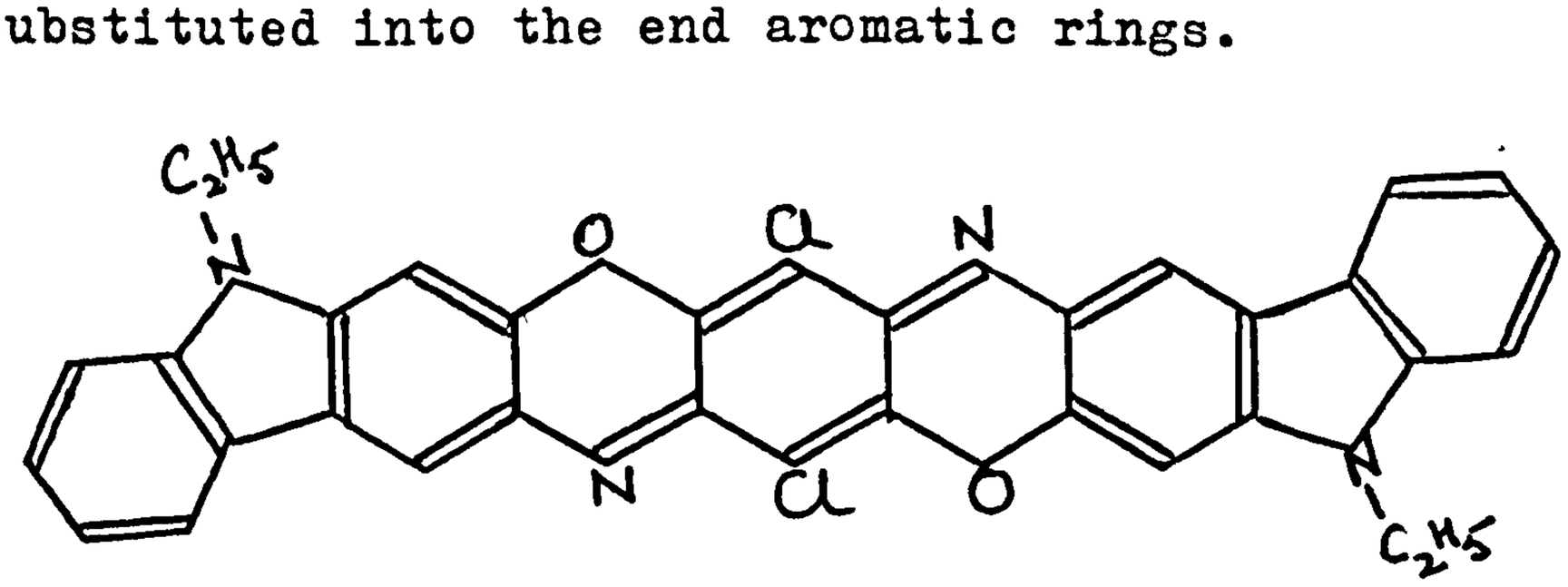


X = H, Cl, Br, I, CH_3, C_2H_5. XLVI

In general arylamines of relatively high molecular weight were employed as these gave products which were of technical use in the dyestuff industry. Sulphonation of

the triphenodioxazines gave water soluble compounds which could be used as direct cellulose dyes, giving a range of shades from violet to blue-green.

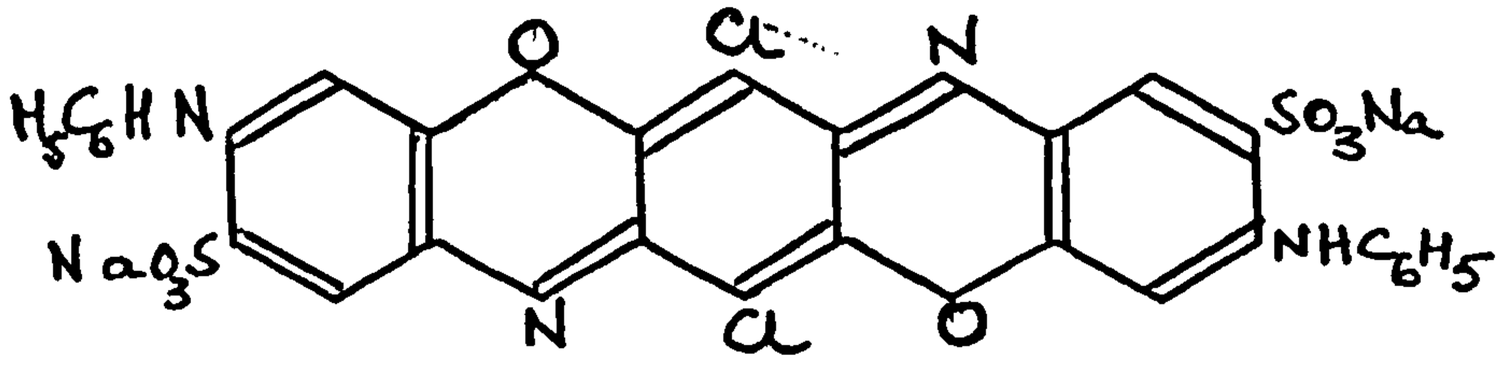
Condensation of 3-amino-9-ethylcarbazole[61,62]. with chloranil gave the corresponding diarylaminoquinone. This was easily cyclised to the triphenodioxazine in o-dichlorobenzene using benzenesulphonyl chloride as a catalyst. The product formed green needles and was marketed as Pigment Violet R. The structure was assumed to be 5,15-diethyl-8,18-dichlorodiindolo [3,2-b; 3',2'-m] triphenodioxazine (XLVII). This could be disulphonated with oleum and the disodium salt marketed as a direct blue cotton dye under the name Sirius Light Blue FFRL. The calcium and barium salts were used as pigments. It was generally assumed that the sulphonic acid groups substituted into the end aromatic rings.



XLVII

p-Aminodiphenylamine underwent a similar process to

the above, but greater use was made of its sulphonic acid derivative. 5-Amino-2-anilinobenzenesulphonic acid was condensed in aqueous medium with chloranil, using magnesium oxide as an acid binder. The arylaminoquinone was isolated as a dirty violet powder. This was cyclised to a triphenodioxazine using 8.3% oleum. The excess sulphonic acid groups were removed leaving a blue direct dyestuff. This was formulated as 3,10-dianilino-6, 13-dichlorotriphenodioxazine-2,9-disodium sulphonate (XLVIII).

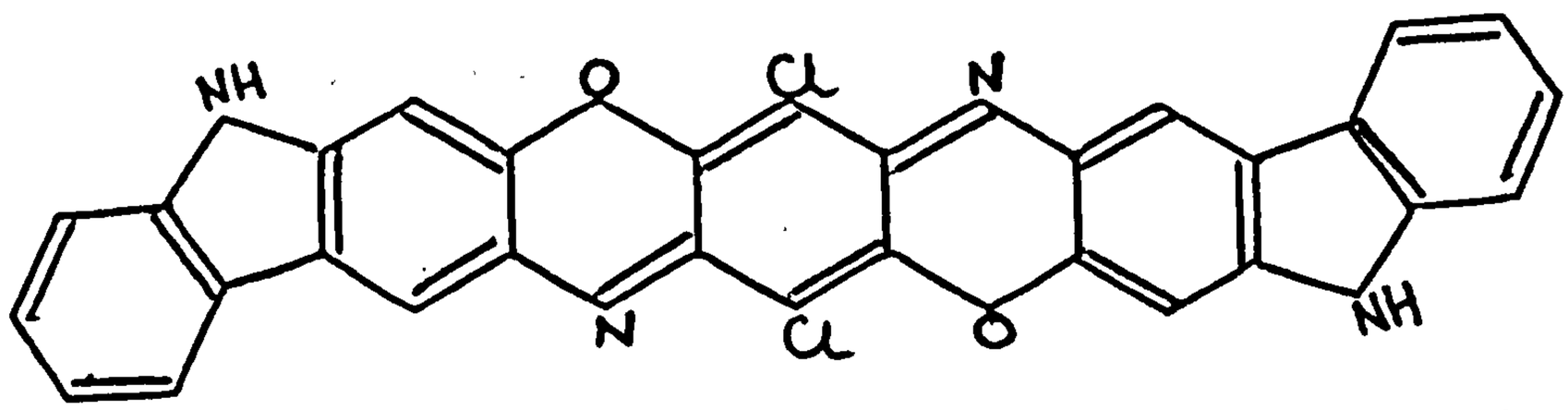


XLVIII

Other 1,4-quinones[63]. were tried besides chloranil. 3-Amino-9-ethylcarbazole was condensed with 2,3,5-trichloro-6-methyl-1,4-benzoquinone and 2,5-dimethyl-1,4-benzoquinone and the condensates cyclised in nitrobenzene, with or without the addition of 2,4-dinitrophenol.

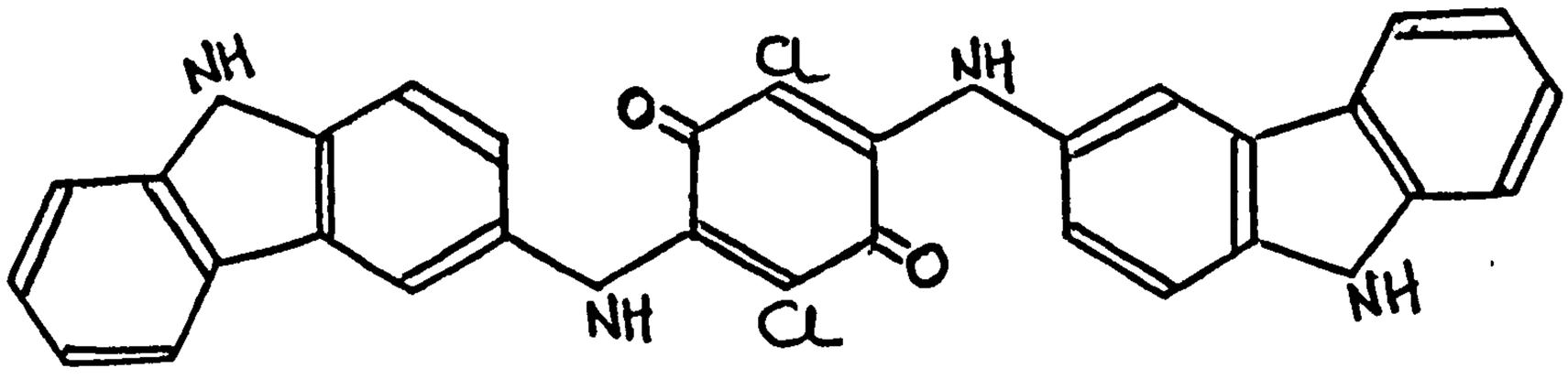
Besides ethylcarbazole a series of triphenodioxazines were prepared from 3-amino-9-acylcarbazole where acyl could be acetyl, benzoyl, p-toluenesulphonyl, and

diphenylcarbaminyl, the products being violet in colour.[64]. 3-Aminocarbazole with chloranil gave a product of type (XLIX). This was refluxed in nitrobenzene, together with p-toluenesulphonyl chloride as a catalyst, to give a dark violet pigment which was assumed to have the structure (L). The product could be trisulphonated with oleum to give a direct dye which produced a reddish blue shade on cotton.



L

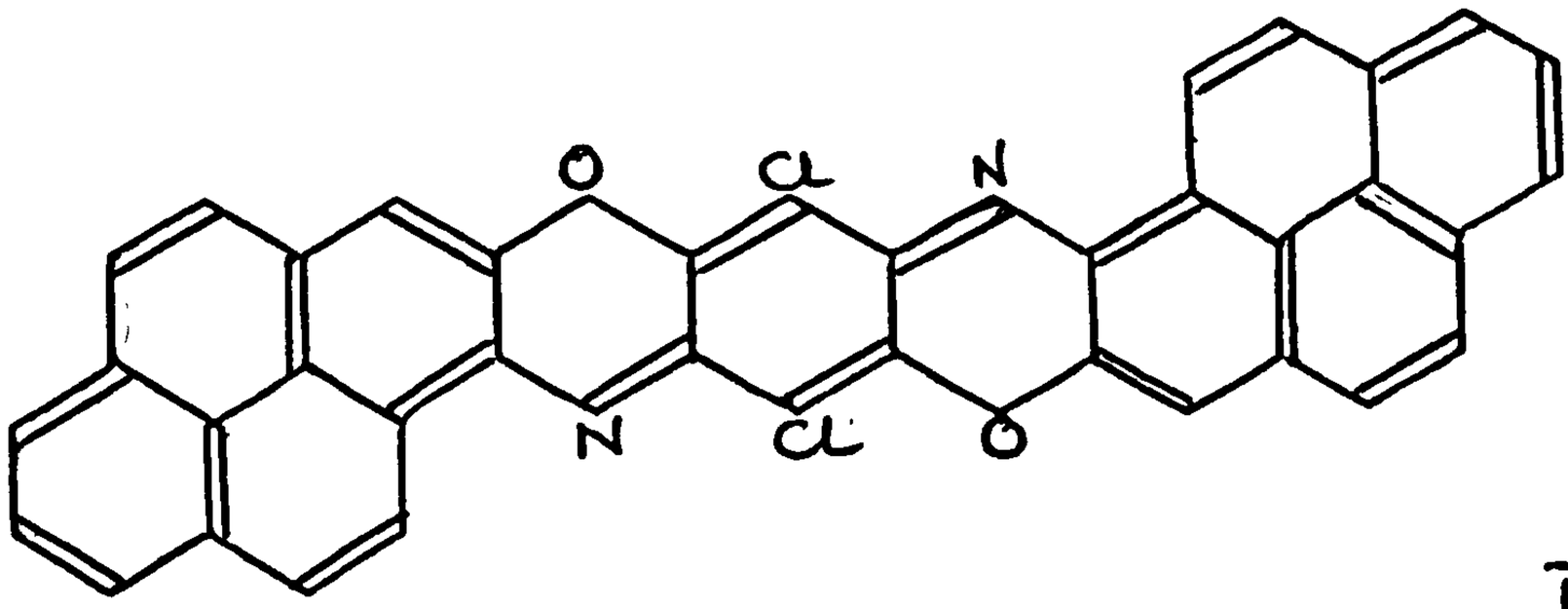
cyclisation



XLIX

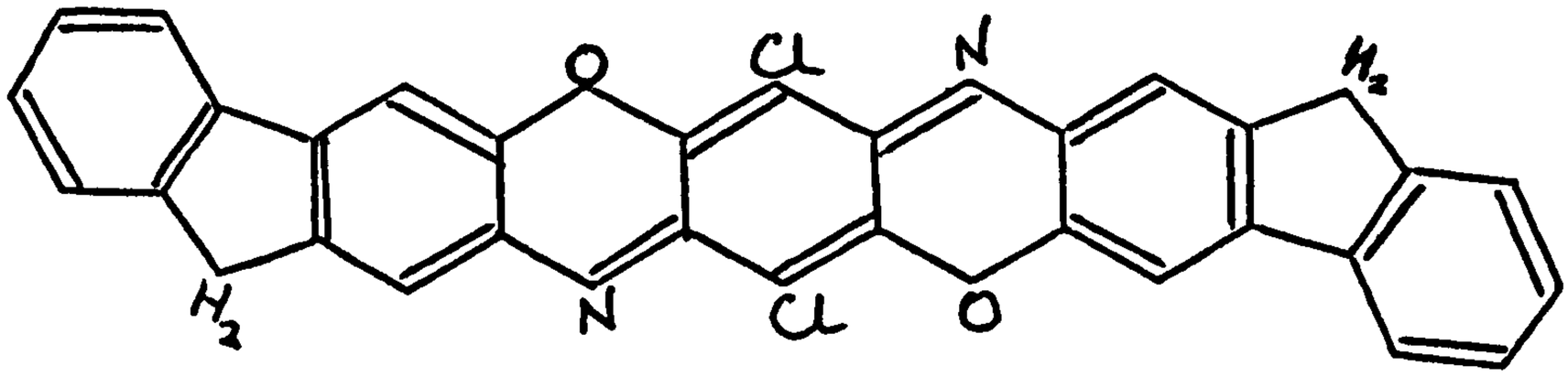
Further amines were used especially those of the polynuclear type[65,66]. such as chrysene and pyrene. 1-Pyrenamine on condensation with chloranil gave the

diarylaminoquinone, which on cyclisation in a high boiling solvent together with a catalyst, gave a product which was formulated as 10,21-dichlorodiphenaleno [1,9-a,b; 1′,9′-l,m] triphenodioxazine (LI). It was sulphonated with oleum and isolated as the sodium salt to give a product which produced a bright greenish-blue shade on cotton.



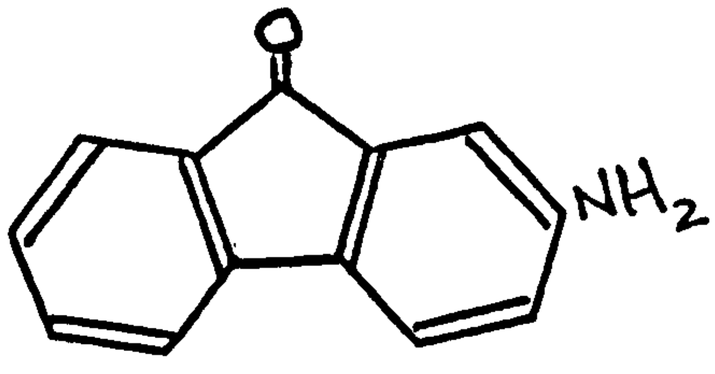
LI

A similar process was tried with 2-aminochrysene but the product was of no technical value. 4-Aminofluoranthrene, 2-aminofluorene, and 2-anthramine[67]. were also used. The cyclised product from the condensation of 2-aminofluorene and chloranil gave a violet pigment which was assumed to be 7,17-dichlorodiindeno [2,3-b; 2′,3′-m] triphenodioxazine (LII).

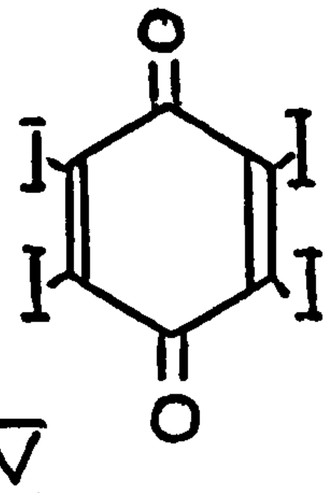


LII

Disulphonation of the product gave as the disodium salt, a direct dye which produced a bright violet shade on cotton.



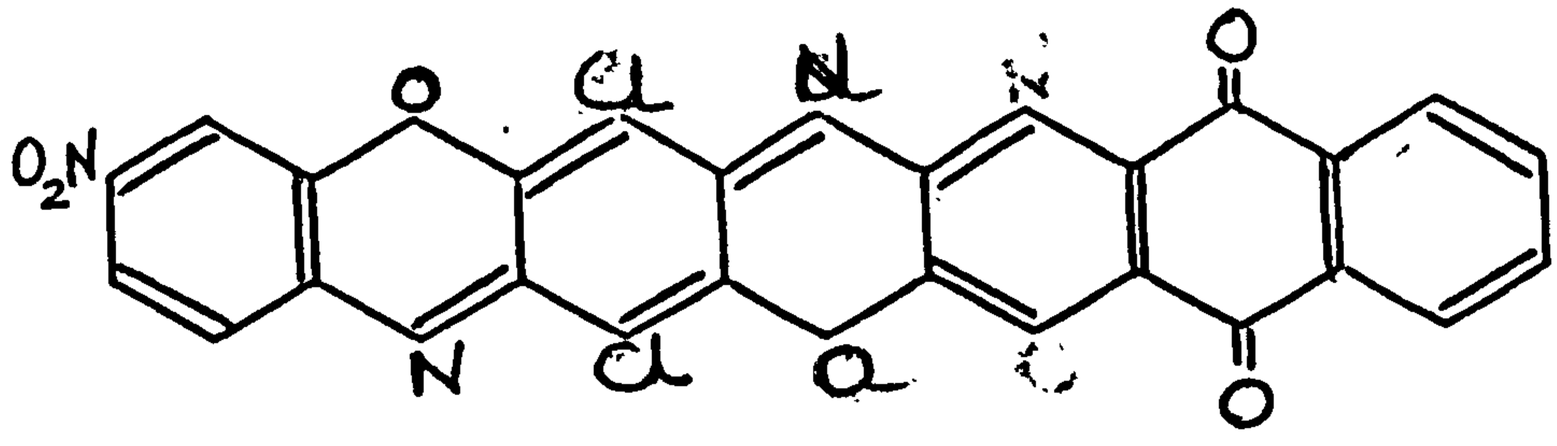
LIII



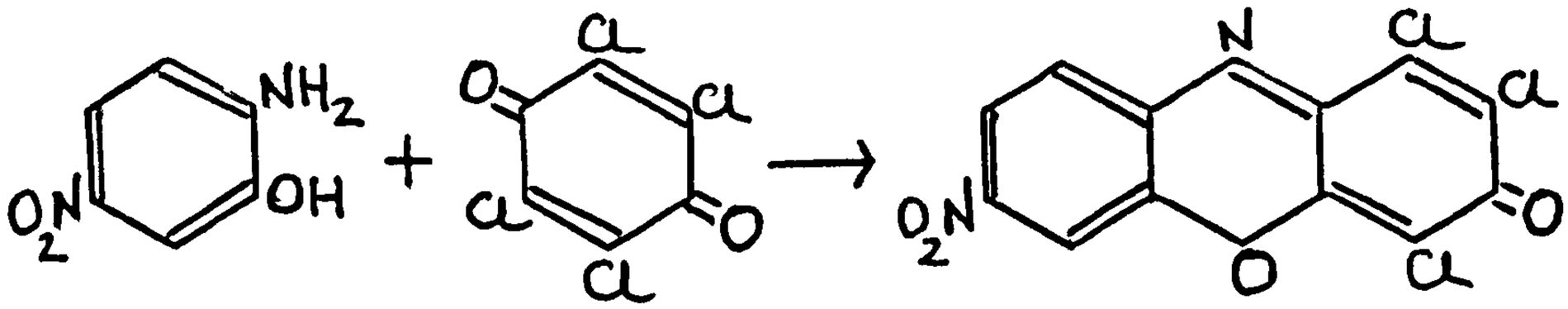
LIV

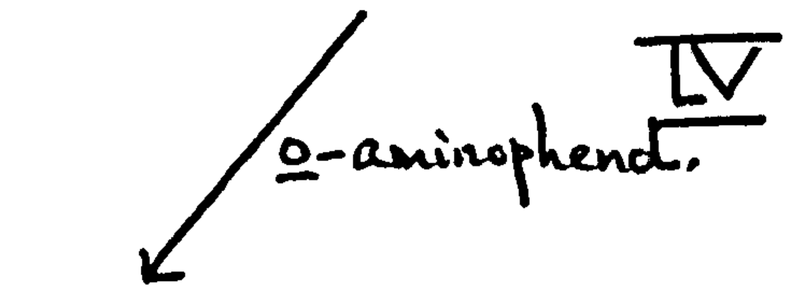
2-Amino-9-fluorenone (LIII) on condensation with 1,4-benzoquinone gave 2,5-di(2-fluorenonamino)-1,4-benzoquinone as a dark coloured powder. This was refluxed in 1-chloronaphthalene with some m-nitrobenzene-sulphonyl chloride to give a deep red-violet pigment. (LIII) could also be condensed with iodanil (LIV) and the resulting condensate mixed with manganese dioxide and benzoyl chloride and refluxed in nitrobenzene, to give deep blue-green needles.

In the search for new triphenodioxazine derivatives Zerweck[68] synthesised several from 3-phenoxazone derivatives. 1,2,4-Trichloro-7-nitro-3-phenoxazone (LV) was the most readily available of the phenoxazone derivatives. It was prepared[69] by condensing one mole of 5-nitro-2-aminophenol with one mole of chloranil at room temperature in ethanol. The product (LV) gave compact red needles from glacial acetic acid which dissolved in concentrated sulphuric acid to give a yellow-green colour. It gave a bright violet shade on wool from an alkaline vat. On condensing with o-aminophenol, 3-nitro-6,13-dichlorotriphenodioxazine (LVI) was formed. (LV) could be condensed with many other amines, i.e., on condensing it with 2-hydroxy-3-aminoanthraquinone in acetic acid and in the presence of sodium acetate, 2,3-diphthaloyl-6,13-dichloro-10-nitrotriphenodioxazine (LVII) was formed. It afforded small brown crystals from nitrobenzene of no melting point which dissolved in concentrated sulphuric acid to give a blue colour.

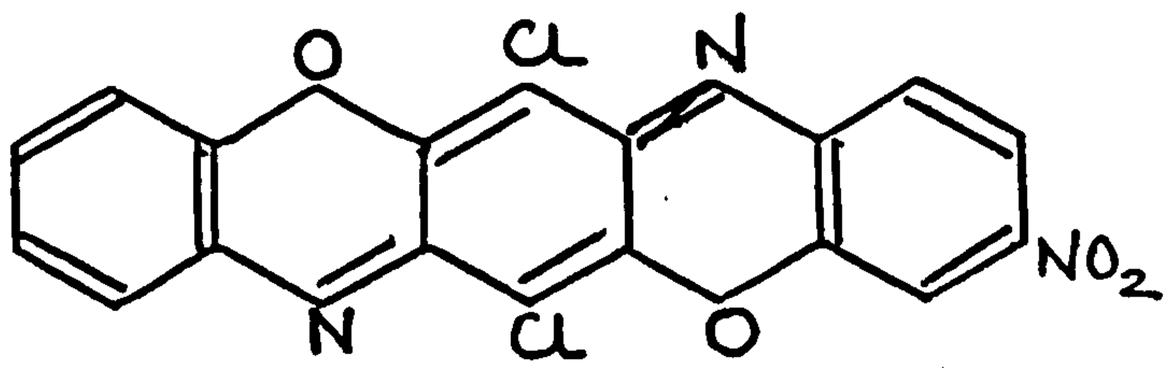


LVII





o-aminophenol. IV

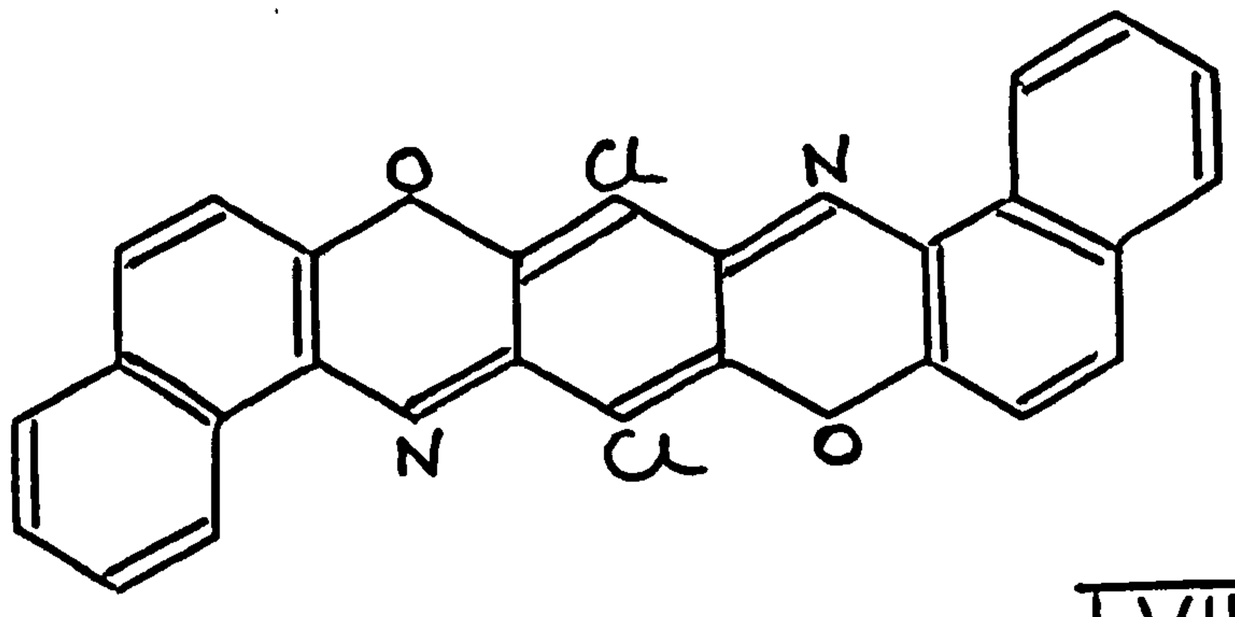


VI

o-Aminophenol and its alkyl and halogen derivatives would not condense with chloranil to the oxazine ring system but gave oxidation products instead. This was presumably due to the greater oxidizing power of the quinone group.

Fierz-David[70] investigated the preparation and properties of triphenodioxazine derivatives and concluded that the cyclisation procedure of the diarylaminoquinone to dioxazine involved some form of complex oxidation. 6,13-Dichlorotriphenodioxazine was prepared by demethylation

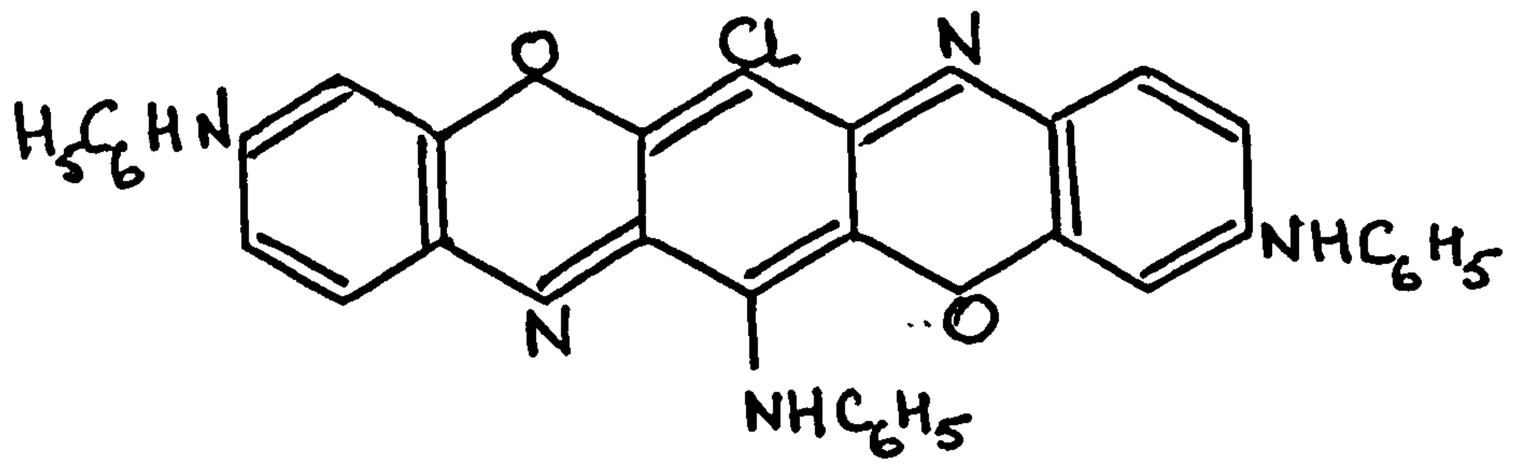
of 2,5-di(o-anisidino)-3,6-dichloro-1,4-benzoquinone with aluminium chloride in pyridine. Extensions of Zerweck's work were carried out. 5-Nitro-2-aminophenol on refluxing with chloranil in ethanol for twenty hours gave 3,10-dinitro-6,13-dichlorotriphenodioxazine as red-violet glistening flakes. It was reduced with alkaline sodium dithionite and then subjected to gentle oxidation with hydrogen peroxide to yield 3,10-diamino-6,13-dichloro-triphenodioxazine as green leaflets from sym-trichlorobenzene. 2,5-Di(1-naphthylamino)-3,6-dichloro-1,4-benzoquinone was obtained as a brown powder in 38.9% yield from the condensation of 1-naphthylamine with chloranil. This dissolved in concentrated sulphuric acid to give a yellow-green colour which gradually changed to a pure blue owing to triphenodioxazine formation. The diarylaminoquinone on refluxing in nitrobenzene gave green needles of 1,2,8,9-dibenzo-6,13-dichlorotriphenodioxazine (LVIII) in 44% yield.



LVIII

Triphenodioxazines were also prepared from amines such as 2-methoxy-4-aminodiphenylamine (Variamine Blue Base).

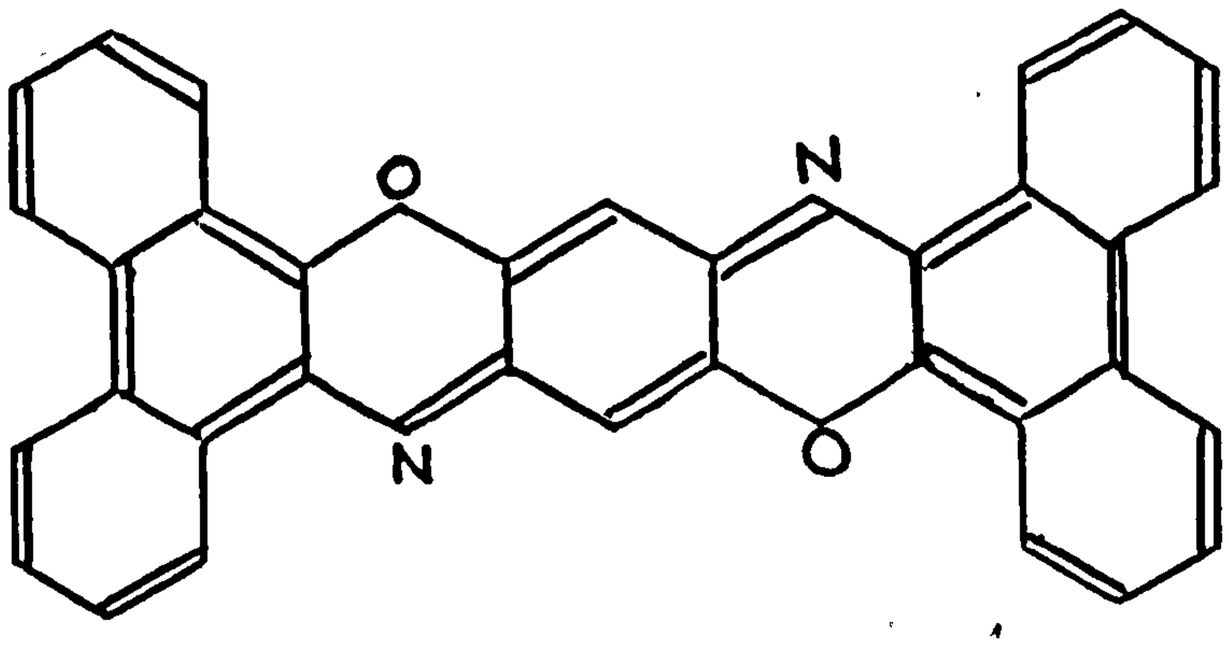
6,13-Dichlorotriphenodioxazine was refluxed with aniline and aniline hydrochloride for fifteen hours. A crystalline blue powder was obtained which was formulated as 3,6,10-trianilino-13-chlorotriphenodioxazine (LIX). The chemical analyses agreed with this structure and it was thought that the 3,10-positions on triphenodioxazine were the most reactive.



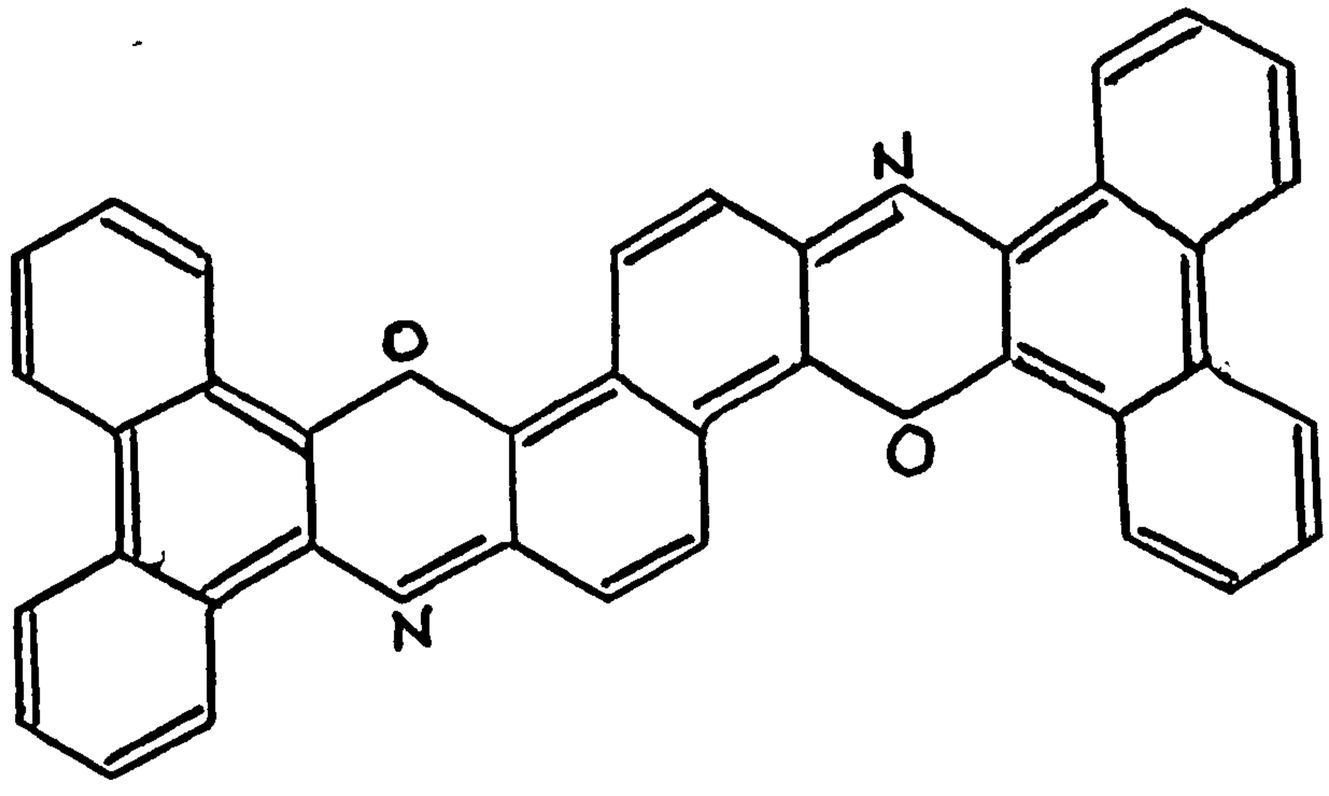
LIX

An American patent[71.] suggested the formation of triphenodioxazine derivatives by condensing a p-diamine, with free o-positions, with an o-quinone. Two moles of p-phenylenediamine on condensation with one mole of phenanthrene-9,10-quinone gave tetrabenzo [a,c,l,n] triphenodioxazine (LX). It was sparingly soluble in

nitrobenzene forming a blue-violet solution from which large dark prismatic needles were formed. Extremely high molecular weight compounds could be formed this way. By condensing 2,6-naphthalenediamine with phenanthrene-9, 10-quinone in refluxing glacial acetic acid, a dark very sparingly soluble powder was formed. This was recrystallised from a large volume of quinoline to give small dark red crystals of diphenanthro [9,10-b; 9,10-k]-1, 7-diaza-4,10-dioxachrysene (LXI).

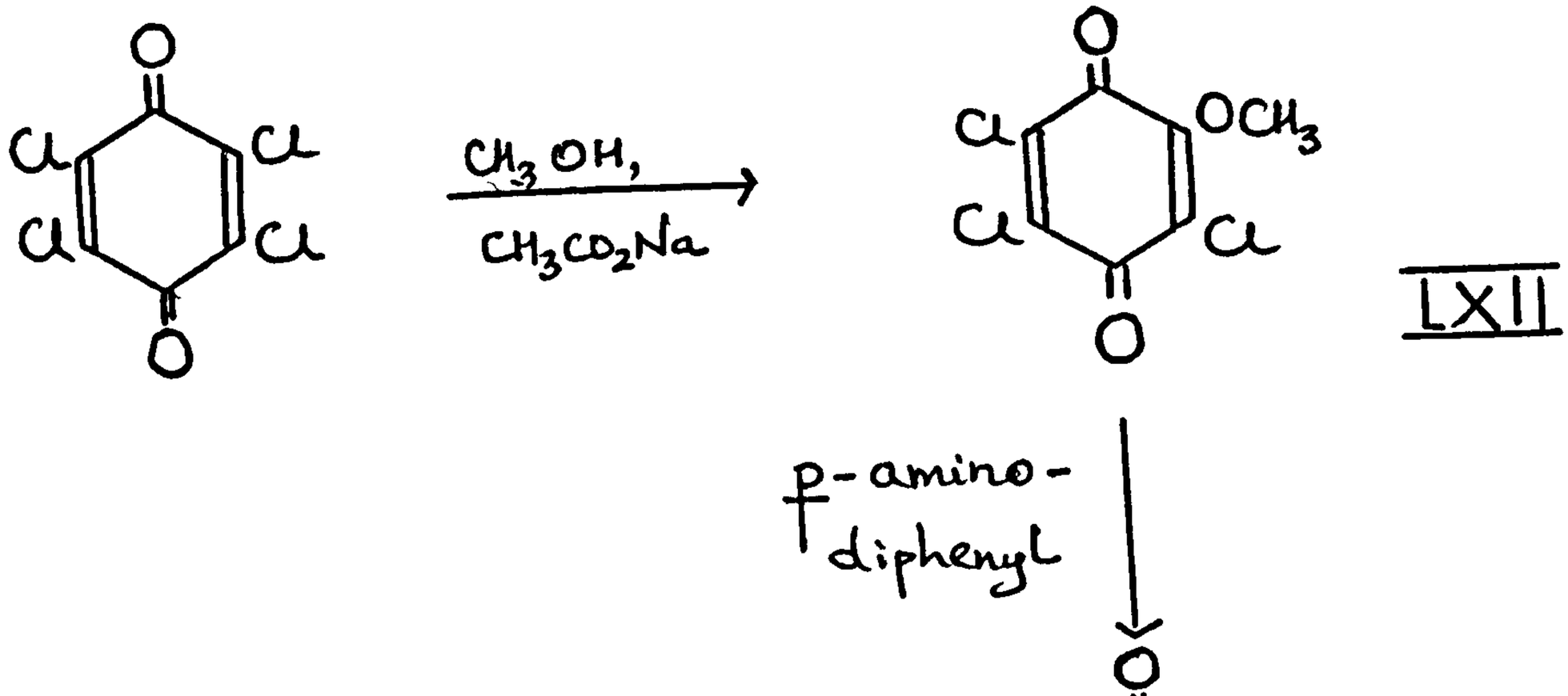


LX



LXI

The preparation of unsymmetrical triphenodioxazines formed the basis of a patent by Sandoz.[72,73,74,75]. Chloranil was refluxed with methanol for some hours to afford orange leaflets of 2-methoxy-3,5,6-trichloro-1, 4-benzoquinone (LXII), m.p. 183-185°. This was dissolved in ethanol, and a solution of p-aminodiphenyl added to it gradually at 45°. After cooling the reaction mixture in ice and filtering, dark violet leaflets of 2-methoxy-5-(4-diphenylamino)-3,6-dichloro-1, 4-benzoquinone (LXIII), m.p. 190-192°, were deposited from the filtrate. A small amount of 2,5-di(4-diphenyl-amino)-3,6-dichloro-1,4-benzoquinone was obtained as an insoluble powder on the filter, the amount formed depending on the temperature of condensation. The final methoxyl group was replaced under more vigorous conditions by refluxing aniline with (LXIII) in ethanol to give 2-anilino-5-(4-diphenylamino)-3,6-dichloro-1,4-benzoquinone (LXIV) as dark crystals. Sulphonated intermediates could also be used to give water soluble products. Two moles of p-aminodiphenyl with (LXII) and condensation with p-phenylenediamine gave 1,4-bis [2,5-dichloro-3-(4-diphenylamino)-1,4-benzoquinonylamino] benzene (LXV) as a deep brown coloured powder, very sparingly soluble in organic solvents. It gave an intense black-brown shade on wool from a colourless vat.



LXII

LXIII

LXIV

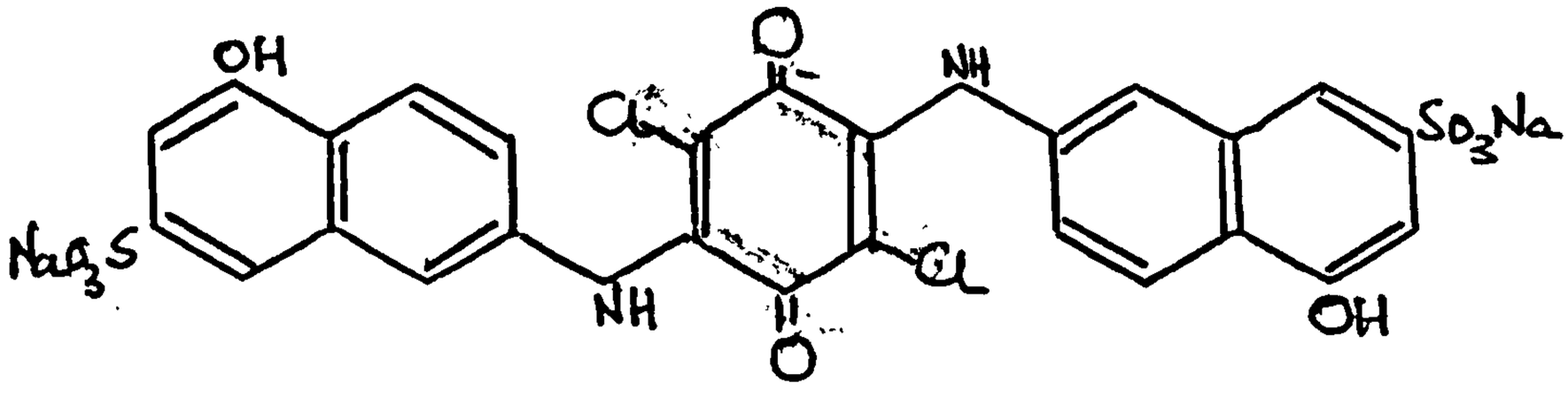
LXV

These arylaminoquinones could be cyclised to the corresponding triphenodioxazines in the usual way.

Azo intermediates were used to provide further triphenodioxazine derivatives[70,76]. 4-Benzeneazo-1-naphthylamine was condensed with chloranil to give the

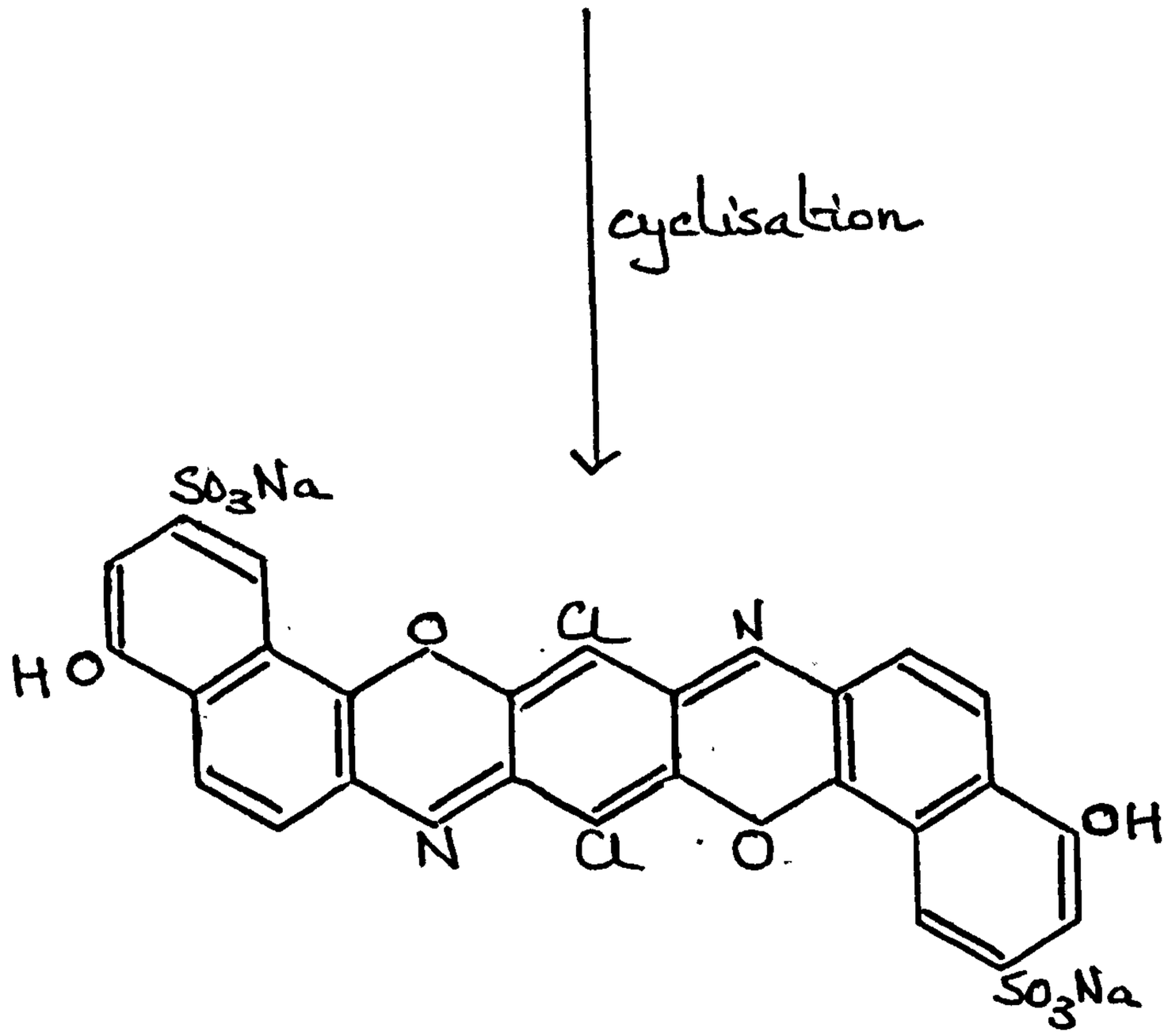
diarylaminoquinone. This was readily cyclised by refluxing in nitrobenzene, together with some p-toluenesulphonyl chloride, for half-an-hour. There was deposited grey-green needles of a blue pigment which was assumed to be 1,2,8,9-dibenzo-3,10-dibenzeneazo-6, 13-dichlorotriphenodioxazine. This could be sulphonated with sulphuric acid to give a direct dyestuff.

Recently Reichel and Balint[77]. used aminonaphthol sulphonic acids as intermediates for preparing triphenodioxazines. 2-Amino-5-naphthol-7-sodium sulphonate was condensed in aqueous alcohol with chloranil to give the water soluble violet diarylaminoquinone (LXVI) in good yield. On refluxing (LXVI) in nitrobenzene in the presence of an oxidizing agent, (LXVII) was formed. It gave red to violet shades on cellulose which could be developed by coupling with diazonium salts. It could be sulphurised under a variety of conditions with the ultimate formation of a dithiazine.



LXVI

LXVI



LXVII

OBJECT OF THE WORK

OBJECT OF THE WORK

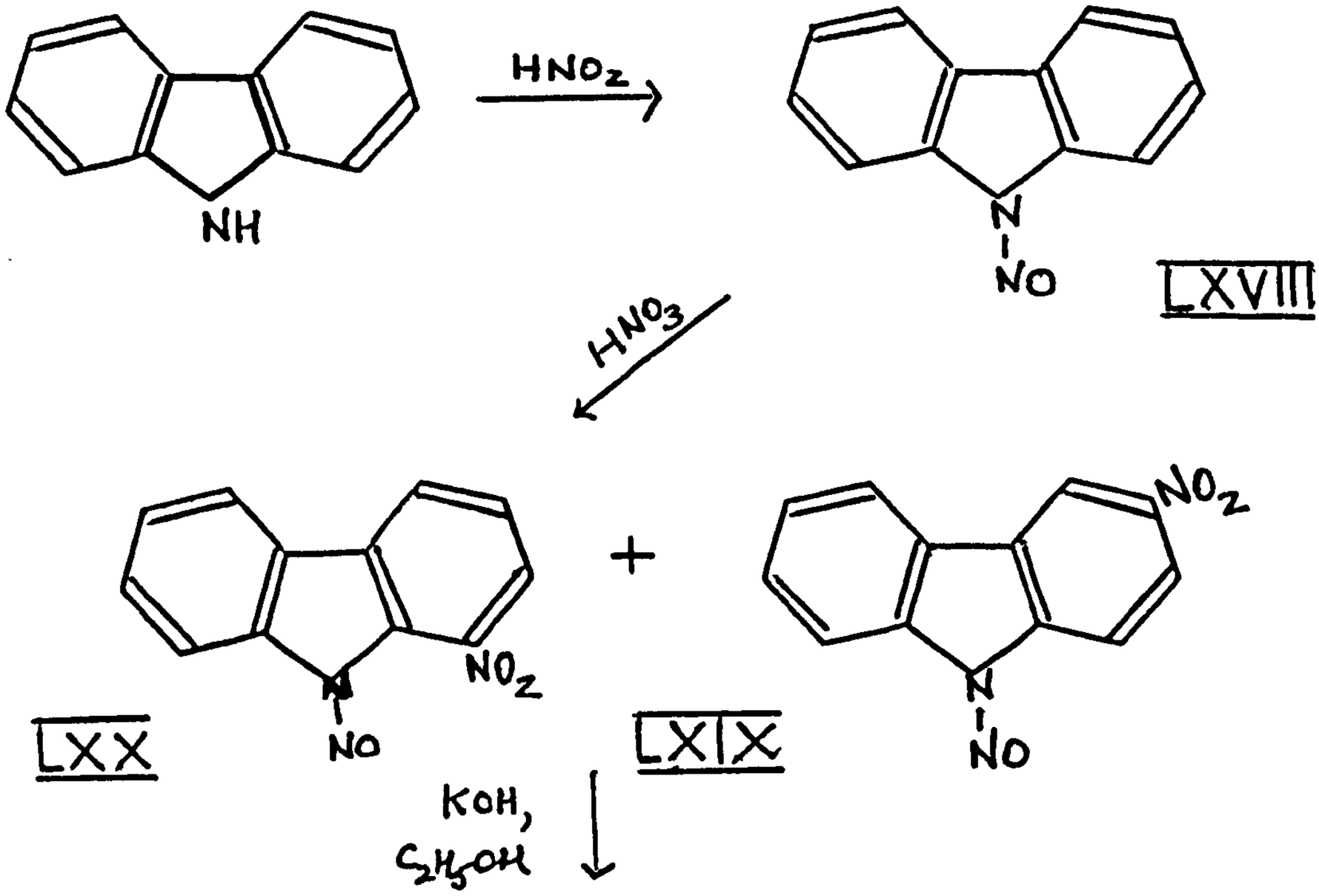
It had been known for some time that when an arylamine was condensed with chloranil, the resulting arylaminoquinone could be cyclised in a high boiling solvent containing an oxidizing agent, to a triphenodioxazine derivative. By variation of the arylamine, triphenodioxazines of high tinctorial power could be obtained. In the present work, it was proposed to prepare several of these triphenodioxazine derivatives in a pure state, examine their properties and attempt to elucidate the mechanism of cyclisation of arylaminoquinones to triphenodioxazines.

EXPERIMENTAL DISCUSSION

EXPERIMENTAL DISCUSSION

The preparation of 3-aminocarbazole from the reduction of 3-nitrocarbazole.

Preparation of 3-nitrocarbazole



The basis of this method involved the direct nitration of carbazole.

Carbazole is reactive to electrophilic reagents in positions 3 and 6. It is less reactive in positions 1, 8, and 9. Nitration initially produces a 3-nitrocarbazole together with a little 1-nitrocarbazole (compare diphenylamine). Further nitration produces 3,6-dinitrocarbazole as the main product.

Ruff and Stein[78.] prepared nitrous fumes from starch and nitric acid and passed these into a solution of carbazole in glacial acetic acid. Yellow needles of 9-nitroso-3-nitrocarbazole (LXIX), m.p. 166.5°, were obtained. This gave on boiling in amyl alcohol yellow needles of 3-nitrocarbazole (LXXI), m.p. 208.5°. Ziersh[79.] nitrated carbazole in glacial acetic acid with concentrated nitric acid at 80°. He filtered the mixture when cool to obtain (LXXI) on the filter, m.p. 205°, the filtrate giving 1-nitrocarbazole (LXXII), m.p. 164°, on pouring into water. Whitner[80.] repeated this work, but obtained the same results by nitrating at 60°. It was thought that it might be possible to obtain a fairly pure product by nitrating carbazole according to the patent literature.[81.] Carbazole was slurried with a dispersing agent in water and then treated with nitric acid (63%) at 78° for 6 hours. The green product so

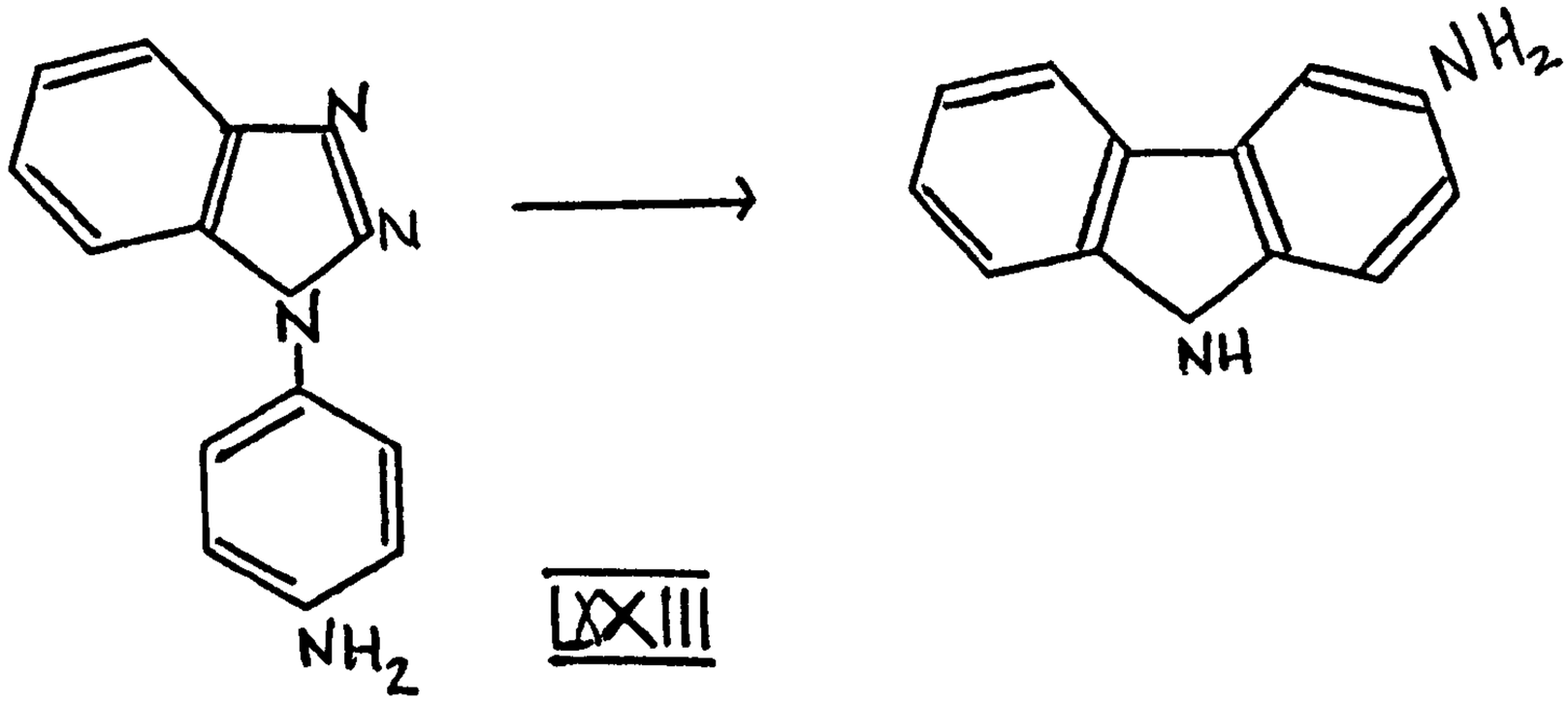
obtained was extremely impure and it was not considered worthwhile to continue with this method. The method chosen was that of Linemann.[82]. If carbazole was treated with sodium nitrite and acid, a 9-nitroso-group was formed. This on nitration, gave mainly a 3-nitro-group as the amount of 1-substitution would presumably be reduced due to steric factors. A suspension of carbazole in glacial acetic acid was treated with an equimolar proportion of aqueous sodium nitrite at 40-60°. Yellow needles of 9-nitrosocarbazole (LXVIII), m.p. 82°, were obtained. It was unnecessary to isolate (LXVIII) so it was treated <u>in situ</u> with concentrated nitric acid (d = 1.40) and glacial acetic acid. After stirring for some time, a green solid was obtained which consisted of 3-nitro-9-nitrosocarbazole (LXIX) and some 1-nitro-9-nitrosocarbazole (LXX). It was found unnecessary to recrystallise this green product and so it was used crude for the next stage. By boiling it with glacial acetic acid, decomposition set in, presumably with the formation of high melting polynitro-compounds. The nitroso-compound was decomposed with alcoholic potassium hydroxide solution to form 3-nitrocarbazole together with about 10-12% of 1-nitrocarbazole. According to Lindemann, purification could be effected by recrystallising from a

set volume of glacial acetic acid, filtering off the 3-nitrocarbazole on cooling, and leaving the 1-nitrocarbazole in the mother liquor. The 3-nitrocarbazole obtained in the present work, melted between 180° and 205° and thin layer chromatography showed it to still contain some 1-nitrocarbazole. The separation of these isomers was effected by using their different solubilities in boiling ligroin (b.p. 80-100°); 3-nitrocarbazole being insoluble whilst 1-nitrocarbazole was sparingly soluble. The mixture was thus separated by extraction with ligroin in a Soxhlet apparatus, the 1-nitrocarbazole (LXXII) being finally obtained on recrystallisation from ethanol as bright yellow needles, m.p. 189-191°. 3-Nitrocarbazole (LXXI) gave yellow needles from ethanol, m.p. 216-218°. Lindemann suggested the product obtained by earlier workers and melting at 164° was possibly a 2- or 4-nitrocarbazole. Morgan and Mitchell[83.] however, have shown it to be an 8:5 molecular complex of (LXXI) and (LXXII).

Reduction of 3-nitrocarbazole to 3-aminocarbazole

3-Nitrocarbazole has been readily reduced under various conditions. Ziersh[79.] reduced an alcoholic solution of it with sodium dithionite but the yield was low. Stannous chloride in acetic acid[78, 82.] has also been used. None of these methods were tried however, as it was thought more convenient to use iron and hydrochloric acid. An excess of finely divided iron was added to an alcoholic solution of 3-nitrocarbazole containing some hydrochloric acid. After refluxing it for 3 hours, crude 3-aminocarbazole was obtained in 94% yield. Recrystallisation gave 3-aminocarbazole as buff crystals, m.p. 254-256°. It was characterised as its acetyl derivative, 3-acetyl-aminocarbazole, m.p. 217-219°.

Ullmann[84.] proved the structure of 3-aminocarbazole by distilling 1-(4-aminophenyl)benztriazole (LXXIII).



LXXIII

The attempted preparation of 8,18-dichlorodiindolo [3,2-b; 3', 2'-m] triphenodioxazine.

Preparation of 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone.

The procedure contained in the B.I.O.S. reports[81] was employed. Two molecular proportions of 3-amino-carbazole were condensed with one molecular proportion of chloranil, in absolute ethanol containing some anhydrous sodium acetate as an acid binder. The mixture was stirred at room temperature for 5 hours. Another process described the experiment as above, but the mixture was refluxed in 50% ethanol. It was thought best to keep the temperature to a minimum as this removed the possibility of any unpleasant side effects that might occur, and also, 3-aminocarbazole was sufficiently reactive to condense with chloranil at room temperature. The product so obtained was extremely intractable and could only be purified by extraction of the soluble impurities with solvents. It was soluble in boiling dimethyl phthalate, but after boiling for a few minutes, rapid conversion to a purple component occurred. Continual boiling resulted in a dulling of the colour with apparent decomposition. It was thought the purple colour was due to a mixture of

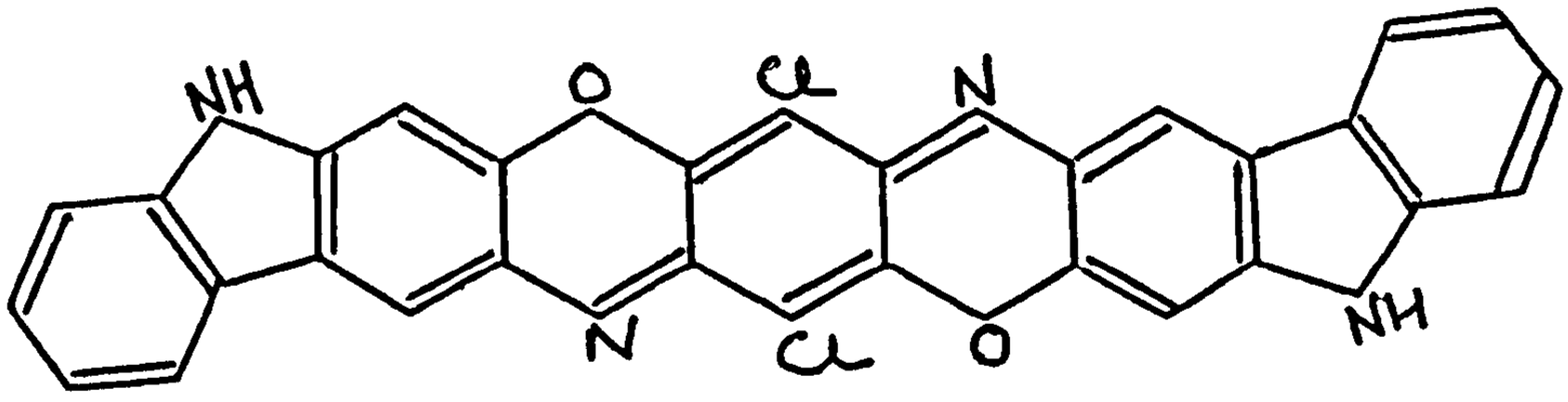
carbazole triphenodioxazine derivatives which rapidly decomposed at the high temperature employed.

The effect of sulphuric acid on 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone.

The quinone was shaken with concentrated sulphuric acid for 24 hours and the resulting deep blue mixture filtered. Some of the quinone remains undissolved and this was left on the filter. The deep blue liquid was poured onto ice-water, and a brown-red powder was obtained, soluble in concentrated sulphuric acid to give a dull blue colour. The powder was neutralised with barium carbonate, filtered, and the filtrate concentrated. The filtrate deposited a small amount of brown solid which was soluble in water to give a white precipitate with sulphuric acid. This indicated the presence of a soluble barium salt but the analysis gave an ash figure which was too high for a sulphonic acid derivative of 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone. Besides sulphonation, some form of cyclisation could have occurred but there was no positive evidence to that effect. It was hoped to repeat this experiment at a later date but time did not permit.

Attempted cyclisation to the triphenodioxazine

2,5-Di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone was refluxed with about 60% of its own weight of p-toluenesulphonyl chloride in dry nitrobenzene as described in the B.I.O.S. reports.[81.] A violet powder was obtained which appeared to be very impure. After extracting it with acetone and 10% alcoholic potassium hydroxide, the resulting product was recrystallised with great difficulty to give shining green needles. The analysis did not agree with the formula for 8,18-dichlorodiindolo [3,2-b; 3′, 2′-m] triphenodioxazine (L). Examination by thin layer chromatography showed there to be two main violet components present. The needles had the characteristics of a triphenodioxazine but the analysis indicated a drop in the chlorine figure with an increase in the carbon, hydrogen, and nitrogen figures. From later work (see page 111), it appeared likely that the product was a mixture of (L) and (LXXIV).



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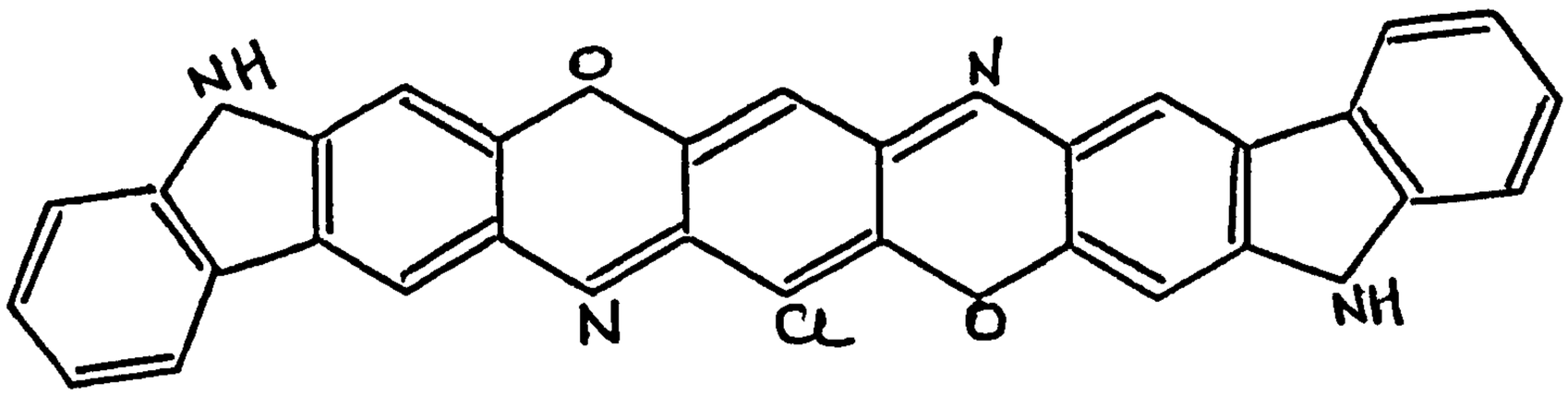
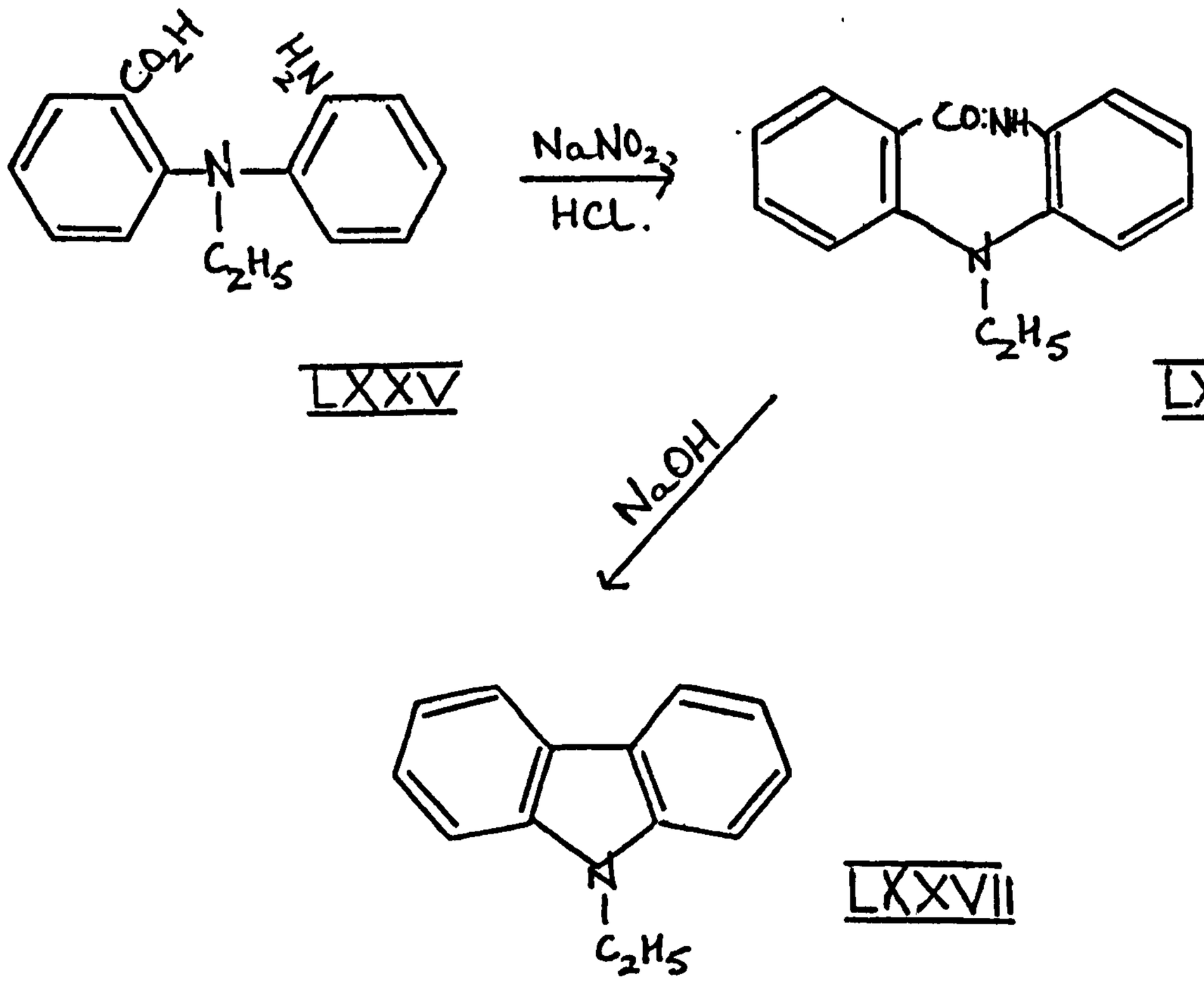


LXXIV

The preparation of 3-amino-9-ethylcarbazole

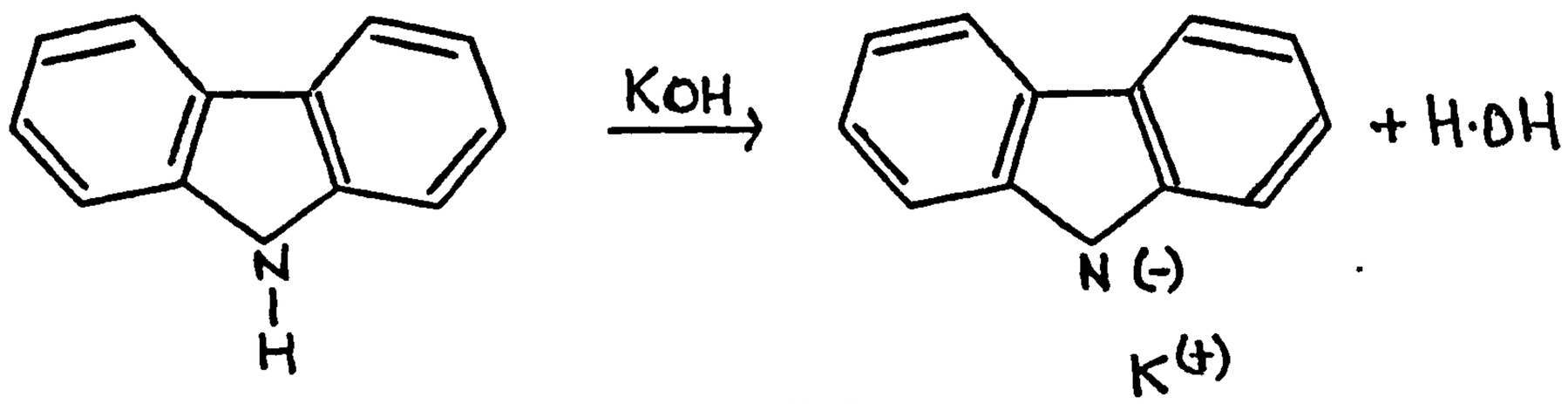
Preparation of 9-ethylcarbazole

It was originally prepared by Graebe[85] who heated carbazole, ethyl iodide, and potassium hydroxide, together in a sealed tube at 160-170°. He obtained it as colourless needles, m.p. 67-68°. Burton and Gibson[86] obtained it by diazotising 2-amino-2′-carboxy-N-ethyldiphenylamine (LXXV), the product rearranging to a lactam (LXXVI). On treating (LXXVI) with sodium hydroxide, 9-ethylcarbazole (LXXVII) was obtained in 41% yield, m.p. 67-68°.



Neither of these methods were used owing to the low yields. The method chosen was a modification of that due to Stephens and Tucker[87]. who heated a mixture of carbazole, sodium hydroxide solution and diethyl sulphate, in acetone for 30 minutes - 1 hour. The mixture was poured into water and (LXXVII) was obtained on recrystallisation as colourless needles, m.p. 66-67°. This method was found to be unreliable as in several cases, the carbazole was incompletely ethylated. It was thought that this was due to the incomplete formation of the carbazole anion with sodium hydroxide.

Carbazole itself will not react with electrophilic reagents at the -N- atom as there is an insufficiency of electrons to cause the attraction of an electron accepting group. The formation of the anion (LXXVIII) rectifies this and the -N- atom now carries a negative charge making it reactive towards electrophilic reagents.



LXXVIII

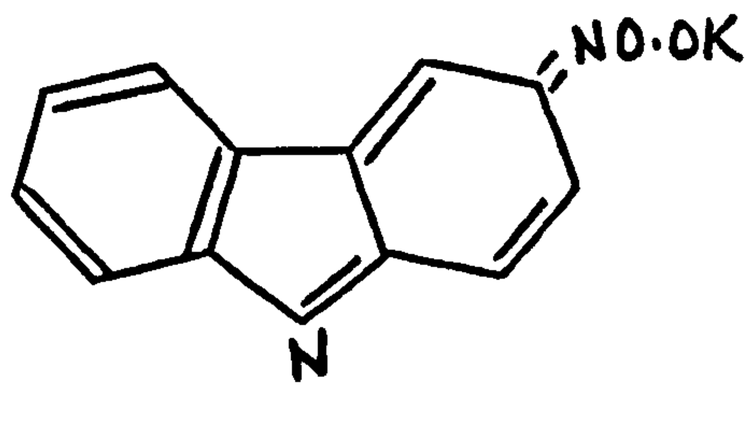
Carbazole was dissolved in acetone and an excess of

potassium hydroxide added. Potassium hydroxide was used as it was more soluble in water than sodium hydroxide and was thought to combine with the carbazole more readily. An olive solution was formed, possibly due to this anion formation, and to this an excess of diethyl sulphate was added. 9-Ethylcarbazole was readily formed in good yield, forming white needles, m.p. 69-70°.

Preparation of 3-nitro-9-ethylcarbazole.

Method 1.

Stevens and Tucker[87] noticed that 3-nitrocarbazole dissolved in potassium hydroxide solution to form a deep red colour which they attributed to an aci-form (LXXIX).



LXXIX

In attempting to isolate the aci-ether, in which they were unsuccessful, they found that alkyl halides readily gave the 9-alkyl derivative of 3-nitrocarbazole. In this method, 3-nitrocarbazole in absolute ethanol was mixed with an excess of potassium hydroxide solution.

The red mixture was refluxed with an excess of diethyl sulphate for some hours. The solution eventually lost its red colour, changing to yellow, and gave on cooling, crystals of 3-nitro-9-ethylcarbazole, m.p. 123-124°.

Method 2.

It was decided to try a method involving the direct nitration of 9-ethylcarbazole as the above method gave a low yield. Morgan and Read[88.] added a solution of 9-ethylcarbazole to 43.4% nitric acid at a low temperature. This preparation was repeated but it was found that replacement of the benzene with toluene gave a much more easily handled mixture since a lower temperature could be attained without freezing of the solvent. 3-Nitro-9-ethylcarbazole was obtained in 50% yield, and was identical to the product obtained by Method 1.

Method 3.

It was also found possible to hitrate 9-ethylcarbazole in glacial acetic acid directly with concentrated nitric acid. Nitration normally occurred in the 1- and 3-positions on carbazole but the 9-ethyl group effectively steered the nitro-group into the 3-position; the 1-position presumably being hindered by the ethyl group.

9-Ethylcarbazole in glacial acetic acid, was treated with an equivalent amount of concentrated nitric acid at room temperature. The advantage in this method was that the reaction mixture was homogeneous and was much easier to control. The yield obtained was at least as good as in Method 2, the product being identical to those obtained in Methods 1 and 2. 3-Nitro-9-ethylcarbazole was obtained as yellow needles, m.p. 127-128°.

Reduction to 3-amino-9-ethylcarbazole.

Lindemann[83.] reduced 3-nitro-9-ethylcarbazole with stannous chloride and acetic acid and the resulting 3-amino-9-ethylcarbazole recrystallised many times from benzene to afford pinkish crystals, m.p. 113-114°. The acetyl derivative was obtained as bluish white needles, m.p. 190°.

The B.I.O.S. report[89.] stated that 3-nitro-9-ethylcarbazole was reduced in ethanol containing 12.5% sodium sulphide solution. A brown crystalline powder, m.p. 88°, was obtained, which was claimed to be 3-amino-9-ethylcarbazole of 96-99% purity. This method was repeated but it was found necessary to use 30% sodium sulphide solution, the mixture being refluxed for 30 hours. The product was obtained in 73% yield and melted over a range of 15°,

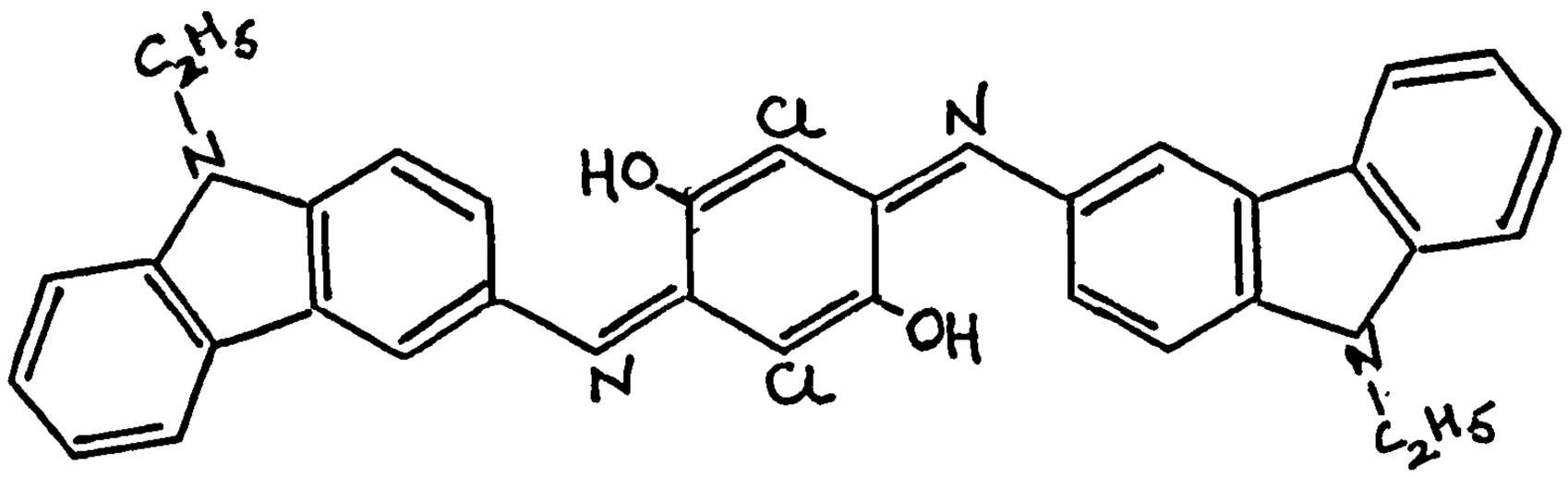
(85-100°), no sharp melting point at 88° being obtained. Recrystallisation of the product from benzene, alcohols, or ether, did not afford a product which remained solid over 100°. A similar effect occurred when sublimation was attempted. It could only be satisfactorily recrystallised from ligroin (b.p. 60-80°) to afford pink needles of 3-amino-9-ethylcarbazole, m.p. 120-121°. It was characterised as its acetyl derivative, m.p. 198-199.5°, and as its hydrochloride.

It was evident that the product Lindemann obtained from benzene was impure, and the product claimed to be 97-99% 3-amino-9-ethylcarbazole, m.p. 88°, by B.I.O.S.[89.], must be completely unfounded as ,from the melting range obtained, it was indicated that the product was very impure.

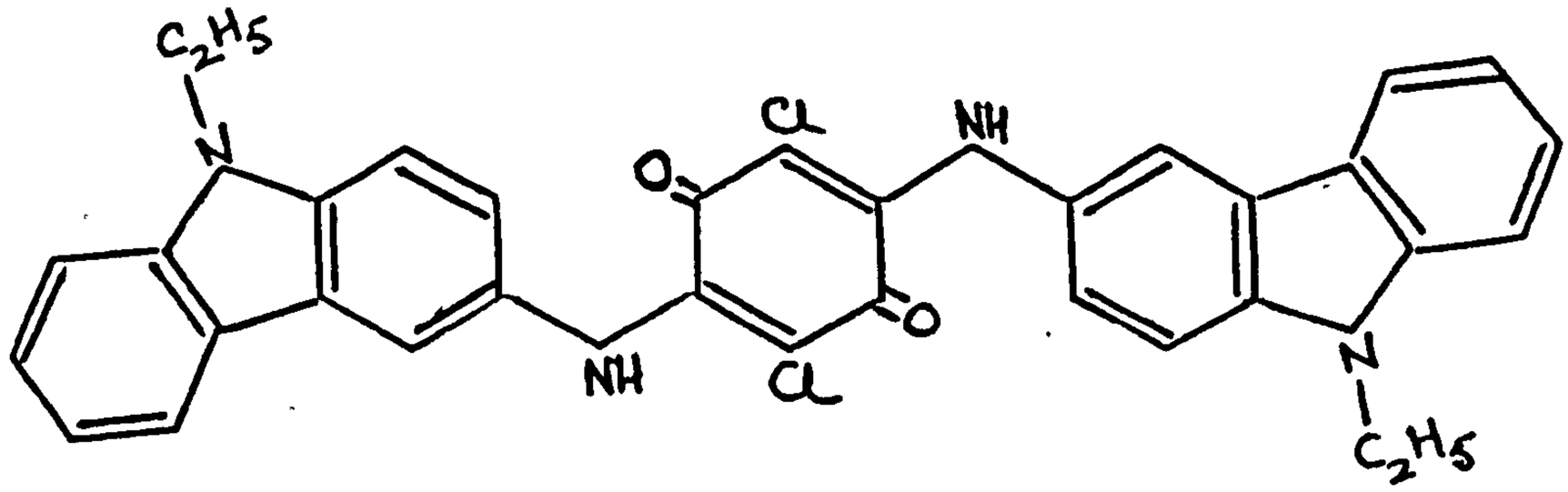
<u>The preparation of 2,5-di(9-ethyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone</u>.

3-Amino-9-ethylcarbazole was condensed with chloranil according to the B.I.O.S. reports.[89]. 3-Amino-9-ethylcarbazole was condensed with a little more than one half molecular proportion of chloranil in ethanol in the presence of sodium acetate as an acid binder. The reaction was carried out under nitrogen to prevent any external oxidation of the amine. After stirring and refluxing a red powder was obtained. This red powder was readily soluble in hot acetone but after some time, a blue-purple solid was deposited which was sparingly soluble. This purple solid was obtained crystalline, m.p. 306-308°, and the analysis agreed with the structure for 2,5-di(9-ethyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone (LXXXI). If LXXXI was heated at the melting point for a few minutes, it appeared to loose hydrogen chloride with the formation of green needles which presumably were a triphenodioxazine derivative. Both the red and purple compounds had identical absorption spectra when examined in dioxan. It appeared that the two components were similar and could either be two different crystal modifications or else were tautomers. (LXXX) would presumably be the red compound as the -OH groups would impart solubility. Infra-

red measurements on (LXXXI) showed the presence of a medium carbonyl vibration at 1638 cm.$^{-1}$, and a strong absorption at 3270 cm.$^{-1}$, for secondary amine vibration, which would indicate that it was (LXXXI). Had time permitted, it would have been of interest to carry out infra-red measurements on the red powder and compare the absorption measurements at 3270 cm.$^{-1}$ and 1638 cm.$^{-1}$, as if it possessed the tautomeric form (LXXX), one would have expected some modifications in the absorption characteristics.



LXXX



LXXXI

The preparation of 5,15-diethyl-8,18-dichlorodiindolo [3,2-b; 3', 2'-m] triphenodioxazine. (Pigment Violet R).

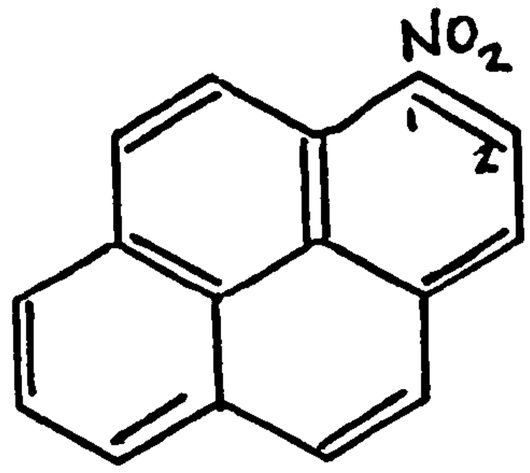
This was prepared according to the B.I.O.S. report.[89] 3-Amino-9-ethylcarbazole was condensed with chloranil under similar conditions to the previous experiment except o-dichlorobenzene was used as the solvent. After condensing at 65° for 2 hours it was refluxed for some time with benzenesulphonyl chloride. Benzenesulphonyl chloride, like p-toluenesulphonyl chloride, being used in the capacity of a condensing agent. The formation of the triphenodioxazine took place readily and 5,15-diethyl-8,18-dichlorodiindolo [3,2-b; 3',2'-m] triphenodioxazine was obtained as microscopic green needles. It was very sparingly soluble in organic solvents, the presence of the ethyl group apparently reducing the solubility. The converse was noticed in the arylaminoquinones, (LXXX) being reasonably soluble in most solvents whilst 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone being insoluble. Here, the introduction of a 9-ethyl group aided solubility.

The triphenodioxazine gave a strong absorption at 1580 $cm.^{-1}$ which indicated the presence of a quinonoid

nitrogen vibration. The absence of a strong band at or around 3270 cm.$^{-1}$, indicated the loss of the secondary amine grouping which gave further indication that cyclisation had taken place.

The preparation of 1-aminopyrene

Preparation of 1-nitropyrene



LXXXII

Graebe[90.] first prepared 1-nitropyrene (LXXXII) by treating pyrene with about an equal quantity of nitric acid (d = 1.20) and then warming with some water on a steam-bath for 2 hours. He obtained a yellow compound, m.p. 140-142°. Goldschmiedt[91.] added an ethereal solution of potassium nitrite to a solution of pyrene in ether, containing some dilute sulphuric acid. 1-Nitropyrene was obtained as yellow needles, m.p. 148-149°. Neither of these methods were tried as there was some doubt over the experimental conditions and the products obtained. It was decided to use the method of Vollmann.[92.] Pyrene, slurried in glacial acetic acid, was treated with slightly less than an equimolar portion of concentrated nitric acid at 50° to afford 1-nitropyrene as yellow needles, m.p.

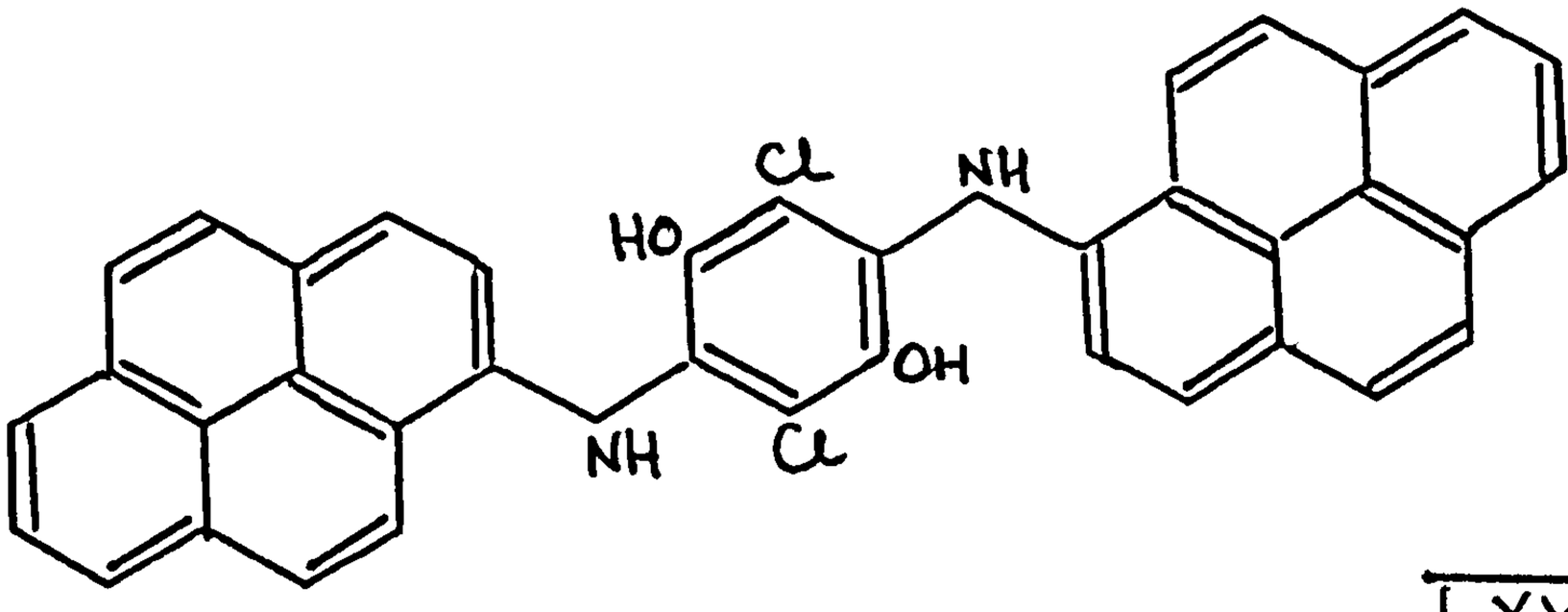
153-154°. On repeating this method and varying the times of nitration, it was found that the pyrene was incompletely nitrated and that the final product contained large amounts of unreacted pyrene. As the work was done on 98-99% pure pyrene, it was thought that the earlier work may have involved work on impurer samples of pyrene thus giving varying results. The experiment was modified by treating pyrene with slightly more than an equimolar portion of concentrated nitric acid at 50° and then raising the temperature to 95° uhtil the 1-nitropyrene begins to separate. 1-Nitropyrene (LXXXII) was obtained as yellow woolly needles, m.p. 152-154°. Care must be taken not to add a large excess of nitric acid or else dinitration would take place.

Reduction to 1-aminopyrene

Vollmann[92] reduced 1-nitropyrene in ethanol with 61% sodium hydrosulphide solution but this apparently gave a poor yield of amine. The method employed was to reduce 1-nitropyrene in ethanol with iron and hydrochloric acid. The product was recrystallised from cyclohexane to give 1-aminopyrene, m.p. 114-116°, in 60% yield. It was characterised by preparing its formyl derivative; 1-formyl-aminopyrene gave very pale green needles, m.p. 228-230°.

The preparation of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone

The condensation was carried out by adapting the method described in the B.I.O.S. report.[93] Two molecular proportions of 1-aminopyrene were condensed with slightly over one molecular proportion of chloranil in the presence of sodium acetate. The B.I.O.S. report stated that the condensation was carried out in 90% ethanol, containing some o-chlorophenol to aid the solubility of 1-aminopyrene in ethanol, at 0-5°, and then at 25°. It was found that the same result could be obtained by carrying out the condensation in absolute ethanol and refluxing, 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone being obtained in 70% yield. It was purified by reducing to 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-quinol (LXXXIII) being obtained as a grey crystalline powder, and the analysis agreeing with (LXXXIII).



LXXXIII

By heating (LXXXIII) in nitrobenzene at 190° for 45 minutes, 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone was obtained as purplish brown needles. Attempts to measure the absorption spectrum of (LXXXIII) in either dioxan or pyridine failed, as the initially colourless solutions gradually turned brown with the formation of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone.

The attempted cyclisation of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone

Method 1.

The patent literature's[65.] procedure was carried out as it was thought that it offered a fairly easy practical method for cyclising the quinone. The quinone was mixed with 50% of its weight of 2,4-dinitrophenol and refluxed in hitrobenzene for 4 hours. On obtaining the final product, its colour and tests indicated it to be starting materials. The experiment was repeated with the time of reflux, 8 hours, but again there was no cyclisation. The patent described the isolation of metallic grey-green needles of the triphenodioxazine but this was not observed. It can only be assumed that failure of this method was probably due to the temperature of cyclisation being insufficiently high.

Method 2.

This method involved the adaption of the B.I.O.S. report.[93.] 2,5-Di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone and 50% of its weight of p-toluenesulphonyl chloride were refluxed for 30 minutes in 1-chloronaphthalene (b.p. 259^{o}). It was essential to avoid exceeding the time of reflux as the resulting triphenodioxazine was very easily

decomposed at the temperature employed. The deep blue product, obtained on filtering the cold reaction mixture, was chromatographed on a steam heated alumina column. It was necessary when chromatographing these compounds to use a heated column as these compounds were only soluble in hot organic solvents such as o-dichlorobenzene. A deep blue band and a violet band were formed, the latter being completely detached from the column. This violet product was soluble in acetone but an insufficient quantity of it was obtained for further investigation. The blue band was eluted and the eluate concentrated to give a bluish green microcrystalline product which analysed correctly for 8,19-dichlorodiphenaleno[1,9-ab; 1',9'-lm]tripheno-dioxazine. The infra-red absorption measurements showed the presence of a strong absorption at 1580 $cm.^{-1}$ which corresponded to a quinonoid nitrogen stretching vibration.

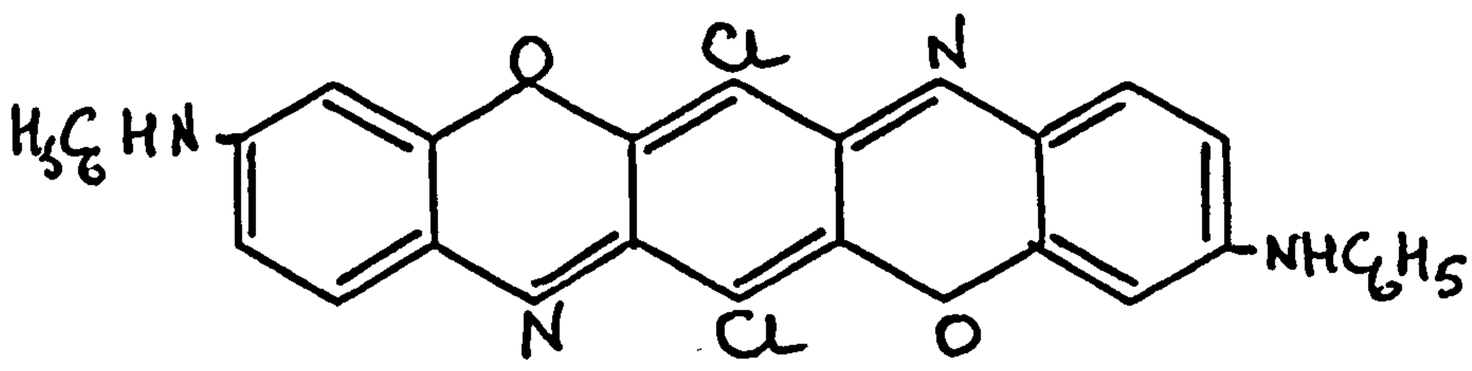
The preparation of 2,5-di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone.

4-Aminodiphenylamine was condensed with a little over one half of a molecular proportion of chloranil in ethanol, containing some sodium acetate as an acid binder. After refluxing the mixture for 8 hours under nitrogen, the arylaminoquinone was obtained as a black crystalline powder in 60% yield. On recrystallisation, 2,5-di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone was obtained as black lustrous needles of high melting point.

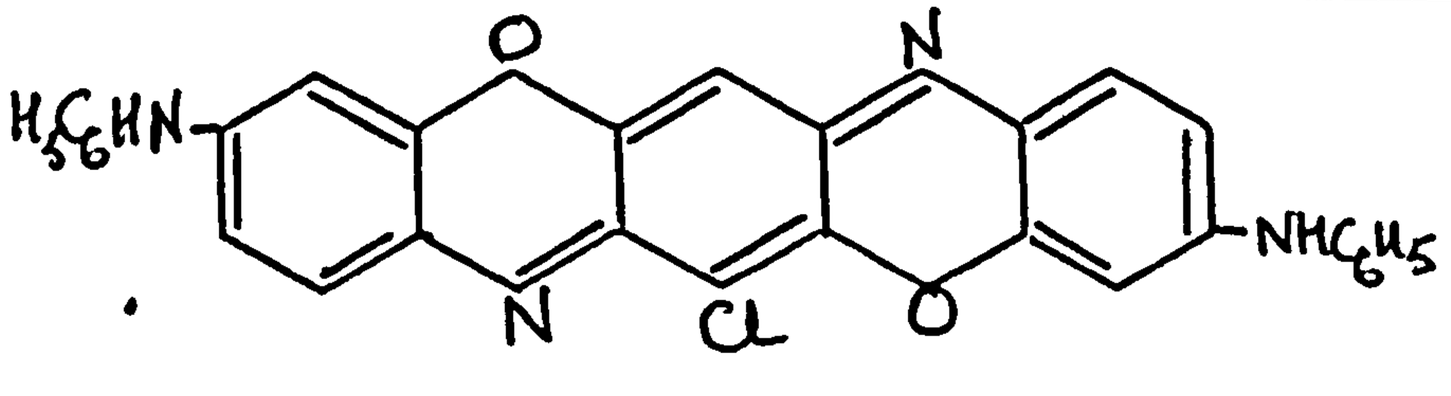
Attempted cyclisation of 2,5-di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone.

The attempted cyclisation was carried out according to the method described in the patent literature.[94] The above quinone was refluxed for 8 hours in nitrobenzene, containing a little phosphorous pentachloride and precipitated manganese dioxide as condensing agents. The resulting mixture was cooled, filtered and washed, to give a greenish crystalline powder. A sample was recrystallised from o-dichlorobenzene to give small bronze needles of no melting point. The chlorine analysis showed that the quantity was half that expected for 3,10-dianilino-6,13-dichlorotripheno-dioxazine (LXXXIV). A sample examined by thin layer

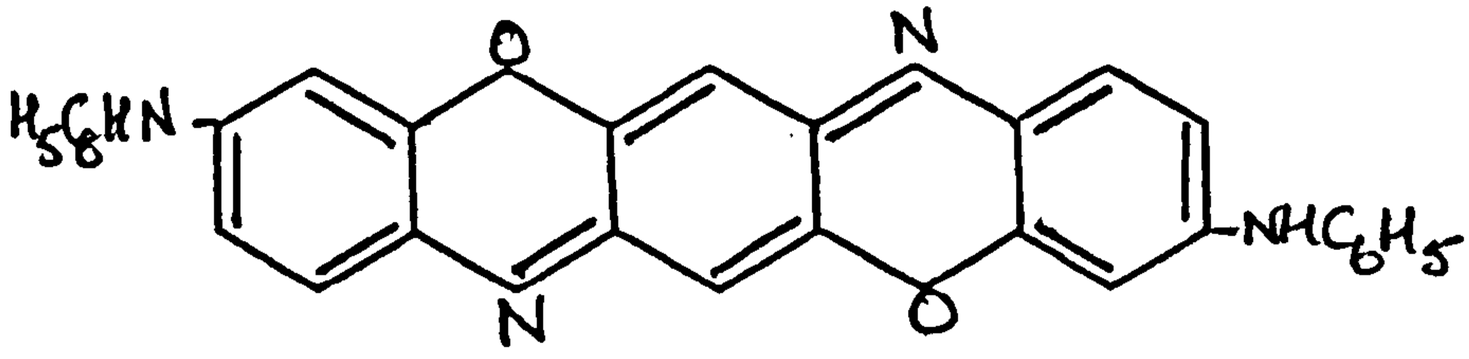
chromatography showed the presence of three main blue components, all occurring very close together on the chromatoplate. In view of the low chlorine figure and the fact that tests and the method of preparation indicated that the compounds were of the triphenodioxazine structure, it seemed very likely they were composed of the structures (LXXXIV), (LXXXV), and (LXXXVI).



LXXXIV



LXXXV

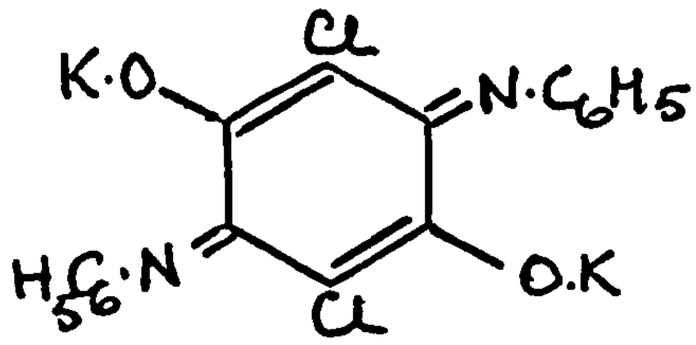


LXXXVI

The condensation of chloranil with aniline.

Knappe and Schultz[39.] condensed four molecular proportions of aniline with one molecular proportion of chloranil in ethanol and obtained 2,5-dianilino-3,6-dichloro-1,4-benzoquinone as black-brown crystals. This method was modified in the patent literature[95.] where one molecular proportion of chloranil was condensed with two molecular proportions of aniline in 1,2,4-trichlorobenzene. Two molecular proportions of anhydrous sodium acetate being employed to remove the hydrogen chloride formed on condensation. The patent claimed that after washing the resulting product with alcoholic potassium hydroxide, 6,13-dichlorotriphenodioxazine was formed. The experiment was carried out using reflux times of 9 hours and 20 hours, but no triphenodioxazine derivative was isolated. The product obtained gave shining black plates, m.p. 330-333°. The analysis agreed with the structure of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone. Infra-red measurements showed the presence of a strong absorption at 1660 $cm.^{-1}$ corresponding to a carbonyl stretching vibration and a further strong absorption at 3270 $cm.^{-1}$ corresponding to a secondary amine stretching vibration which substantiated

the conclusion that the product was 2,5-dianilino-3,6-dichloro-1,4-benzoquinone. Solubility in alcoholic potassium hydroxide solution indicated formation of the tautomer (LXXXVII).



LXXXVII

Solutions of alcoholic potassium hydroxide could be therefore used to remove the arylaminoquinone from a mixture of an arylaminoquinone and a triphenodioxazine, the latter being insoluble. The continued heating of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone at its melting point resulted in the loss of hydrogen chloride with the formation of new products. The investigation of this reaction is described on page 94 .

The condensation of 2,6-dichloro-1,4-benzoquinone with aniline.

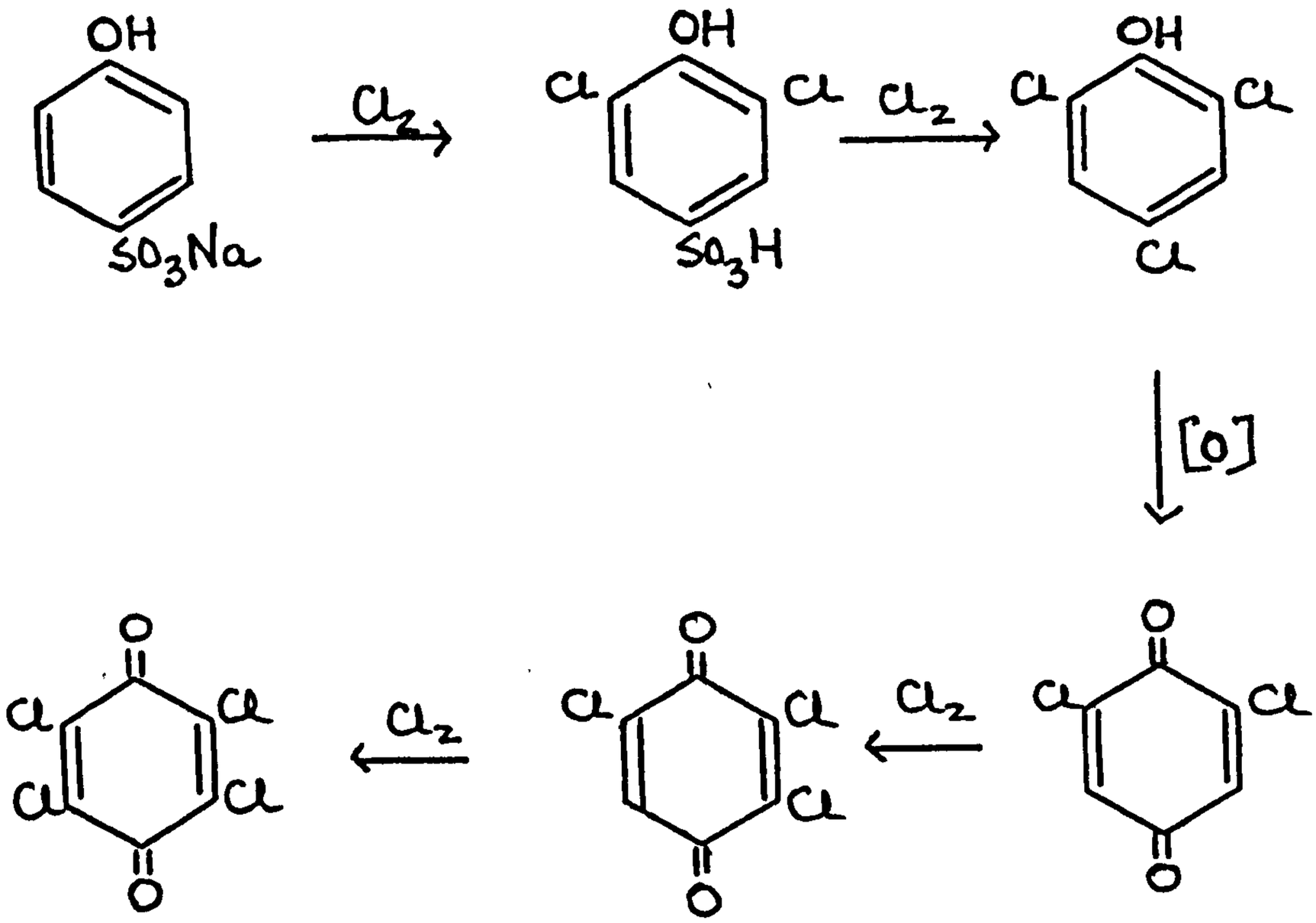
Preparation of 2,4,6-trichlorophenol.

Method 1.

o-Chlorophenol was heated on a steam-bath whilst a stream of chlorine was passed through it until the o-chlorophenol had absorbed two atoms of chlorine. This gave 2,4,6-trichlorophenol as white needles, m.p. 58-61° (literature quoted 68°). The low melting point was probably due to the presence of dichlorophenols. In view of the impurity of the product it was decided to use another method.

Method 2.

According to Datta and Mitter,[96] phenol-p-sulphonic acid could be chlorinated in aqueous solution quantitatively to 2,4,6-trichlorophenol. Sodium phenol-p-sulphonate was dissolved in about eight times its own weight of water and a stream of chlorine was then passed through. 2,4,6-Trichlorophenol was eventually precipitated and formed white needles, m.p. 65-67°. A quantitative yield could not be obtained, due to the gradual formation of halogenated quinones caused by the gradual build up of hypochlorous acid, which acted as an oxidizing agent and led to the ultimate formation of chloranil.



The use of the free acid, varying the volume of water used and the rate of chlorination, did not improve the yield which was generally 35% on an average. The final product was much purer than in method 1, if it was isolated before oxidation took place.

Preparation of 2,6-dichloro-1,4-benzoquinone.

The original method of Faust,[21] who treated 2,4,6-trichlorophenol with fuming nitric acid and then added the dark coloured product to water in order to obtain 2,6-dichloro-1,4-benzoquinone, was not attempted, as it was obvious that an impure product was obtained.

A.R. Ling[97] treated a solution of 2,4,6-trichlorophenol in ethanol with fuming nitric acid and this gave a purer product. This method was tried and found to be satisfactory. 2,4,6-Trichlorophenol in absolute ethanol was cooled to below 0^{o} and fuming nitric acid (d = 1.51) added very carefully, avoiding any rise in temperature and thus letting the reaction get out of control. Yellow crystals separated out and 2,6-dichloro-1,4-benzoquinone was obtained as yellow prismatic needles, m.p. 120-121^{o}. It was essential to ensure that the 2,4,6-trichlorophenol was completely free of chlorine or else high halogenated 1,4-benzoquinones were formed on oxidation.

Condensation of 2,6-dichloro-1,4-benzoquinone with aniline.

This compound was described by Niemeyer[40] who condensed aniline with 2,6-dichloro-1,4-benzoquinone in either ethanol or acetic acid to afford red-brown crystals, m.p. 262^{o}, of 2,5-dianilino-3-chloro-1,4-benzoquinone. The experiment was carried out by dissolving 2,6-dichloro-1,4-benzoquinone in absolute ethanol containing some sodium acetate and adding aniline dropwise. After refluxing for 5 hours, 2,5-dianilino-3-chloro-1,4-benzoquinone was obtained as purple needles, m.p. 269-270^{o}.

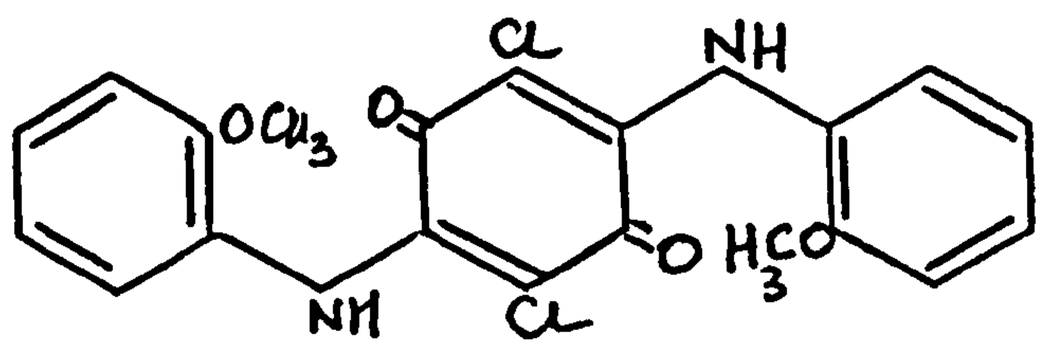
The condensation of 1,4-benzoquinone with aniline.

Aniline was condensed with an excess of 1,4-benzoquinone in absolute ethanol. After refluxing for some time, 2,5-dianilino-1,4-benzoquinone was obtained as plates, m.p. 354-356°, which were very sparingly soluble in organic solvents. Infra-red measurements indicated a strong carbonyl stretching vibration at 1643 cm.$^{-1}$ and a medium secondary amine stretching vibration at 3260 cm.$^{-1}$.

H. and W. Snida[45.] obtained 2,5-dianilino-1,4-benzoquinone by a similar method to above as purple crystals, m.p. 345°.

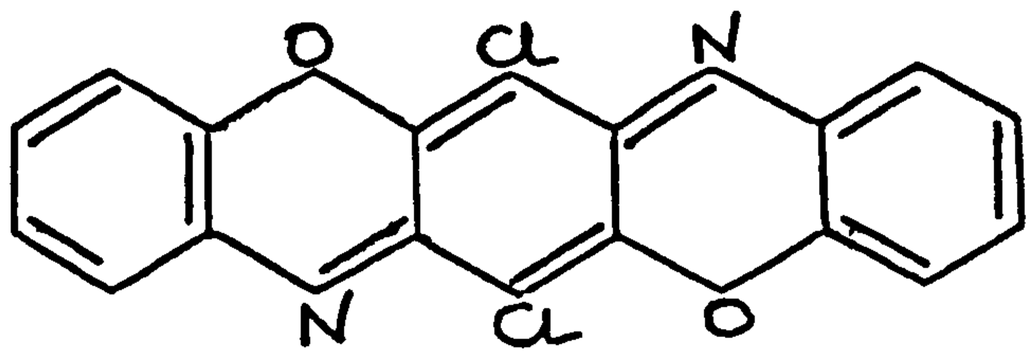
The preparation of 6,13-dichlorotriphenodioxazine

In 1937, Fierz-David and Blangley[70.] described a new method of preparing triphenodioxazines involving the cleavage of ethers. It had been known for some time,[98.] that aromatic ethers, especially those which contained a strong negative substituent in the o-position, were readily dealkylated with anhydrous aluminium chloride to the corresponding phenol. o-Anisidine was condensed with chloranil and the resulting 2,5-di(o-anisidino)-3,6-dichloro-1,4-benzoquinone (LXXXVIII) demethylated and ring closed with aluminium chloride to 6,13-dichloro-triphenodioxazine (LXXXIX).



LXXXVIII

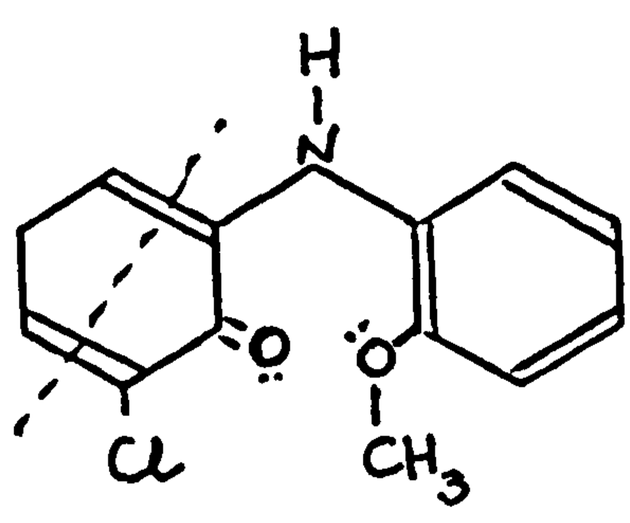
↓ $AlCl_3$



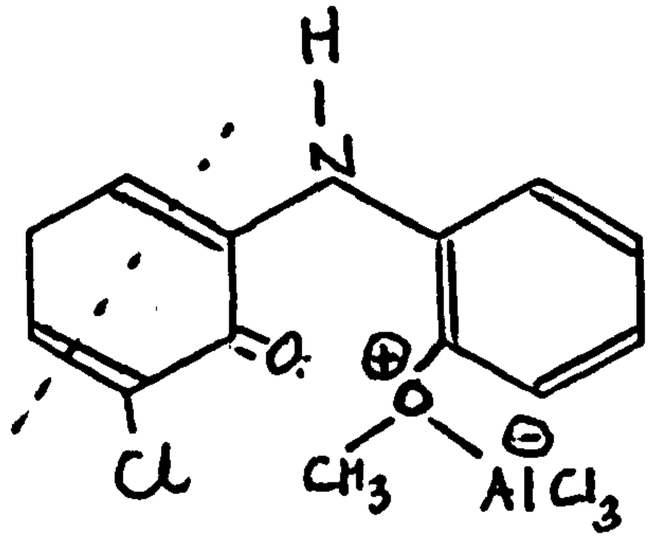
+ $2CH_3OH$

LXXXIX

The mechanism of this dealkylation is not fully understood but it is suggested that it may proceed by the following scheme:-

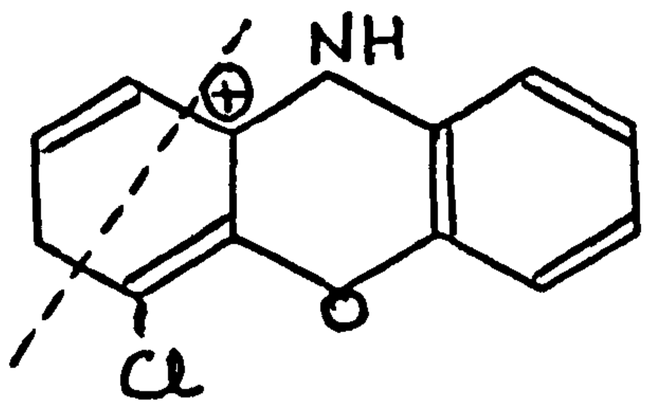


$AlCl_3$

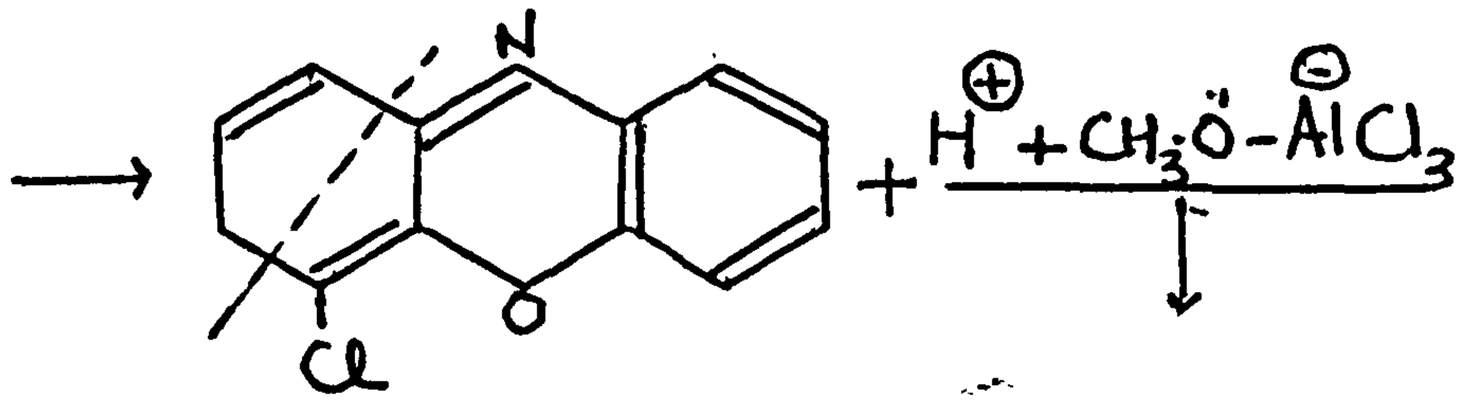


XC

XCI



XCII



By considering one half of (LXXXVIII), it is assumed that the lone pair of electrons on the methoxy

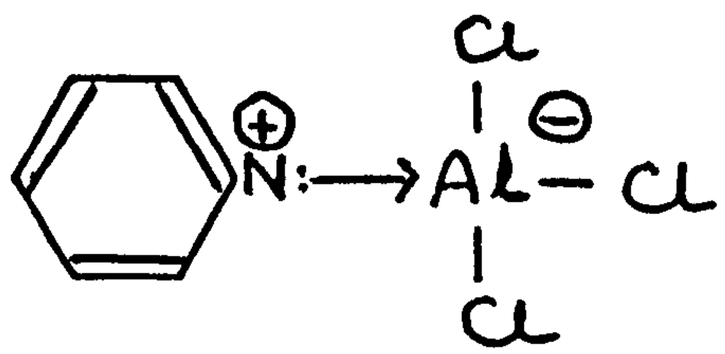
group attract aluminium chloride with the formation of the coloured complex (XC). At this stage there may be association between the carbonyl group and aluminium chloride but it is assumed that the ether split is the initiating step. The complex could then loose the charged entity CH_3-O-$AlCl_3^{(-)}$ with the formation of the carbonium ion (XCl). Mesomeric shifts would then involve ring closure and rearrangement of bonds, and the (+) migrating as shown in (XCll). The charge is then lost as a proton with the formation of the oxazine ring, which is in a more stable form of resonance. The proton destroys the entity CH_3-O-$AlCl_3^{(-)}$ as shown, with formation of methanol. Although only one half of the structure is shown, both halves must cyclise simultaneously.

Condensation of o-anisidine with chloranil

o-Anisidine was added to a half molecular proportion of chloranil and some sodium acetate, in o-dichlorobenzene. The mixture was refluxed for 3 hours and on cooling and filtering, 2,5-di(o-anisidino)-3,6-dichloro-1,4-benzoquinone was obtained as plates, m.p. 257-259°, in 70% yield. Fierz-David in the original paper[70]. made no mention of the purification and subsequent analysis of the product he obtained by condensing chloranil with o-anisidine.

Cyclisation to 6,13-dichlorotriphenodioxazine

The quinone was cyclised in pyridine with anhydrous aluminium chloride. Pyridine afforded a suitable solvent for aluminium chloride owing to the formation of the pyridine soluble complex (XCIII).



XCIII

One molecular proportion of the quinone was added gradually to a little less than eight molecular proportions of aluminium chloride in pyridine. The resulting blue mixture was refluxed for 20 hours, cooled, and the aluminium chloride removed with hydrochloric acid to leave 6,13-dichlorotriphenodioxazine in good yield. There was some evidence that 6-chlorotripheno-dioxazine was formed in small amounts.

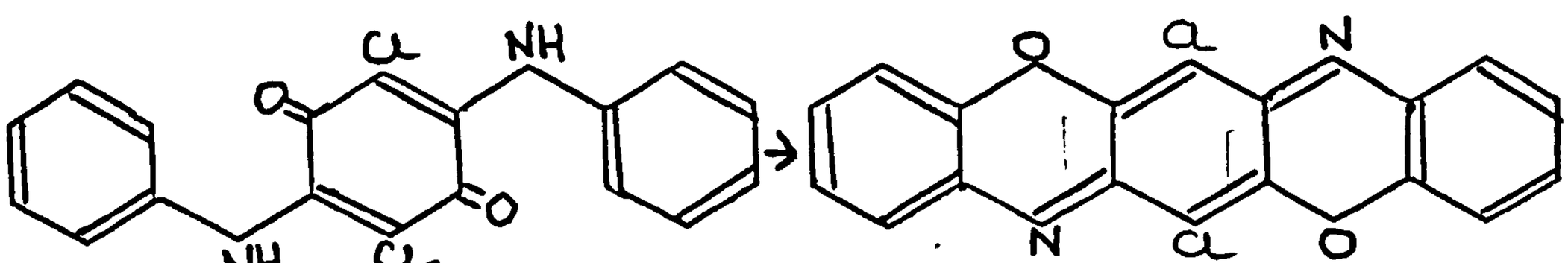
6,13-Dichlorotriphenodioxazine was readily reduced in xylene with an excess of phenylhydrazine to form the colourless 7,14-dihydro-6,13-dichlorotriphenodioxazine. This compound was unstable and if warmed or left to stand in air, it gradually lost hydrogen with the formation of the red triphenodioxazine.

The condensation of chloranil with o-phenetidine

The condensation was carried out under similar conditions to the o-anisidino derivative. o-Phenetidine was added to one half molecular proportion of chloranil and sodium acetate in o-dichlorobenzene. After refluxing for 3 hours, standing and filtering, 2,5-di(o-phenetidino)-3,6-dichloro-1,4-benzoquinone was obtained as black lustrous plates, m.p. 211-213°. It was readily soluble in organic solvents compared to 2,5-dianilino-3,6-dichloro-1,4-benzoquinone, with a corresponding reduction in melting point. This was presumably due to the alkoxy group hindering the attractive forces between the arylaminoquinone.

The pyrolysis of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone in diphenyl ether.

This experiment was carried out in order to assess the effect of a high temperature solvent on 2,5-dianilino-3,6-dichloro-1,4-benzoquinone. The quinone was dissolved in diphenyl ether and refluxed for the required time interval under an atmosphere of nitrogen. Samples were withdrawn at the required time intervals and the optical density at the peak wavelength of 6,13-dichloro-triphenodioxazine (655 mμ) in concentrated sulphuric acid measured. It was thought at this time that the following mechanism took place:-



+ 4H

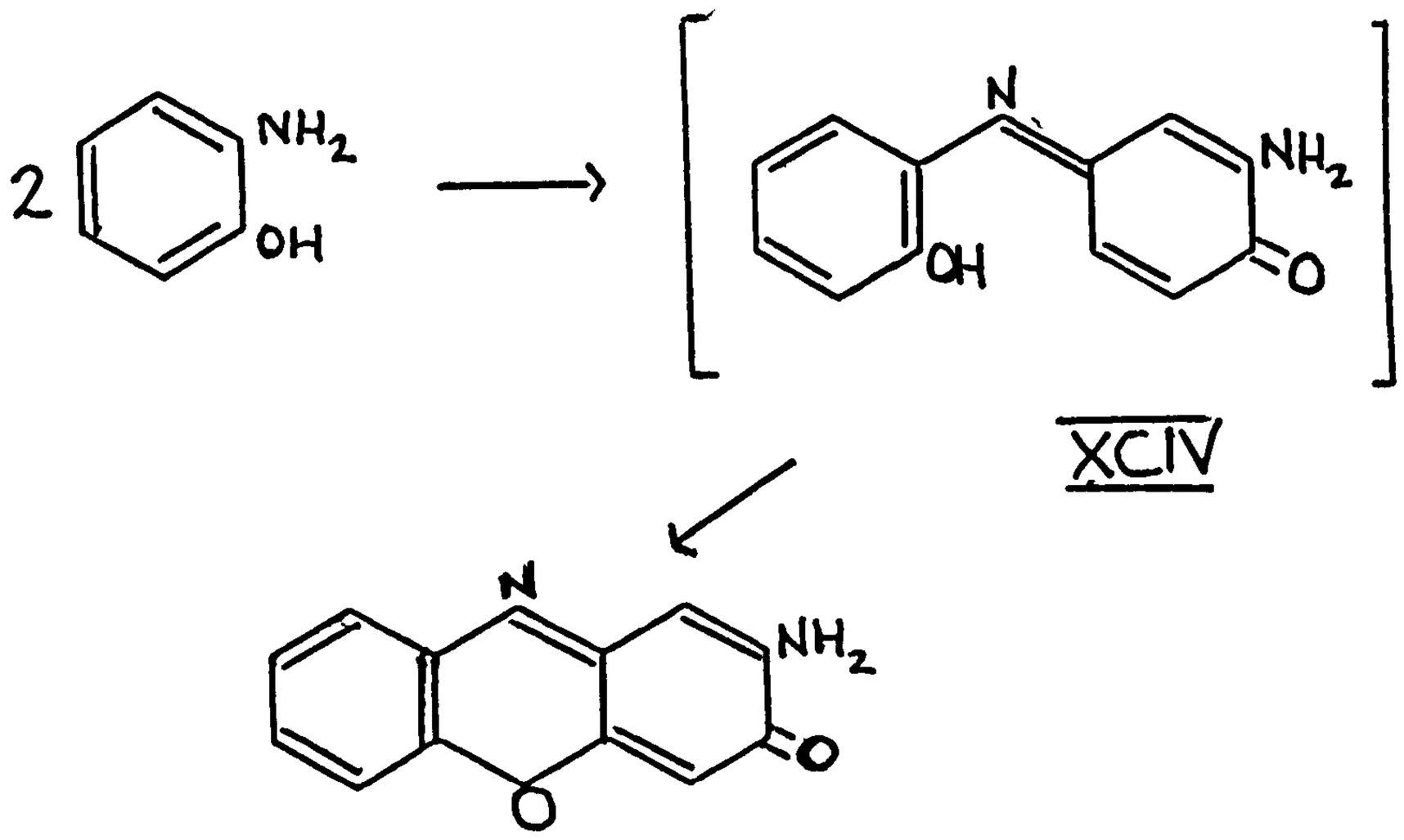
From the results obtained, the maximum optical density measured was 0.47 which very roughly was equivalent to 0.47/1.95 or 24.2% cyclisation, where 1.95 was $E^{0.001\%}_{1\ cm.}$ for 6,13-dichlorotriphenodioxazine in sulphuric acid at 655 mμ. After 48 hours, decomposition

appeared to take place. It was thought that only about 30% of the starting material appeared to cyclise, the remaining 70% was inert and required the action of compounds such as p-toluenesulphonyl chloride for further cyclisation. It was also noticed that 2,5-dianilino-3,6-dichloro-1,4-benzoquinone appeared much less reactive in its cyclising characteristics than the higher molecular weight arylaminoquinones such as 2,5-di(9-ethyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone.

The preparation of triphenodioxazine

Preparation of 2-amino-3-phenoxazone.

o-Aminophenol was oxidized with mercuric oxide according to the method of Fischer and Jonas.[2] o-Aminophenol was dissolved in benzene and refluxed with yellow mercuric oxide for 7 hours. It was thought that the intermediate indoaniline (XCIV) was formed during the oxidation to 2-amino-3-phenoxazone.



The phenoxazone was obtained as small dark red needles, m.p. 250-252°, in 35% yield.

Condensation to triphenodioxazine.

o-Aminophenol hydrochloride was intimately mixed with 2-amino-3-phenoxazone in a mortar and then heated

together at 180° for 5 minutes. The resulting mass was extracted with methanol and water, to remove most of the impurities, and then the resulting solid chromatographed from o-dichlorobenzene. Fischer[3]. purified his product by sublimation but it was felt that chromatographic purification afforded a purer product in better yield. A steam heated alumina column was used as triphenodioxazine was virtually insoluble in cold o-dichlorobenzene. The resulting triphenodioxazine, which formed a strong orange-red-band on the column, was eluted to give a yellow-orange, strongly green fluorescent, eluate. It was obtained on concentrating the eluate, as glistening red plates. The condensation of o-aminophenol hydrochloride and 2-amino-3-phenoxazone only gave triphenodioxazine as no other isomer was ever formed. Triphenodioxazine was much less soluble than the corresponding 6,13-dichloro-derivative.

A new synthesis of triphenodioxazine.

It was hoped that the method for preparing 6,13-dichlorotriphenodioxazine[70]. might be extended to the preparation of triphenodioxazine.

Condensation of o-anisidine with 1,4-benzoquinone.

o-Anisidine was added gradually to an excess of 1,4-benzoquinone in absolute ethanol. After refluxing for 5 hours, a dark powder was obtained which on purification gave 2,5-di(o-anisidino)-1,4-benzoquinone as purple needles, m.p. 249-250°.

Cyclisation to triphenodioxazine.

One molecular proportion of 2,5-di(o-anisidino)-1,4-benzoquinone was added to a little less than eight molecular proportions of aluminium chloride in pyridine. On refluxing for 18 hours, the initial blue-violet mixture turned to a dull purple. On cooling, the aluminium chloride was removed with hydrochloric acid and the product purified to give a dark powder. A sample was chromatographed from o-dichlorobenzene to afford triphenodioxazine as red glistening plates. Comparison on thin layer chromatography with the product obtained

by the condensation of 2-amino-3-phenoxazone with o-aminophenol hydrochloride showed them to be identical. A considerable amount of impurity was present as was indicated on the alumina column, and this may have been due to the time of reflux during cyclisation, being too long.

The effect of heating 2,5-dianilino-3,6-dichloro-1,4-benzoquinone at its melting point.

As had already been noticed, both 2,5-dianilino-3,6-dichloro-1,4-benzoquinone and 2,5-di(9-ethyl-3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone both underwent some form of decomposition with loss of hydrogen chloride when heated at the melting point. It was thought advisable to study this effect with the anilino-derivative as any cyclisation taking place would be presumably slower than the carbazole derivative, and the solubility of the products in organic solvents would be greater owing to their lower molecular weight. A sample of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone was heated in a bath of boiling di-n-butyl phthalate for 4 minutes under a stream of nitrogen. The hydrogen chloride evolved was absorbed in standard sodium hydroxide solution and determined volumetrically. An attempt was made to measure any other gas by using a gas burette employing a water meniscus, the water dissolving any hydrogen chloride. No gas was found present and it can be assumed that no hydrogen was given off.

The product obtained was examined by thin layer chromatography and showed the presence of three orange

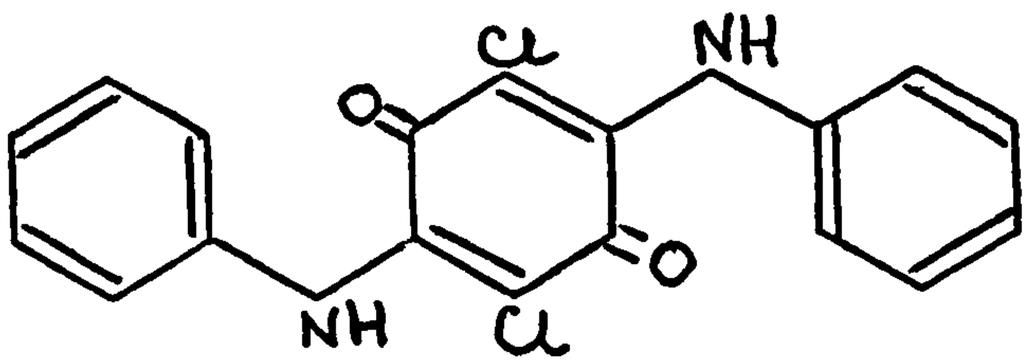
components and a yellow component. The product was chromatographed from o-dichlorobenzene on a steam heated alumina column. A dark purple band was formed together with a red band, the latter being fractioned at. The purple band was extracted and rechromatographed to afford a purple immobile band and a violet mobile band. The violet band was eluted to give a very small amount of violet solid which when examined by thin layer chromatography showed the presence of three violet components. It was thought that these were further decomposition products of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone occurring as a side reaction. The purple band was extracted with great difficulty to afford 2,5-dianilino-1,4-benzoquinone. These arylaminoquinones were extremely difficult to chromatograph owing to their strong retentive power on alumina.

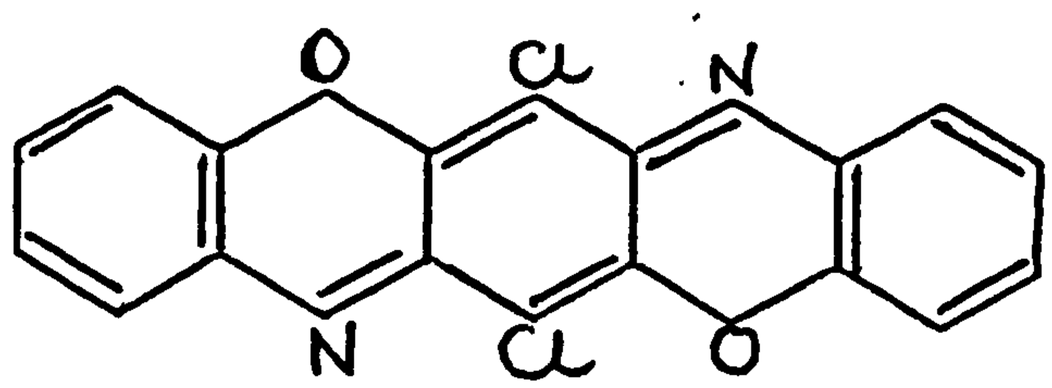
The first fraction from the red band consisted of 6,13-dichlorotriphenodioxazine (LXXXIX) as shown by analysis and comparison with an authentic sample by thin layer chromatography. The second fraction contained 6,13-dichlorotriphenodioxazine and a further orange component which was shown to be 6-chlorotriphenodioxazine (XCV). The third fraction contained, in addition to the forementioned dioxazines, a further orange component

which compared with triphenodioxazine (I) when examined by thin layer chromatography.

The three dioxazines gave no visible separation on the column but appeared as a diffuse red band, visible separation only occurring when they were chromatographed on a thin layer of Kieselgel G. The only qualitative method of separation involved fractional chromatographing of the components and continual testing of the consistency of the eluates by use of thin layer chromatography. Even this procedure could not completely separate triphenodioxazine, especially as it was present in such small amounts.

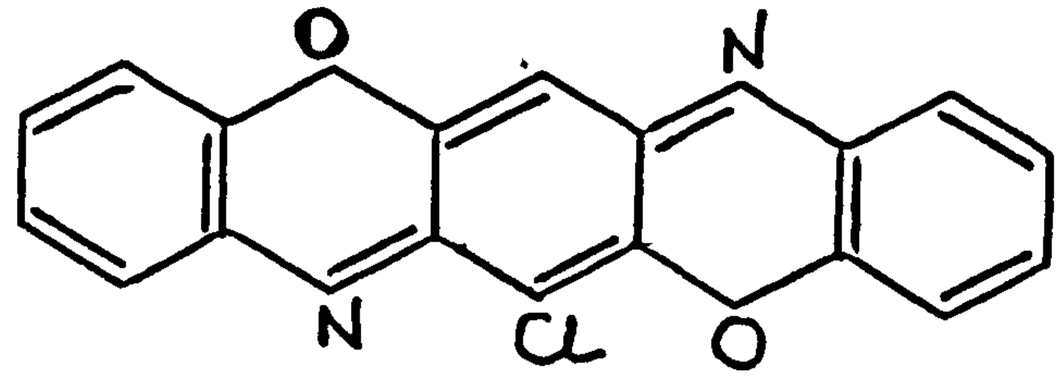
It appeared that the pyrolysis of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone occurred with the formation of the following products:-





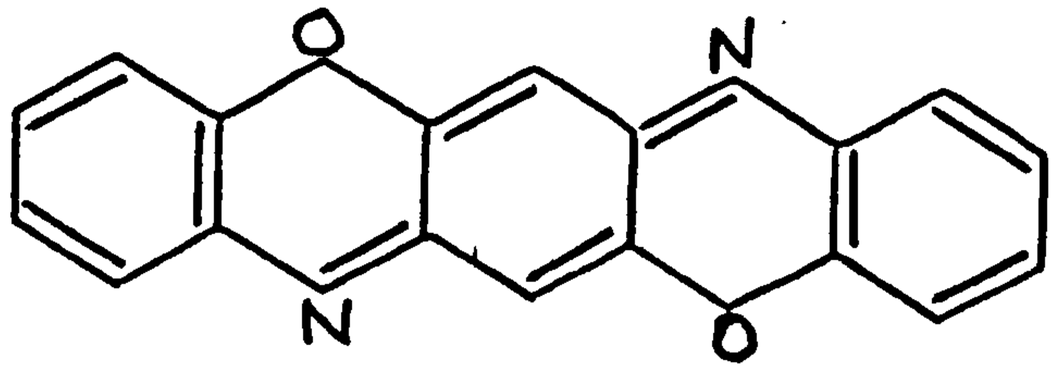
LXXXIX

+



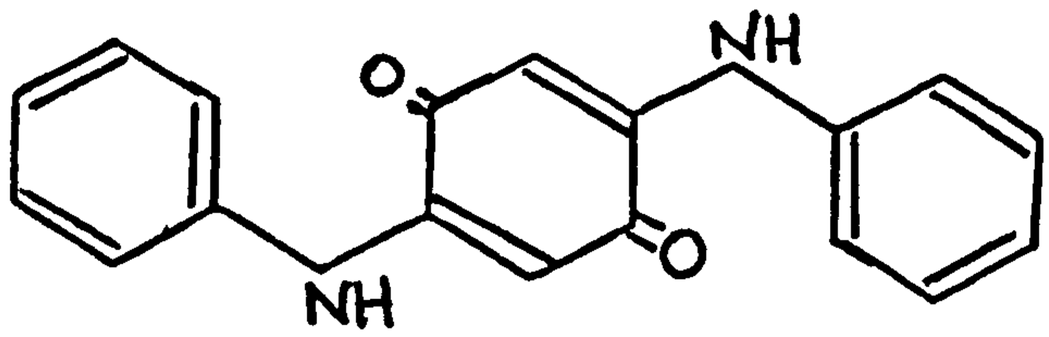
+

XCV



+

I



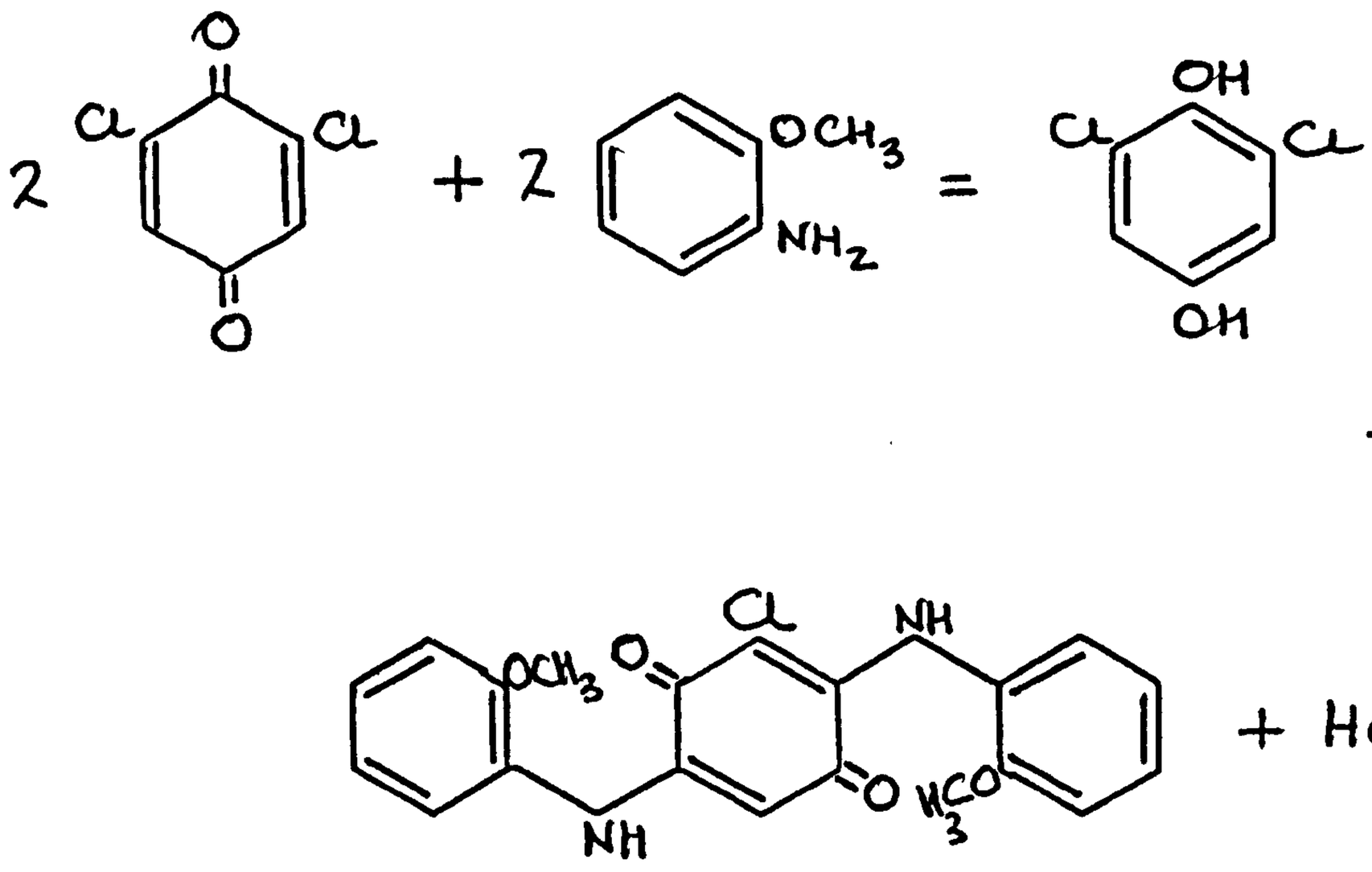
+ HCl

The synthesis of 6-chlorotriphenodioxazine.

This method involved the demethylation of a suitable o-anisidinoquinone as already carried out in the case of 6,13-dichlorotriphenodioxazine and tripheno-dioxazine.

Condensation of o anisidine with 2,6-dichloro-1,4-benzoquinone.

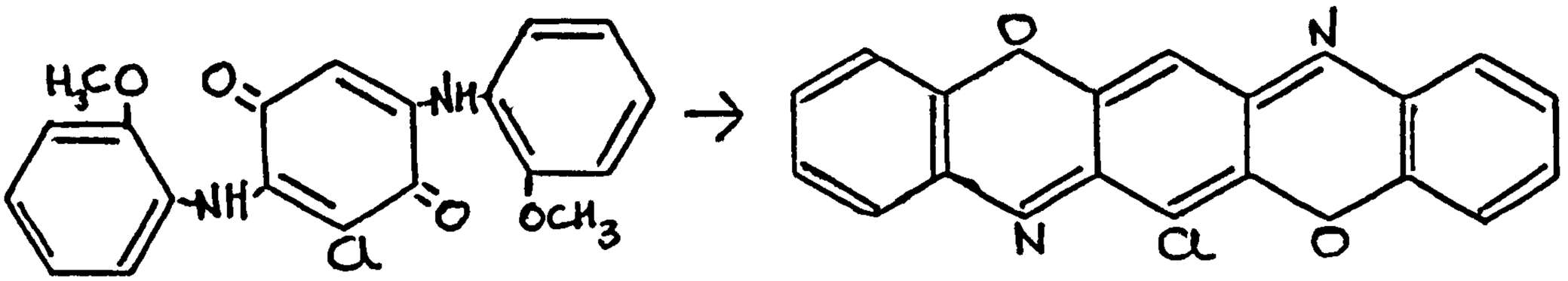
An equimolar portion of o-anisidine was added to 2,6-dichloro-1,4-benzoquinone in ethanol, containing some sodium acetate. The reaction was thought to follow the given scheme:-



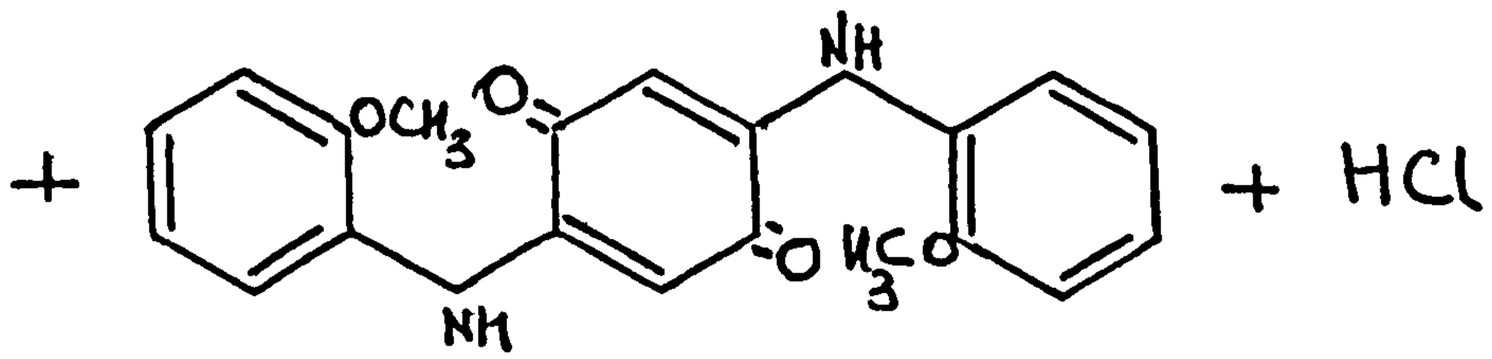
After refluxing for 5 hours, the mixture was cooled, filtered, and a sample purified to give 2,5-di(o-anisidino)-3-chloro-1,4-benzoquinone as small brown plates, m.p. 189-190°.

Cyclisation to 6-chlorotriphenodioxazine.

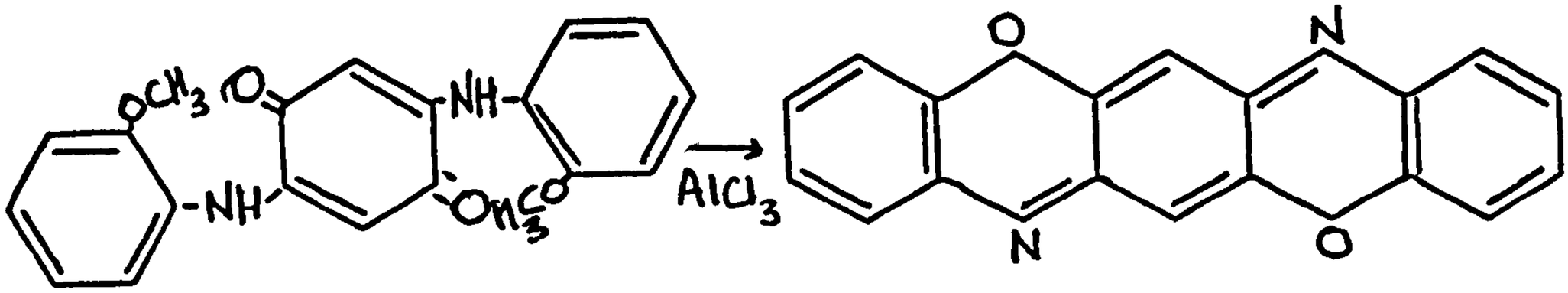
One molecular proportion of 2,5-di(o-anisidino)-3-chloro-1,4-benzoquinone was added to nine molecular proportions of aluminium chloride dissolved in pyridine. The resulting blue-violet mixture was refluxed for 20 hours, cooled, and the aluminium chloride removed with hydrochloric acid to leave a red-brown powder. A sample examined quantitatively and qualitatively by thin layer chromatography showed the presence of 6-chloro-triphenodioxazine with about 20% of triphenodioxazine as impurity. The triphenodioxazine could occur as a side reaction, viz:-



XCV



A small amount of 2,5-di(o-anisidino)-3-chloro-1,4-benzoquinone was dissociated by heat into (XCV) and 2,5-di(o-anisidino)-1,4-benzoquinone.

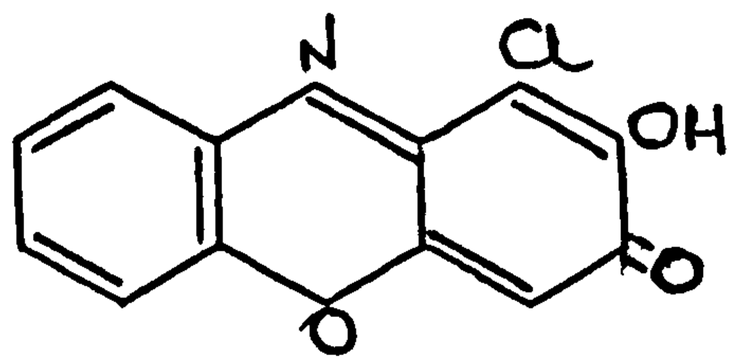


I

The 2,5-di(o-anisidino)-1,4-benzoquinone then ring closes under the influence of aluminium chloride forming triphenodioxazine.(I).

The crude product was chromatographed hot from o-dichlorobenzene to give red needles of 6-chlorotripheno-dioxazine (XCV), identical to the product obtained by the pyrolysis of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

It would have been of interest to prepare (XCV) by the condensation of o-aminophenol hydrochloride with 1-chloro-2-hydroxy-3-phenoxazone (XCVI), (XCVI) being prepared according to the method by Kehrmann,[4]. but time did not permit.



XCVI

The effect of heating 2,5-dianilino-1,4-benzoquinone at its melting point.

As 2,5-dianilino-3,6-dichloro-1,4-benzoquinone appeared to dissociate after heating at its melting point for some minutes, it was that it would be interesting to examine the effect with 2,5-dianilino-1,4-benzoquinone.

2,5-Dianilino-1,4-benzoquinone was heated at 360° for five minutes under an atmosphere of nitrogen. It was cooled, powdered, and a sample dissolved in o-dichlorobenzene and examined by thin layer chromatography. This showed only the presence of unchanged starting material.

The effect of a boiling solvent on 2,5-dianilino-1,4-benzoquinone.

Nitrobenzene.

2,5-Dianilino-1,4-benzoquinone was refluxed in nitrobenzene for 24 hours. The product obtained on cooling and filtering, was examined by thin layer chromatography. This showed only the presence of unchanged starting material and a sample was recrystallised to give 2,5-dianilino-1,4-benzoquinone as purple plates, m.p. 354-356°. By altering the time of reflux to 48 hours, there was still no change in the starting material. The oxidizing power of nitrobenzene obviously playing no part in the attempted cyclisation of 2,5-dianilino-1,4-benzoquinone.

Diphenyl ether.

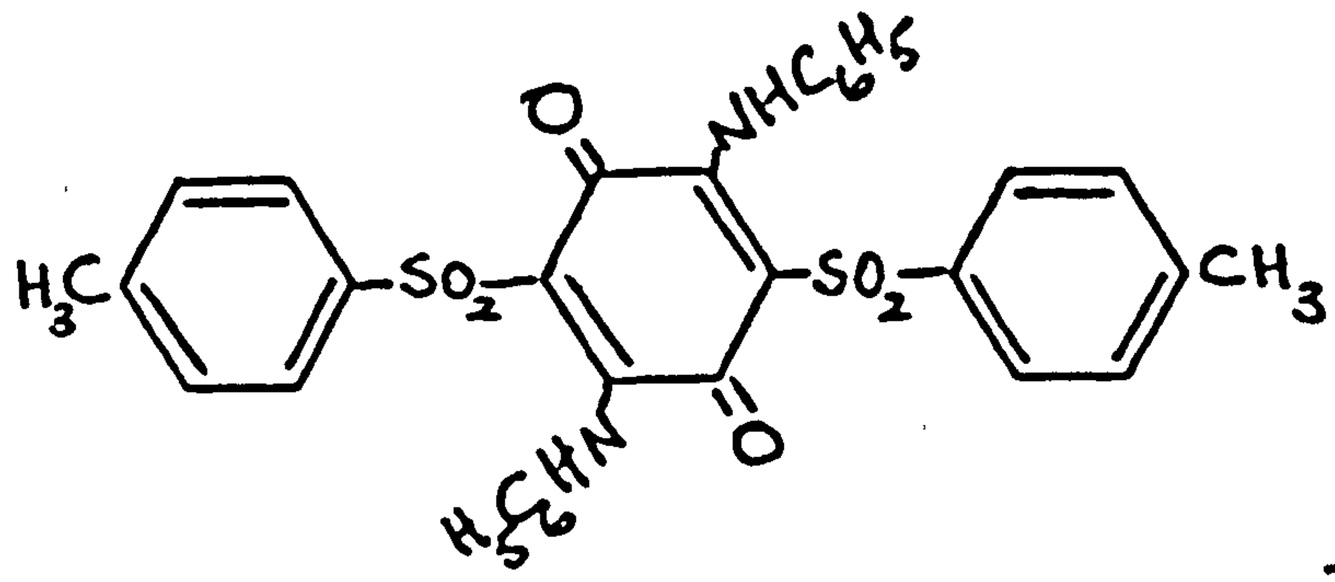
The experiment was repeated under the same conditions as above except that instead of nitrobenzene being employed as a solvent, diphenyl ether was used. Again, no cyclisation took place and the starting material was recovered unchanged.

The effect of condensing agents on 2,5-dianilino-1,4-benzoquinone.

p-Toluenesulphonyl chloride

Method 1.

In this method it was proposed to attempt to condense p-toluenesulphonyl chloride via the reactive chlorine to 2,5-dianilino-1,4-benzoquinone. It was thought possible that the following structure (XCVII) could occur, which could act as an intermediate during cyclisation.



XCVII

One molecular proportion of 2,5-dianilino-1,4-benzoquinone was refluxed in benzene with two molecular proportions of p-toluenesulphonyl chloride in the presence of sodium acetate. After 24 hours, unchanged starting material was recovered indicating that the H atoms on the quinone ring were unreactive.

Method 2.

The above experiment was repeated, without the presence of sodium acetate, using diphenyl ether as the solvent. After refluxing for 2 hours the experiment was abandoned owing to the considerable decomposition that took place.

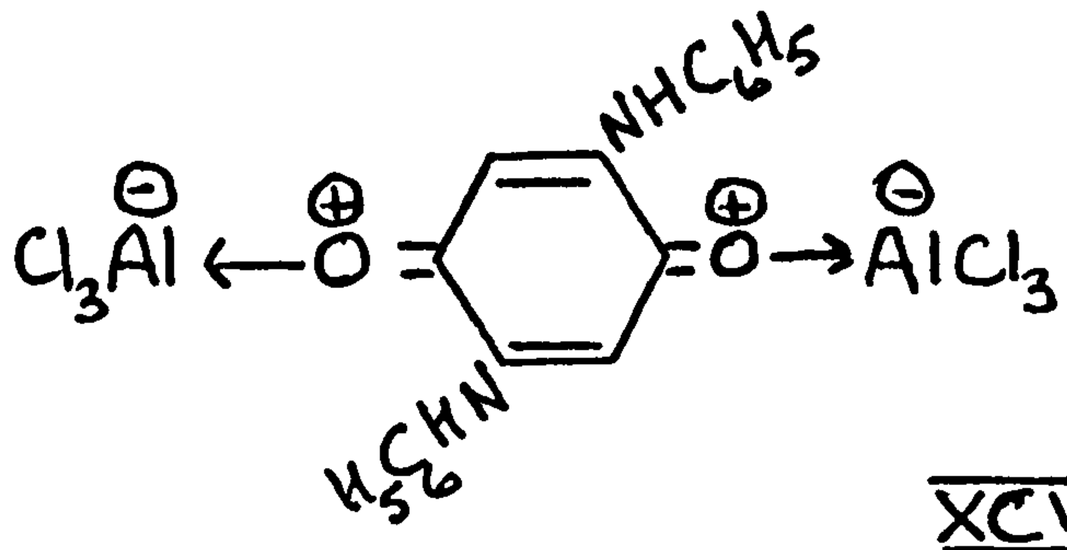
Method 3.

In this method, the solvent used was 1,2,4-trichlorobenzene, and the refluxing period extended to 24 hours. A deep red-violet solution was formed which on examination by thin layer chromatography showed the presence of at least thirteen components, ranging in colour from orange, through red to blue. The orange component compared to triphenodioxazine. The mixture could be completely decolourised on reducing with alkaline sodium dithionite, but the colour returned on standing. This seemed to indicate that the mixture was composed of oxazines and, or substituted quinones, as these were all readily reduced. An attempt was made to chromatograph the material on an alumina column but no separation occurred. The only way to separate these components was to employ a thick layer of Kieselgel G as in thin layer chromatography. This involved a large

number of thick layer plates being made but unfortunately there was not time to procede further, although preliminary experiments did show this method to be possible if a 1.5 mm. thick layer of Kieselgel G was used.

Anhydrous aluminium chloride

2,5-Dianilino-1,4-benzoquinone was added to an excess of anhydrous aluminium chloride in pyridine and the resulting bright orange-red mixture refluxed for 24 hours. It was cooled, treated with hydrochloric acid, and the resulting solid examined by thin layer chromatography. This showed only the presence of unchanged starting material. The bright orange-red mixture was presumably due to the complex (XCVIII) which was unable to cyclise under these conditions. This contrasts with the effect of aluminium chloride on 2,5-di(o-anisidino)-1,4-benzoquinone.



XCVIII

The above experiment was repeated using o-dichlorobenzene as solvent but again there was no change in the starting material.

The effect of diphenyl ether (b.p. 258°) as a solvent on 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

It was decided in this experiment to determine the products formed and if identified, to estimate approximately by thin layer chromatography, the proportion in which they were formed.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone was refluxed in diphenyl ether for the required time interval. Any evolved hydrogen chloride could be determined by absorbing in $\frac{N}{5}$ sodium hydroxide and calculating the amount neutralised from a back titration with $\frac{N}{5}$ hydrochloric acid.

6-Chlorotriphenodioxazine and 2,5-dianilino-3-chloro-1,4-benzoquinone could be identified chromatographically by separating them on a steam heated alumina column using o-dichlorobenzene as the eluting solvent. All the dioxazines could be completely eluted from the column and the resulting eluant examined by thin layer chromatography. The arylaminoquinones remain on the column and these were extracted with o-dichlorobenzene and the extract examined by thin layer chromatography.

This method gave separable methods for identifying the dioxazines and arylaminoquinones but was not sufficient for a quantitative determination, and in this case, 6-chlorotriphenodioxazine and 2,5-dianilino-3-chloro-1,4-benzoquinone were estimated as a mixture.

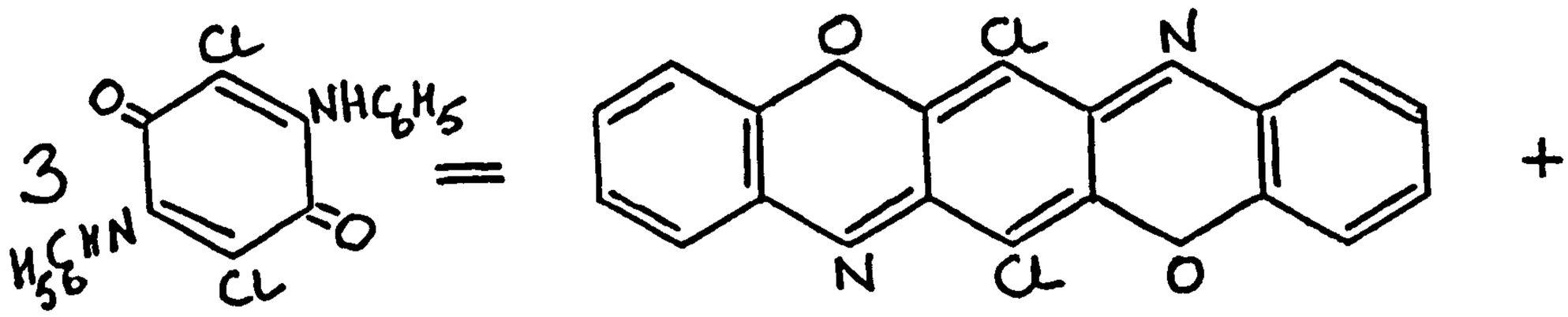
After heating for the required time, the product was examined quantitatively and qualitatively by thin layer chromatography. After 3 hours, a small amount of hydrogen chloride was evolved with some 6,13-dichloro-triphenodioxazine and a trace of 2,5-dianilino-3-chloro-1,4-benzoquinone. Refluxing for 6 hours produced more 6,13-dichlorotriphenodioxazine with a reduction in the starting material and an increased quantity of 2,5-dianilino-3-chloro-1,4-benzoquinone and some 6-chloro-triphenodioxazine. After 10 hours, more hydrogen chloride was formed and only 6,13-dichloro-, 6-chloro-triphenodioxazine and 2,5-dianilino-1,4-benzoquinone were found to be present. 24 hours refluxing gave more or less the same result, although there was perhaps an increased amount of insoluble decomposition product forming on the base of the chromatoplate.

From previous experiments, it was seen that

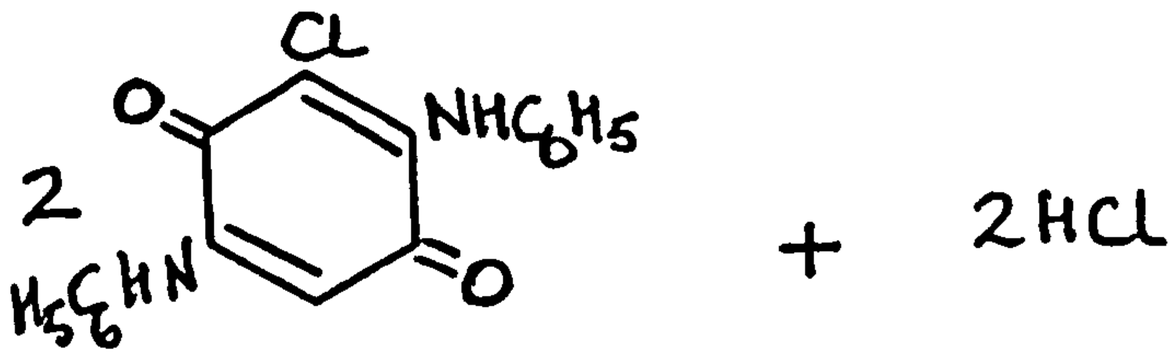
2,5-dianilino-1,4-benzoquinone was stable under these conditions and that the triphenodioxazines could be sublimed at high temperatures without decomposition. Thus it appeared that some form of dissociation took place with the elimination of hydrogen chloride.

The following scheme is proposed from the observations made:-

(i)

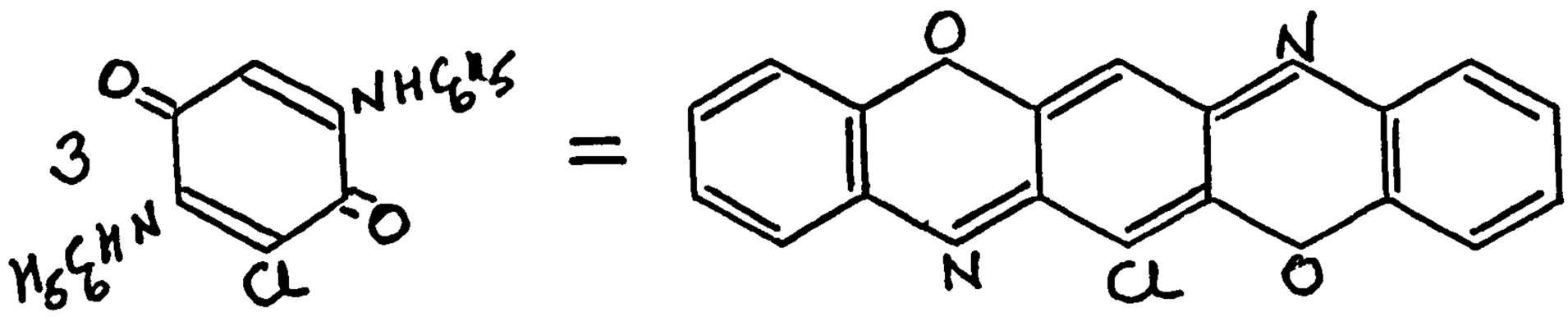


LXXXVI

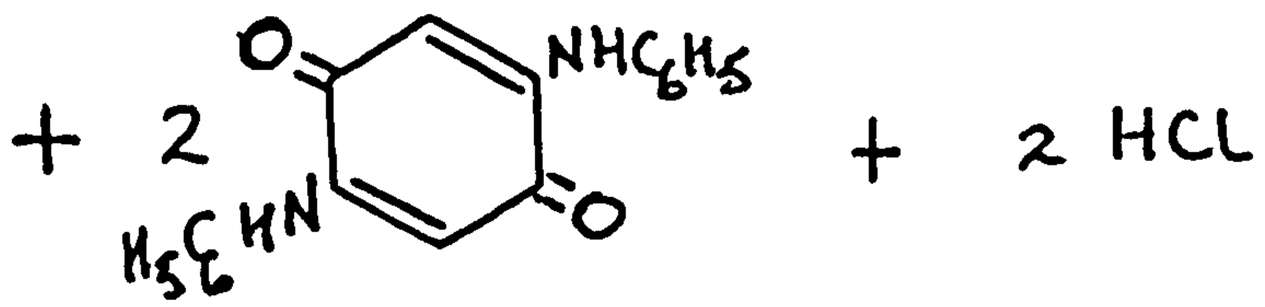


In (i), three moles of starting product dissociate into one mole (LXXXIX) together with two moles of 2,5-dianilino-3-chloro-1,4-benzoquinone and two moles of hydrogen chloride; the equation being balanced to avoid the elimination of any molecular hydrogen.

(ii)



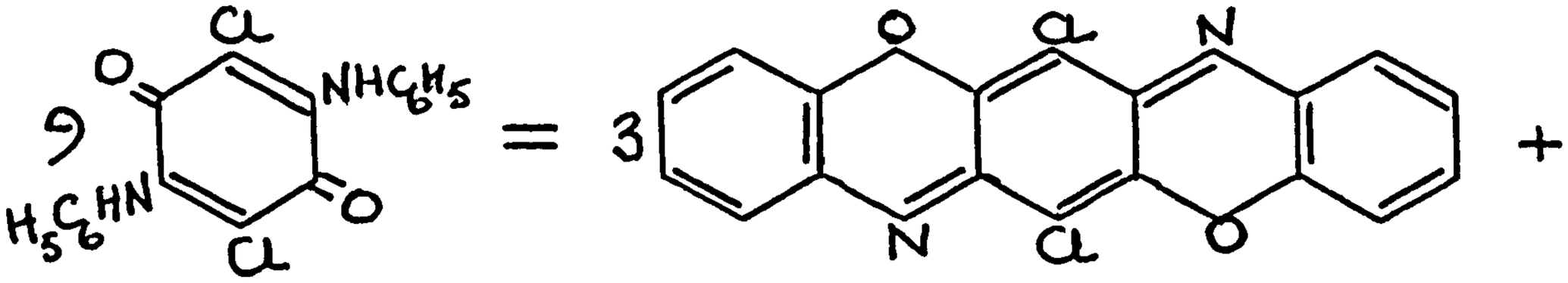
XCV



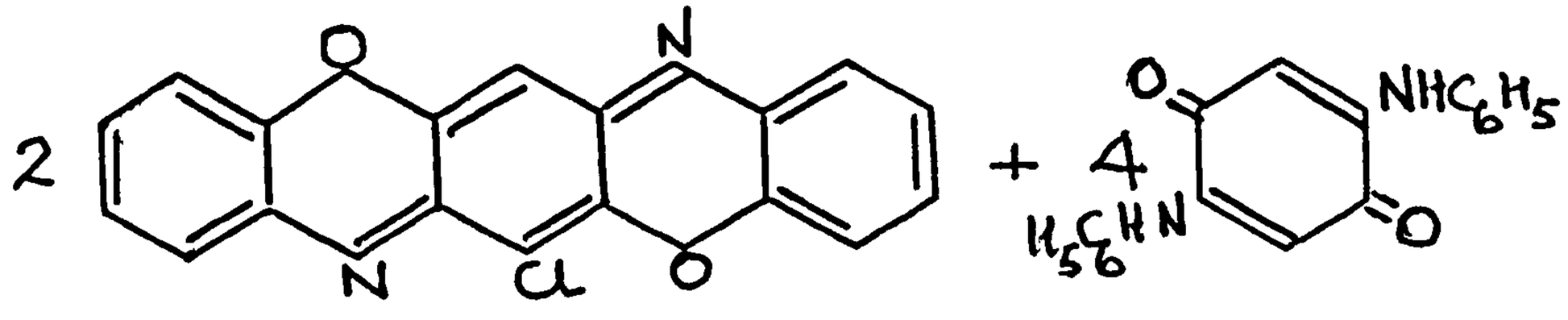
In stage (ii), three moles of 2,5-dianilino-3-chloro-1,4-benzoquinone dissociate similarly as (i) into one mole of (XCV), two moles of 2,5-dianilino-1,4-

benzoquinone and two moles of hydrogen chloride. Stages (i) and (ii) are combined to give the complete effect in (iii).

(iii)



LXXXIX



XCV

+ 10 HCL

As stage (iii) would occur at 10 hours and 24 hours in the experiment, one can calculate from stage (iii) what the relative proportion of products should be and the quantity of hydrogen chloride evolved from a 2g. sample of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

Component.	g.Molecular proportion as in (iii)	Relative concentration. (R_c)	R_c as observed in 10 hours	R_c as observed in 24 hours
LXXXIX.	3 x 355	1.000	1.000	1.000
XCV.	2 x 320.5	0.602	0.585	0.557
2,5-Dianilino-3-chloro-1,4-benzoquinone	4 x 290	1.090	0.967	1.130

From equation (iii), 9 x 359 g. of starting product evolve 10 x 36.5 g. of hydrogen chloride, viz:- 2 g. of starting product evolves $\frac{365 \times 2}{3231}$ g., i.e., 0.2260 g. The amount of hydrogen chloride observed was 0.2603 g.

The high hydrogen chloride figure could perhaps be attributed to side reactions and some decomposition, which would account for the non-elutable material noticed on the base of the chromatoplate.

The above scheme, (iii), would explain the production of more than one triphenodioxazine and the subsequent loss of hydrogen and chlorine on cyclisation of the arylamino-quinones formed from chloranil. It would also account for the observed fact that it is impossible to achieve high yields of triphenodioxazines by thermal cyclisation.

The effect of nitrobenzene (b.p. 211°) as a cyclising solvent on 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

As was previously noticed, 1,2,4-trichlorobenzene (b.p. 213°) had very little effect when 2,5-dianilino-3,6-dichloro-1,4-benzoquinone was refluxed in it. It was proposed in this experiment to use nitrobenzene, which although it had a similar boiling point to 1,2,4-trichlorobenzene, it was also an oxidizing agent.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone was refluxed in nitrobenzene under an atmosphere of nitrogen for the required time interval. Any hydrogen chloride which was evolved was absorbed in $\frac{N}{5}$ sodium hydroxide and determined volumetrically. The product was dissolved in o-dichlorobenzene and estimated quantitatively and qualitatively by thin layer chromatography.

No reaction occurred after heating for 9 hours, but on heating for 24 hours the formation of 6,13-dichloro-triphenodioxazine (LXXXIX) occurred together with a little 2,5-dianilino-3-chloro-1,4-benzoquinone and 6-chlorotri-phenodioxazine (XCV). After 48 hours, all the starting material had disappeared with the formation of (LXXXIX), (XCV), 2,5-dianilino-3-chloro-1,4-benzoquinone, tripheno-

dioxazine (I) and a little 2,5-dianilino-1,4-benzoquinone. 72 hours heating produced a similar effect with more hydrogen chloride but a loss in 2,5-dianilino-3-chloro-1,4-benzoquinone, the latter proving much more difficult to cyclise in nitrobenzene than in diphenyl ether.

The production of triphenodioxazine must presumably arise from an oxidation process involving the nitrobenzene, but no reduction products of nitrobenzene were ever identified probably due to the large excess of nitrobenzene employed. As nitrobenzene must act in an oxidizing capacity when compared to the innertness of 1,2,4-trichlorobenzene, some of the hydrogen lost in the cyclisation must be lost as water as well as hydrogen chloride. This could account for the formation of triphenodioxazine (I).

The effect of p-toluenesulphonyl chloride on the cyclisation of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

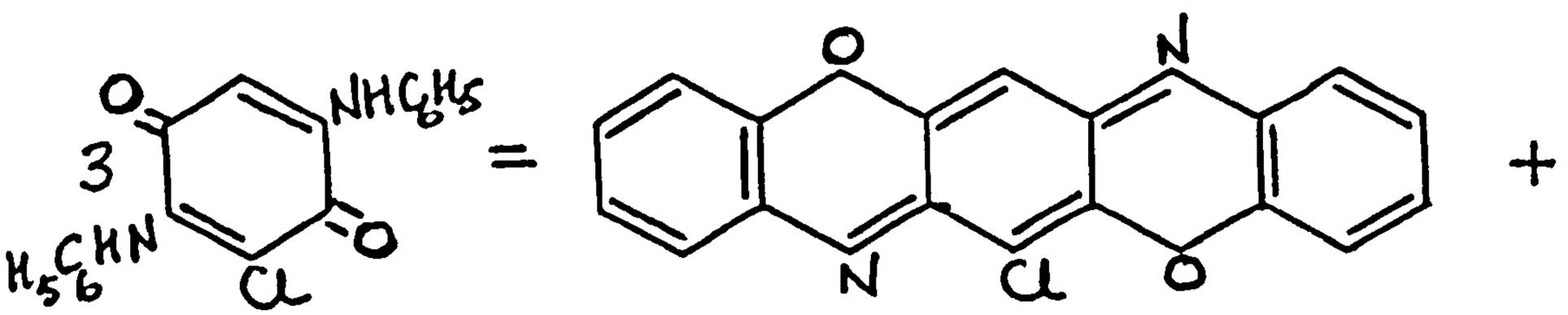
2,5-Dianilino-3,6-dichloro-1,4-benzoquinone was refluxed for 6 hours in the required solvent containing p-toluenesulphonyl chloride. The product so obtained was dissolved in o-dichlorobenzene and examined quantitatively by thin layer chromatography.

o-Dichlorobenzene (b.p. 183°) as a solvent had little effect but cyclisation occurred similarly with 1,2,4-trichlorobenzene and nitrobenzene with the formation of 6,13-dichlorotriphenodioxazine (LXXXIX), a little 2,5-dianilino-3-chloro-1,4-benzoquinone and 6-chlorotriphenodioxazine (XCV), together with unchanged starting material. It appeared from these observations that the use of nitrobenzene as a solvent had little effect over 1,2,4-trichlorobenzene and that the rate of cyclisation in the presence of p-toluenesulphonyl chloride was following a thermal effect. By using diphenyl ether as solvent, all the starting material had disappeared with the formation of (LXXXIX), (XCV), triphenodioxazine (I) and a little 2,5-dianilino-1,4-benzoquinone, the latter presumably accounting in this case for most of (I). The factors contributing to the cyclisation in this case

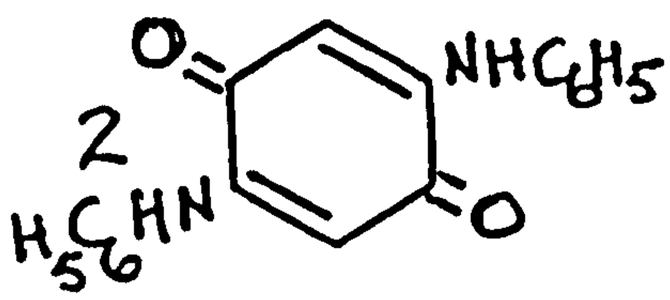
must be very complex as besides the apparent effect of p-toluenesulphonyl chloride, there is the thermal effect of refluxing in diphenyl ether.

The effect of diphenyl ether on 2,5-dianilino-3-chloro-1,4-benzoquinone.

2,5-Dianilino-3-chloro-1,4-benzoquinone was refluxed in diphenyl ether for 24 hours under an atmosphere of nitrogen. Any hydrogen chloride which was evolved was absorbed in $\frac{N}{5}$ sodium hydroxide and determined volumetrically. The product so obtained was examined quantitatively and qualitatively by thin layer chromatography to give 6-chlorotriphenodioxazine (XCV) and 2,5-dianilino-1,4-benzoquinone. The latter was in a large excess and did not appear to follow the given equation (ii).



XCV



However this was probably due in the first place to decomposition arising out of the reluctance of 2,5-dianilino-3-chloro-1,4-benzoquinone to cyclise and causing an increased volume of hydrogen chloride, and in the second place to the low yield of the product, resulting from the increased solubility of (XCV) in solvents.

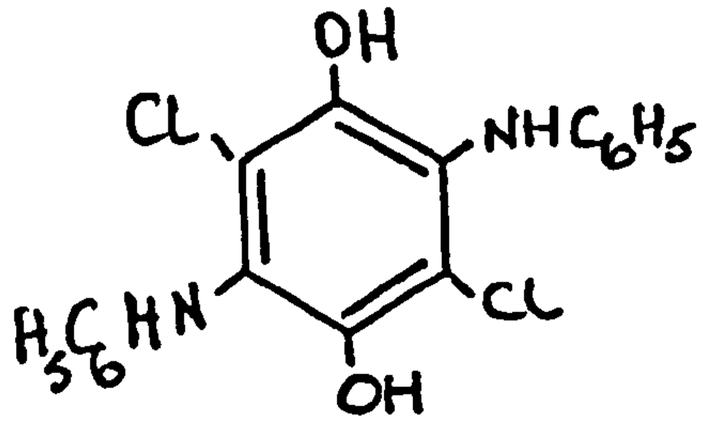
The products were identified further by chromatographing hot on alumina from o-dichlorobenzene, and the resulting analyses of the purified products so obtained, agreeing with the presence of (XCV) and 2,5-dianilino-1,4-benzoquinone.

The experiment was repeated under the same conditions but using nitrobenzene as solvent. Unchanged starting material was recovered.

<u>The hydrogenation of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone</u>.

From the previous cyclisation experiments it was observed that chlorine was removed from the arylamino-quinone nucleus and was replaced by hydrogen. It was thought worthwhile trying to reproduce these conditions by attempting to hydrogenate 2,5-dianilino-3,6-dichloro-1,4-benzoquinone in the presence of a catalyst. A catalyst was necessary as molecular hydrogen was insufficiently reactive.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone was dissolved in toluene containing some Raney nickel catalyst. A rapid stream of hydrogen was bubbled through and a sample of the solution when examined, was found to be colourless. This was due to the formation of 2,5-dianilino-3,6-dichloro-1,4-quinol (XCIX).



XCIX

After 8 hours, the product was filtered hot and

concentrated, causing the solution to gradually turn brown with the formation of the quinone. The product obtained was ground to a homogeneous powder, and a sample, subjected to elemental analysis, gave a reduction of 4.6% in the chlorine figure of the starting material. A sample examined by thin layer chromatography showed the presence of approximately equal amounts of starting material and 2,5-dianilino-3-chloro-1,4-benzoquinone, together with a trace of 2,5-dianilino-1,4-benzoquinone.

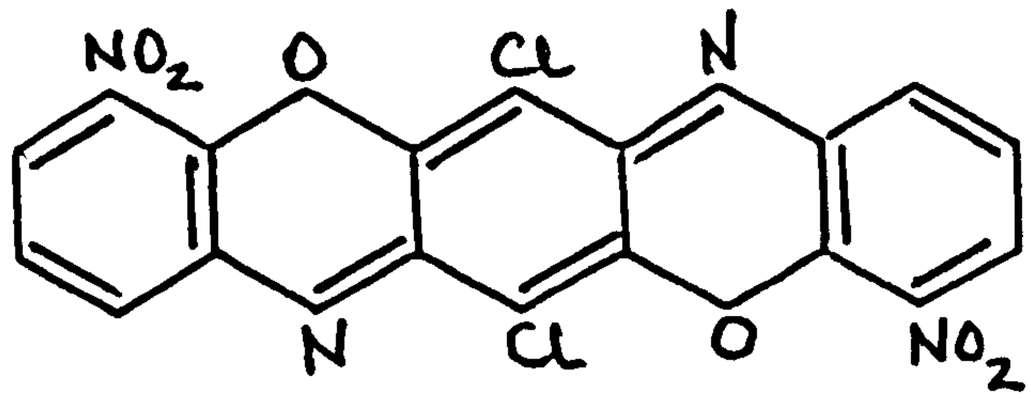
It appears the chlorine is again replaced by hydrogen but the last chlorine may be more difficult to replace resulting in a very small amount of 2,5-dianilino-1,4-benzoquinone.

The condensation of m-nitroaniline with chloranil.

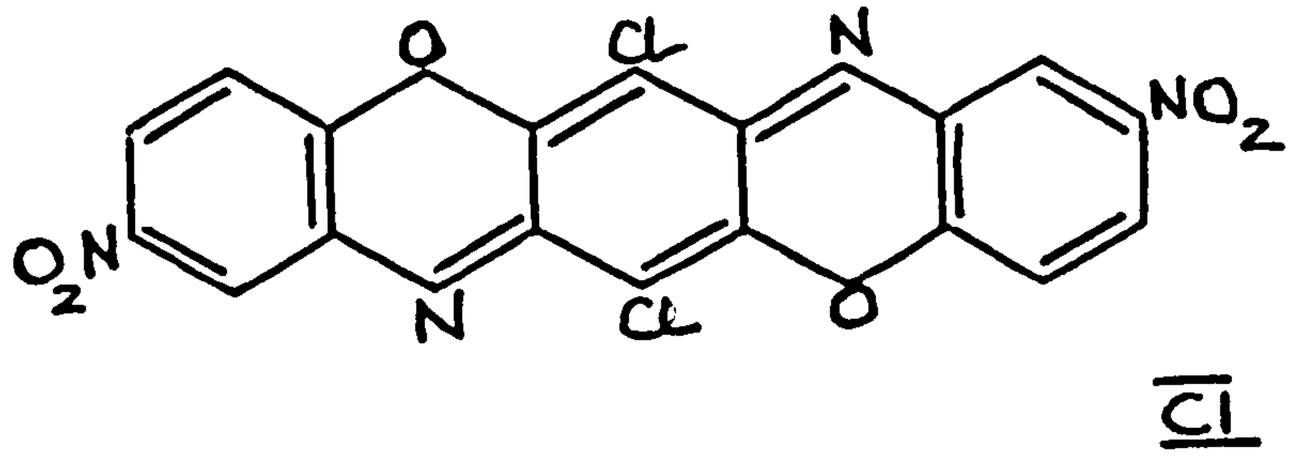
m-Nitroaniline was condensed with a solution of chloranil in ethyl alcohol containing some sodium acetate. The mixture was refluxed for 3 hours and on filtering, 2,5-di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone was obtained as bronze plates, m.p. 322-324°, in 43% yield. A large amount of ethanol-soluble violet material was formed and had there been time, it would have been of interest to examine it. It probably consisted of phenoxazone derivatives.

Attempted cyclisation of 2,5-di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone.

It was thought that the influence of the m-nitro-group would activate the o-positions to the -NH- group and consequently make cyclisation easier. Theoretically it was possible to obtain two isomers, (C) and (Cl).



(C)



Cl

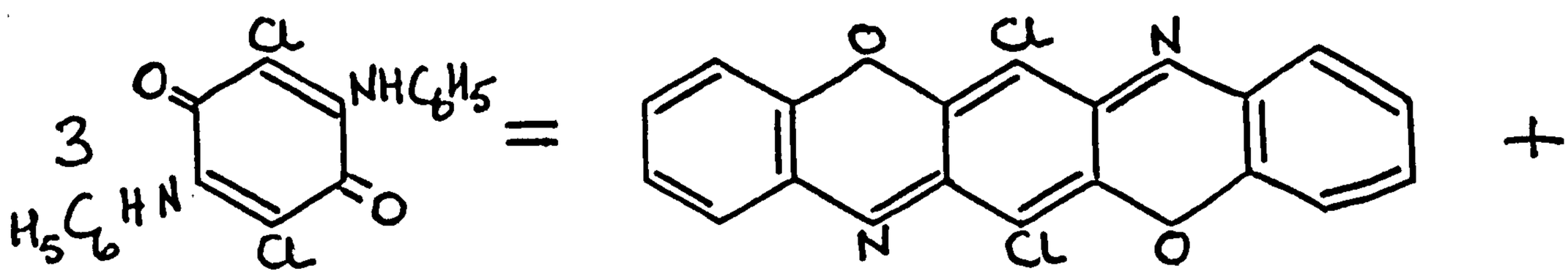
2,6-Di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone was refluxed for 8 hours in nitrobenzene containing p-toluenesulphonyl chloride. After cooling and filtering, the product on examination by thin layer chromatography showed the presence of a small amount of two orange components, but the quantity was too small for further investigation. It would have been of interest to repeat the reaction using an inert solvent such as diphenyl ether, as cyclisation did not appear to take place readily under the given conditions.

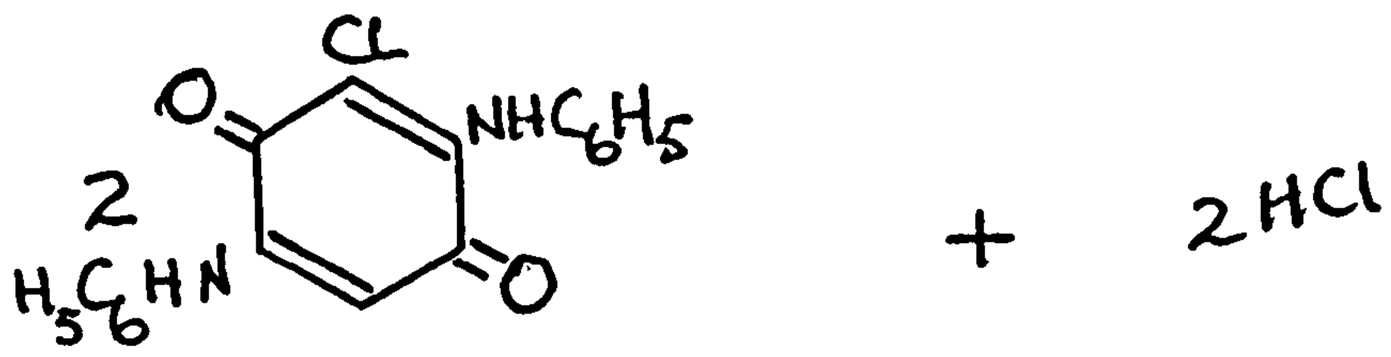
CONCLUSION

From the experiments carried out it can be seen that 2,5-dianilino-3,6-dichloro-1,4-benzoquinone and 2,5-dianilino-3-chloro-1,4-benzoquinone cyclise on heating under various conditions to give 6,13-dichloro-triphenodioxazine, 6-chlorotriphenodioxazine, and 2,5-dianilino-1,4-benzoquinone. The triphenodioxazines must be formed by the loss of four -H- atoms from the parent diarylaminoquinone, and the hydrogen is apparently lost as hydrogen chloride with the formation of 2,5-dianilino-1,4-benzoquinone, which itself is stable to the conditions employed. Removal of the chlorine from the quinone ring thus increased the difficulty of cyclisation due to the inability to loose hydrogen chloride. If the thermal cyclisation is carried out in an oxidizing solvent such as nitrobenzene, cyclisation again takes place but at a lower temperature. There is some evidence to suggest that some of the hydrogen may be lost as water, leading, in addition to the formentioned products, to the production of triphenodioxazine. The presence of an agent such as p-toluenesulphonyl chloride aids the cyclisation, the production of triphenodioxazine in this case being the effect of p-toluenesulphonyl chloride on 2,5-dianilino-1,4-benzoquinone.

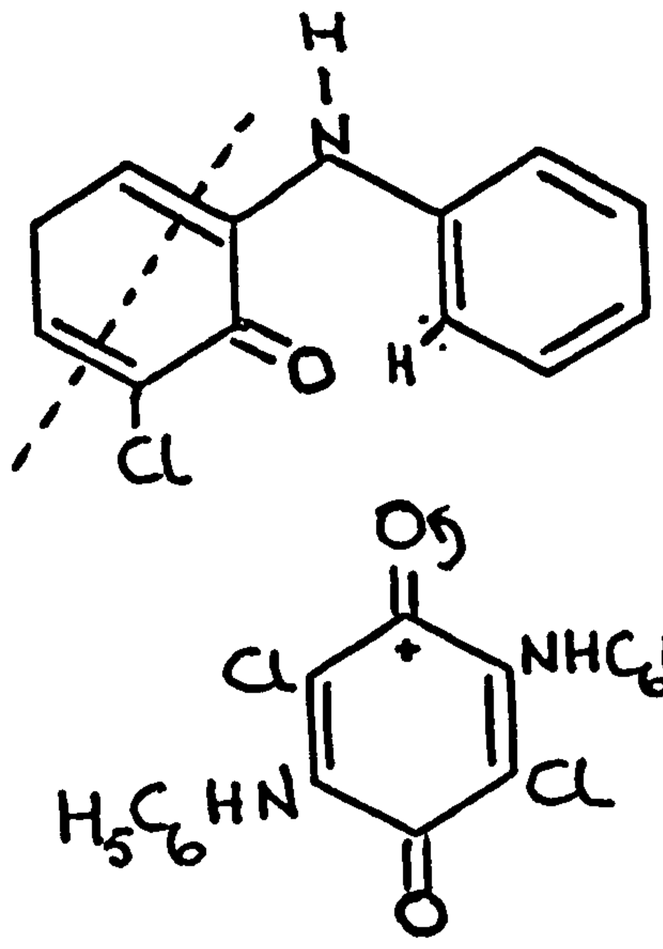
Further evidence of this loss of chlorine was shown by the hydrogenation of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone; 2,5-dianilino-3-chloro-1,4-benzoquinone being formed with a trace of 2,5-dianilino-1,4-benzoquinone. Steric effects may play a part here in that the bulky -Cl- atom is lost in preference to the smaller -H- atom, resulting in a more stable compact structure.

The first stage of the thermal cyclisation has been suggested by this equation:-

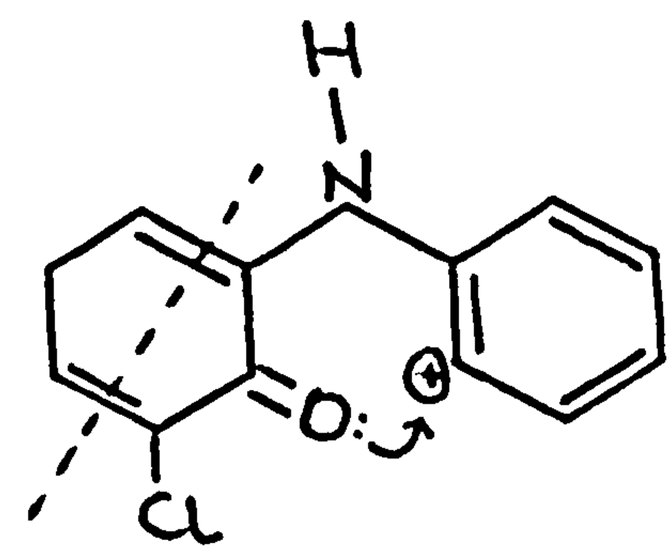




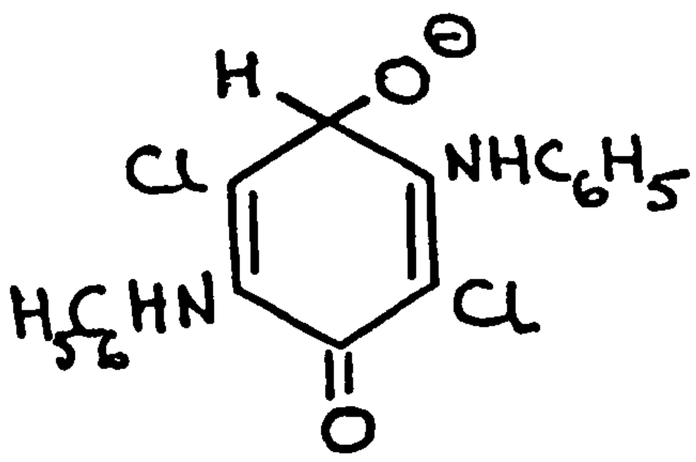
By considering one half of the diarylaminoquinone molecule the following mechanism is suggested:-

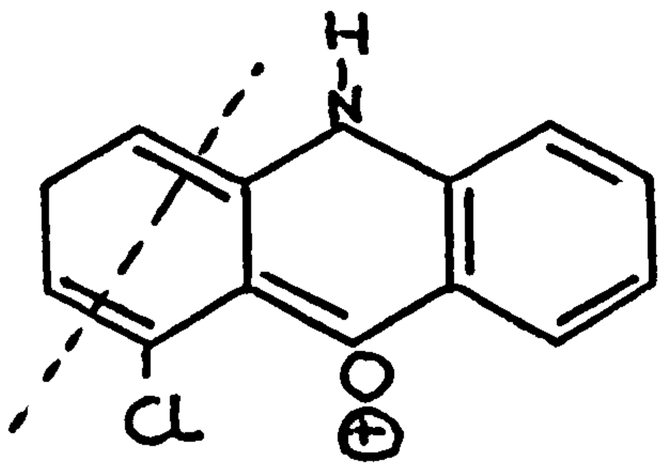


(i) The o-H- atom to the -NH- group is attracted by the oxidizing power of another diarylaminoquinone molecule.

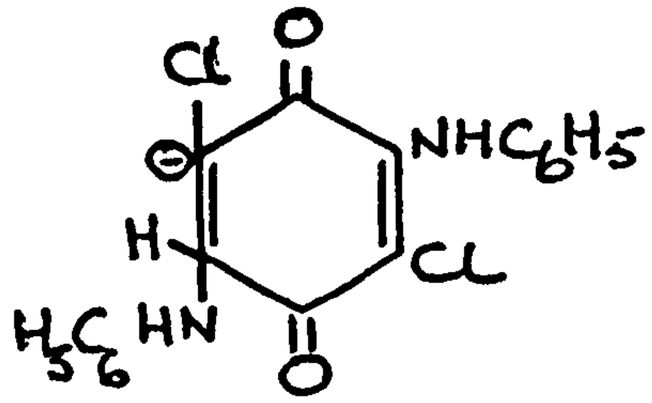


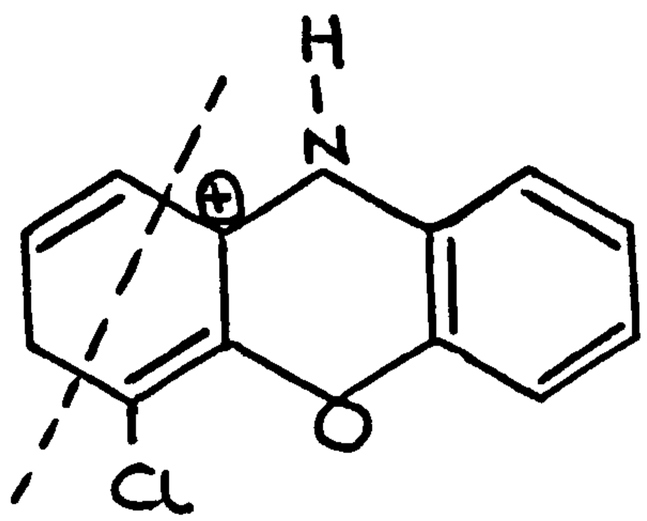
(ii) The-H- bond is broken leaving a carbonium ion whilst the other diarylaminoquinone is reduced with the formation of $-O^{(-)}$.



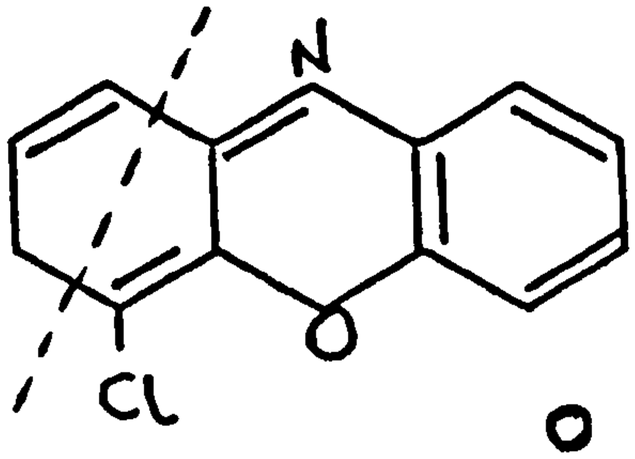


(iii) Ring closure of the carbonium ion occurs with the formation of an oxonium salt whilst the other diarylamino-quinone rearranges to form a carbanion.

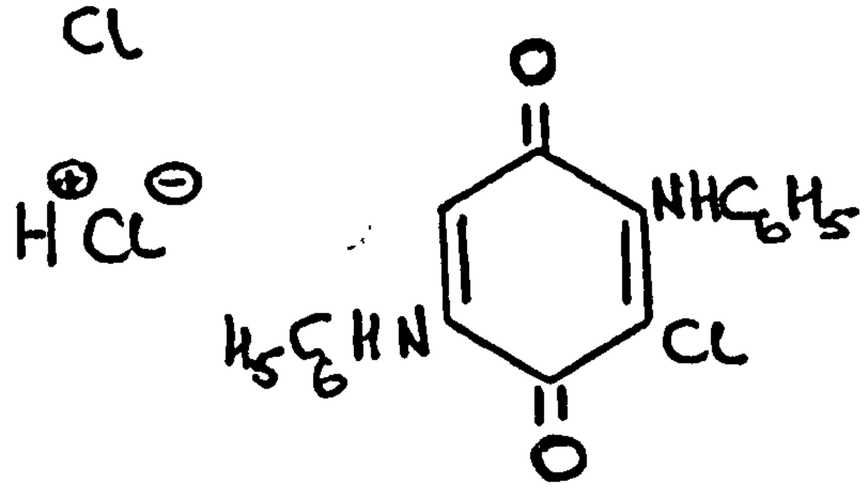




(iv) The charge on the oxonium compound migrates with the corresponding rearrangement of bonds.



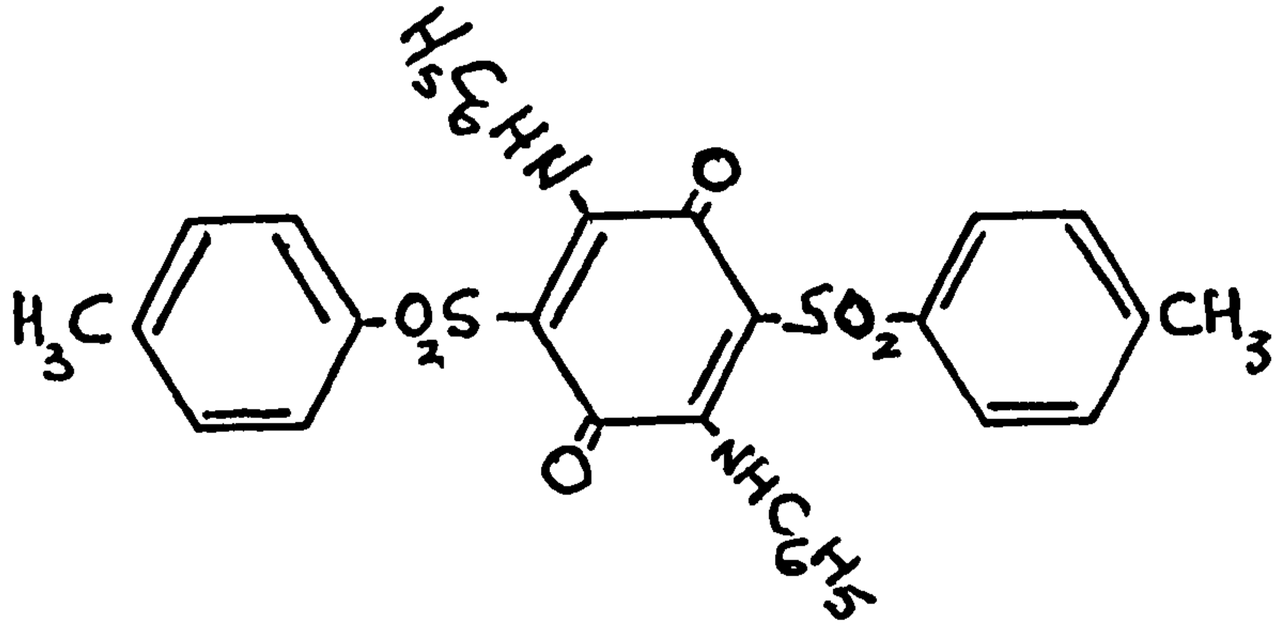
(v) The (+) charge is lost as a proton with the formation of the oxazine ring. This proton attacks the carbanion which looses its (-) as Cl^-, forming hydrogen chloride.



Two diarylaminoquinone molecules must participate in the cyclisation of a further diarylaminoquinone so as to form the dioxazine.

The cyclisation of 2,5-dianilino-1,4-benzoquinone is very difficult by thermal effects alone as this would involve the elimination of $-H^{(-)}$ which seldom occurs.

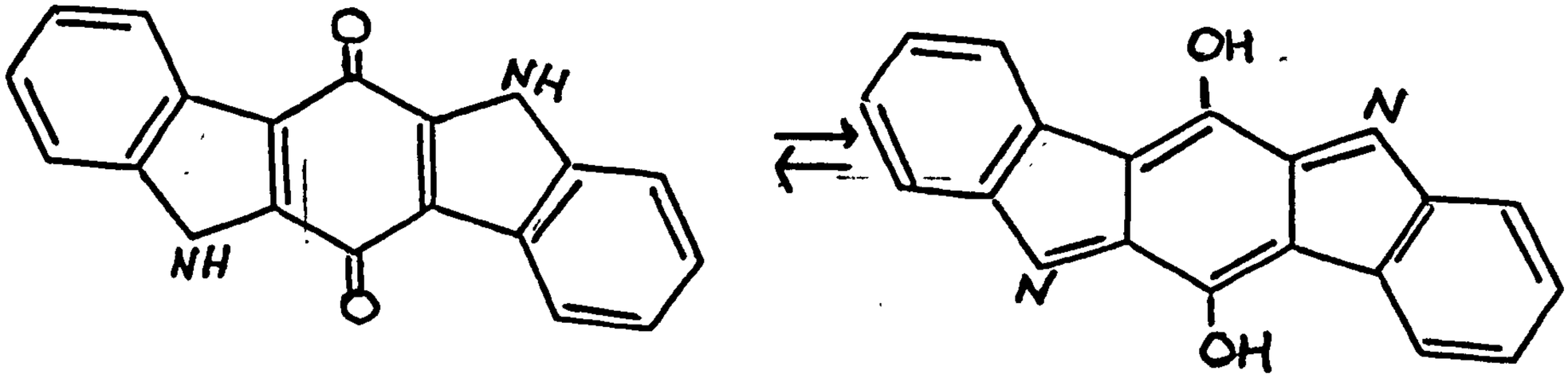
Although the action of p-toluenesulphonyl chloride on 2,5-dianilino-1,4-benzoquinone does not occur in benzene there is the possibility that the sulphone derivative may occur at higher temperatures.



Cyclisation of this can now take place by the elimination of the $p\text{-}CH_3.C_6.H_4.SO_2^{(-)}$ group with the final formation of sulphinic acid.

It would be possible to obtain a further product on cyclisation by elimination of the chlorine groups, the

oxygens taking no part in the ring formation. This would result in the loss of two molecules of hydrogen chloride from 2,5-dianilino-3,6-dichloro-1,4-benzoquinone to form the tautomeric indolo [2,3-b]carbazole-1,4-quinone (CII).



CII

It would be of great interest to examine the thermal effect with 2,5-dianilino-3,6-dimethyl-1,4-benzoquinone and the N-alkylarylaminoquinones to see if they cyclise and what products are produced. Further work could be done involving the use of electron accepting agents such as aluminium chloride and boron trifluoride on the chlorinated diarylaminoquinones.

EXPERIMENTAL

EXPERIMENTAL PROCEDURE

Visible and ultra-violet absorption spectra were measured using a Unicam S.P. 500 spectrophotometer and the absorption coefficients recorded as optical density for 1 mg. substance in 100 ml. solvent.

Infra-red absorption spectra were measured using a Unicam S.P. 200 spectrophotometer employing a disc made up from 1 mg. substance in 200 mg. A.R. potassium chloride.

Melting points were observed between microscope cover slips on an aluminium block and were uncorrected. Where no melting point was recorded, the compound did not melt below 360°.

Microanalyses were carried out by the microanalytical laboratory, The Department of Chemistry, The University of Leeds.

Column chromatography was carried out by using May and Baker "Aluminium Oxide for Chromatography", and thin layer chromatography employed "Kieselgel G nach Stahl", a purified form of silica supplied by Camlab (Glass) Limited.

THIN LAYER CHROMATOGRAPHY

Thin layer chromatography is a process involving the separation of a mixture of components on a thin layer of substrate such as alumina or silica. Its advantages over column and paper chromatography are its high resolving power, rapidity of separation, and flexibility of application. It can be employed to separate a very small quantity of substance and a component can be estimated qualitatively and quantitatively. The preparation of a "plate" involves the laying down of a thin homogeneous layer of substrate on a rectangular sheet of polished plate glass. The plates were prepared by a slight modication of the original method by Stahl.* Kieselgel G nach Stahl (60 g.) was shaken slowly in a corked flask for 2 hours with distilled water (180 c.c.). Sufficient of the resulting creamy paste was placed to cover the base of a doctor blade, placed at one end of the glass plate (18 x 20 cm.), which had been well cleaned free from grease and then polished. The blade was swept swiftly across the glass forming a layer of 0.3 mm. average thickness of Kieselgel G. The plate was dried in air for 20 minutes and then activated at 80-90^{o} for 1 hour. It was best used immediately,

when cool, but it could be kept for 2-3 days provided the Kieselgel G was activated by heating at 80-90° for 1 hour before use.

The substance to be examined was dissolved in a suitable solvent (throughout the present work, hot o-dichlorobenzene was used almost exclusively as a solvent for examination by thin layer chromatography), and drops of this solution (0.5-2.0 μL in capacity) placed on the plate, 2.5-3.0 cm. from one end. It was advisable not to chromatograph solutions whose concentrations were greater than 1% and also to keep the size of the spot on the plate, resulting from a drop of the solution, down to a minimum, as "tailing" effects occurred which resulted in an incomplete separation. A glass tank (25 cm. tall x 19 cm. diameter), containing sufficient A.R. toluene not to cover the spots on the plate when the plate was immersed in the tank, was required with a tightly fitting lid, so as to ensure a saturated atmosphere of toluene within it. The plate was placed in the tank and eluted with the ascending toluene, dried, and could be re-eluted if the resulting separation was insufficient.

In the described work, chromatographing tripheno-dioxazine and anilino-1,4-benzoquinone derivatives required at least two complete elutions with toluene to give the required separation as their R_f values were very low.

$$R_f = \frac{\text{Height in cm. of spot above the base line.}}{\text{Height in cm. of solvent level above the base line.}}$$

R_f values were never calculated as reproducible values were not easily obtained except under the strictest conditions.

Indentification of a product was best carried out by placing a drop of the unknown solution in o-dichlorobenzene on the thin layer and placing alongside it, a drop of the known component in o-dichlorobenzene, and eluting them together with toluene. Visible comparisons of the R_f values could then be made. If they appeared the same, admixture of the known and unknown solutions of the components were examined on the plate and if they were identical, only one spot appeared on the plate.

Quantitative measurements were obtained by placing a strip of the unknown solution along one base of the plate, instead of individual spots, and then eluting with

toluene until the required separation was obtained. The chromatoplate was dried and the component bands separated mechanically and individually extracted with dioxan. The dioxan extract was made up to a known volume in a graduated flask and optical density measurements made at the required wavelength. From this data, the relative concentrations of the products on the chromatoplates could be obtained. The concentration of the solution to be chromatographed was only important in that it should not be too high, or else incomplete separation would occur, or that it should not be too low, causing bands which were too faint to have their absorption spectra measured. This method was claimed to give an accuracy of 2.8%** but in this thesis, the relative values were of importance only in giving a qualitative picture of the reaction rate.

An example of some chromatoplates which have been photographed by Kodakchrome can be seen on page 201.

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* E. Stahl, Chem.-Ztg., 82, 232-329 (1958).

** E.V. Truter, "Thin Film Chromatography", Cleaver-Hume Press L.t.d., London, 1963, 32-40.

The preparation of 3-aminocarbazole

Preparation of 3-nitro-9-nitrosocarbazole

Carbazole (100 g.) was heated to incipient boiling with glacial acetic acid (800 c.c.). The whole was mechanically stirred, and then the solution was cooled quickly to 40-60°. Sodium nitrite (42 g.) was added in small portions over 1 hour at this temperature. The mixture turned yellow and gradually thickened owing to the separation of golden-yellow needles of 9-nitroso-carbazole. The solid was then dissolved by raising the temperature to 55-60°; and a mixture of nitric acid (83 c.c., d = 1.40) and glacial acetic acid (83 c.c.) was added dropwise over 2 hours. The mixture was then stirred for 1 hour at room temperature and for 30 minutes at 10°. The green solid (circa 115 g.) was collected and washed with water and 50% ethanol and then used for the next stage after draining on the filter. It contained mainly 3-nitro-9-nitrosocarbazole with some 1-nitro-9-nitrosocarbazole present as impurity.

Preparation of 3-nitrocarbazole

Crude 3-nitro-9-nitrosocarbazole (circa 115 g.) was refluxed with stirring in 95% ethanol (1 L.) and 40%

potassium hydroxide solution (400 c.c.) for 30 minutes. The deep red solution was poured whilst hot into a large excess of cold water (5 L.) and well stirred. The nitro-compound was precipitated as yellow flakes. It was filtered under suction, washed with hot water, and dried at 80° to give a yellow powder (103 g.). It was mainly 3-nitrocarbazole with 8-12% of 1-nitrocarbazole as impurity and it required further purification.

Crude 3-nitrocarbazole (103 g.) was recrystallised from glacial acetic acid (1.5 L., charcoal). The product (77 g.) had a melting range, 180-205°, and a spot of an acetone solution of it placed on a thin layer of Kiselgel G and eluted with benzene, showed the presence of two yellow bands, the weaker presumably being 1-nitrocarbazole. This product was further purified by extracting it (77 g.) in a Soxhlet apparatus with ligroin (b.p. 80-100°) until the extract was colourless. The extract was evaporated to low bulk and on cooling, deposited yellow crystals (6 g.), m.p. 166-186°. These were further extracted with ligroin (b.p. 80-100°) until the extract was colourless. The extract was concentrated, cooled, and the resulting crystals recrystallised from absolute ethanol to give

1-nitrocarbazole as bright yellow microcrystalline needles (2.4 g.), m.p. 189-191°.

The initial extracted material was recrystallised from absolute ethanol to afford small yellow needles of 3-nitrocarbazole (58 g., 44% overall), m.p. 216-218°. A sample was examined by thin layer chromatography and showed the presence of only one compound. (Found: N, 13.15. Calc. for $C_{12}H_8N_2O_2$:N, 13.2%).

Reduction to 3-aminocarbazole

3-Nitrocarbazole (20 g.) was dissolved, by heating and stirring on a steam-bath, in 95% ethanol (600 c.c.). Concentrated hydrochloric acid (40 c.c.) was added carefully and then finely divided iron filings (20 g.) were added in four portions, 5 minutes being allowed between each addition. The mixture was refluxed for 3 hours and then cooled to 50° and made alkaline to Brilliant Yellow paper by the addition of a solution of potassium hydroxide (40 g.) in 95% ethanol (250 c.c.). It was filtered hot by suction and the filter washed with three portions of boiling 95% ethanol (250 c.c.). The filtrate and washings were combined and evaporated to low bulk on a steam-bath. This afforded a dark solid

(16 g., 94%), m.p. 248-254°. It was recrystallised from absolute ethanol (charcoal) to afford buff leaflets of 3-aminocarbazole, m.p. 254-256° (decomp.). (Found: N, 15.55. Calc. for $C_{12}H_{10}N_2$:N, 15.4%).

3-Aminocarbazole (0.5 g.) was dissolved in glacial acetic acid (1.5 c.c.). Acetic anhydride (1.0 c.c.) was added together with a crystal of sodium acetate. The whole was heated in a test-tube on a water-bath with occasional shaking for 30 minutes. The mixture was poured into iced water (20 c.c.) with stirring and allowed to stand. There was deposited a reddish brown product (0.2 g.) which was twice recrystallised from 95% ethanol giving pinkish white prisms of 3-acetylamino-carbazole, m.p. 217-219°. (Found: N, 12.5. Calc. for $C_{14}H_{12}N_2O$:N, 12.5%).

The attempted preparation of 8,18-dichlorodiindolo [3,2-b; 3',2'-m] triphenodioxazine

Preparation of 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone.

3-Aminocarbazole (10 g., 0.055 mole.) was well mixed with anhydrous sodium acetate (5.7 g., 0.07 mole.) in a mortar and added to absolute ethanol (135 c.c.) and stirred on a steam-bath for 15 minutes. It was cooled to room temperature and chloranil (7.2 g., 0.029 mole.) was added. The whole was stirred at room temperature under an atmosphere of nitrogen for 5 hours and then filtered under suction. It was washed with boiling water to remove inorganic material and then extracted with acetone in a Soxhlet apparatus until the extract was colourless. It left a purple powder (13.1 g., 88%) which did not melt below 400°. (Found: C, 66.15; H, 3.4; N, 10.15; Cl, 12.95. $C_{30}H_{18}N_4Cl_2O_2$ requires C, 67.0; H, 3.35; N, 10.4; Cl, 13.2%).

Attempts to purify this compound by recrystallisation failed. It was completely insoluble in all low boiling solvents except pyridine, but no crystals were obtained by the use of pyridine. It was soluble in

dimethyl formamide and dimethyl phthalate, but prolonged boiling in these solvents quickly changed the original brown-red to a violet solution with a strong red fluorescence, due to the formation of triphenodioxazine derivatives. The compound could not be reduced to the quinol with phenylhydrazine but it could be "vatted" with an alkaline solution of sodium dithionite to give a yellow solution. No suitable analysis could be obtained from the compound on oxidation to the quinone. The compound dissolved in concentrated sulphuric acid to give a dull blue-violet colour and a yellow-brown colour in pyridine, λ_{max} 342,460 mμ (log ε 4.31, 4.04. Fig.1).

Attempted cyclisation to the triphenodioxazine

2,5-Di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone (12 g.), p-toluenesulphonyl chloride (8 g.) and dry nitrobenzene (150 c.c.), were stirred in a flask fitted with an air condenser and a silica gel tube. The mixture was raised to reflux temperature in 2 hours and refluxed for 3 hours. It was cooled to 100-130°, filtered, and washed with acetone and 10% potassium hydroxide solution alternately until the washings were only faintly coloured, and then finally washed with

water and dried to give a dark violet powder (8 g.) with a faint green reflex. The product was recrystallised with difficulty from pyridine to give green shining needles. (Found: N, 11.85; Cl, 11.1. $C_{30}H_{14}N_4Cl_2O_2$ requires N, 10.4; Cl, 13.3%). A sample of the product in pyridine was examined by thin layer chromatography and showed after eluting for some time with o-dichlorobenzene, two violet bands. No attempt was made to separate these two bands in view of their low solubility.

The effect of sulphuric acid on 2,5-di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone

2,5-Di(3-carbazolylamino)-3,6-dichloro-1,4-benzoquinone (4 g.) was shaken with concentrated sulphuric acid (300 c.c.) for 24 hours. The deep blue mixture was centrifuged, the supernatent liquor collected, and the undissolved solid discarded. The deep blue liquid was added with stirring to ice-water (500 c.c.) mixture and allowed to stand for 2 hours., and then centrifuged to give a brownish red powder (1 g.). This powder was soluble in water to give a brown-red solution, and also to give a blue solution in concentrated sulphuric acid. It was taken up in boiling distilled water (350 c.c.) and barium carbonate added until neutral to litmus, filtered, and the filter washed with two portions of distilled water (100 c.c.). The washings and filtrate were combined and the resulting red solution concentrated under vacuum to give a dull brown solid (circa 0.1 g.), which was soluble in water to give a white precipitate with dilute sulphuric acid. (Found: Ash, 84.1%).

The preparation of 3-amino-9-ethylcarbazole

Preparation of 9-ethylcarbazole

Carbazole (30 g.) was dissolved by heating and stirring in acetone (325 c.c.). When it was all in solution, the heat source was removed and a solution of potassium hydroxide (42 g.) in water (20 c.c.) added carefully. After 5 minutes, diethyl sulphate (36 c.c.) was run into the olive coloured solution, and immediately the mixture began to solidify due to the separation of 9-ethylcarbazole. The mixture was stirred for 15 minutes and thenwater (circa. 250 c.c.) added to dissolve the solid. The solution was poured into ice-water (2 L.) and allowed to stand for 12 hours, then filtered and washed with 15% methanol. The resulting white solid (circa 30 g.) was recrystallised from absolute methanol (charcoal) to afford white needles (24 g., 68%) of 9-ethylcarbazole, m.p. 69-70°. (Found: N, 7.05. Calc. for $C_{14}H_{13}N$:N, 7.2%).

Preparation of 3 nitro-9-ethylcarbazole.

Method 1.

3-Nitrocarbazole (7 g.), absolute ethanol (100 c.c.) and 20% potassium hydroxide solution (100 c.c.), were

stirred under reflux conditions. To the bluish red solution, diethyl sulphate (50 c.c.) was added and the mixture refluxed 5-8 hours. The yellow solution was allowed to stand, cooled to 10^{o}, filtered and washed with water and aqueous methanol to yield yellow crystals (48 g.). A sample was recrystallised from absolute ethanol to yield yellow needles of 3-nitro-9-ethylcarbazole, m.p. 123-124^{o}.

Method 2.

9-Ethylcarbazole (36 g.) was slurried in toluene (70 c.c.) and stirred 1 hour at room temperature and then cooled in ice-salt mixture to -5-0^{o}. Nitric acid (44 c.c., 43.4% HNO_3, d = 1.270 - 1.275) was added over 3 hours, and the mixture was stirred overnight allowing the ice-bath to melt and reach room temperature. It was cooled again to 0^{o}, the green solid was filtered, and recrystallised from absolute ethanol (charcoal) to yield greenish yellow needles (21 g., 47%), m.p. 125-126^{o}. Thin layer chromatography showed this product to be identical to that obtained from method 1.

Method 3.

9-Ethylcarbazole (24 g.) was dissolved by heating and stirring in glacial acetic acid (130 c.c.) and then cooled quickly to room temperature, a further quantity of

glacial acetic acid (20 c.c.) being added. A mixture of nitric acid (9 c.c., d = 1.40) and glacial acetic acid (9 c.c.) was added dropwise over 1½ hours, and then the green mixture warmed to 70° for 30 minutes, and stirred at room temperature overnight. It was filtered, washed with aqueous methanol, and dried to give green crystals (27 g., 91%), m.p. 118-122°. This was recrystallised from a large volume of absolute ethanol (charcoal) to give yellow-green needles (17 g., 58% overall), m.p. 127-128°, identical to the products from methods 1 and 2. (Found: N, 11.65. Calc. for $C_{14}H_{12}N_2O_2$:N, 11.65%).

<u>The preparation of 3-amino-9-ethylcarbazole</u>.

3-Nitro-9-ethylcarbazole (20 g.), 95% ethanol (190 c.c.) and 30% sodium sulphide solution (60 g., 60 g. $Na_2S,9H_2O$ dissolved in its own water of crystallisation plus 5-10 c.c. of water), were refluxed for 30 hours. The solution was cooled to 40°, the lower inorganic layer separated in a separating funnel and discarded, and the ethanol layer stirred in an ice-bath for 30 minutes. It was filtered, washed with water and 5% methanol, and dried in vacuum to yield a brown crystalline powder (14.5 g., 73%) m.p. 85-100°.

The product could not be recrystallised from benzene, alcohols, or ether, to give a product which melted over 100°. It could only be best recrystallised from ligroin (b.p. 60-80°) (charcoal) to yield pinkish white needles of 3-amino-9-ethylcarbazole, m.p. 120-121°, (Lindemann, 113-114°). (Found: N, 13.1. Calc. for $C_{14}H_{14}N_2$:N, 13.3%).

Crude 3-amino-9-ethylcarbazole (15.5 g.), glacial acetic acid (16 c.c.) and acetic anhydride (30 c.c.) were refluxed with a few drops of concentrated sulphuric acid for 30 minutes. It was allowed to cool and then added to ice-water mixture (350 c.c.) with stirring whence a dark solid (16.7 g.) was deposited on standing. It was recrystallised from methanol (charcoal) to afford small white needles (6.7 g.), m.p. 198-199.5°, (Lindemann, 190°). (Found: N, 10.95. Calc. for $C_{16}H_{16}N_2O$:N, 11.1%).

3-Amino-9-ethylcarbazole (1.0 g.) was boiled with 2N. hydrochloric acid (circa 40 c.c.), cooled, and the resulting solid recrystallised from water to afford grey needles of 3-amino-9-ethylcarbazole hydrochloride. (Found: N, 11.5. Calc. for $C_{14}H_{14}N_2.HCl$: N, 11.35%).

The preparation of 2,5-di(9-ethyl-3-carbazolyl-amino)-3,6-dichloro-1,4-benzoquinone.

3-Amino-9-ethylcarbazole (5 g., 0.024 mole.), anhydrous sodium acetate (2.3 g., 0.028 mole.) and chloranil (4.4 g., 0.018 mole.), were stirred at 45° under an atmosphere of nitrogen in absolute ethanol (100 c.c.). After 4 hours the deep brown mixture was refluxed for 4 hours, filtered hot, and washed with hot water and ethanol to afford a red powder (5 g., 70%), soluble in acetone. It was recrystallised from acetone to afford purple needles, sparingly soluble in acetone, m.p. 306-308°, and its absorption spectrum identical to the red powder. Prolonged heating at the melting point caused 2,5-di(9-ethyl-3-carbazolyl-amino)-3,6-dichloro-1,4-benzoquinone to loose hydrogen chloride and change to green needles of a triphenodioxazine derivative. The purple needles dissolved to give a yellow-brown colour in dioxan (1) and a blue colour in concentrated sulphuric acid (2). (Found: C, 68.85; H, 4.45; N, 9.25% $C_{34}H_{26}N_4O_2Cl_2$ requires C, 68.8; H, 4.4; N, 9.45). Light absorption: (1) λ_{max} 265,300,340,460 mμ (log ε 4.67,4.50,4.30,4.07. Fig. 2). (2) λ_{max} 400,610,650 mμ (log ε 3.92,4.45,4.52 Fig. 3). ν_{max} 1638 cm.$^{-1}$(m), ·C:O· stretching; 3270 cm.$^{-1}$(s), secondary amine stretching.

The preparation of 5,15-diethyl-8,18-dichlorodiindolo [3,2-b; 3',2'-m] triphenodioxazine.

(Pigment Violet R)

3-Amino-9-ethylcarbazole (5 g.), anhydrous sodium acetate (2.3 g.) and dry o-dichlorobenzene (75 c.c.) were stirred at 60-65° for 2 hours. The mixture was then heated to 115° in 2½ hours, benzenesulphonyl chloride (2.5 g.) added, and the mixture raised to reflux temperature and refluxed for 3½ hours. It was filtered hot (100°), washed with boiling water and with boiling acetone, and dried to give a dark green solid (5 g.). It was recrystallised from o-dichlorobenzene to give small glistening green needles of no melting point. (Found: N, 9.75; Cl, 12.4. $C_{34}H_{22}N_4O_2Cl_2$ requires N, 9.5; Cl, 12.1%). It dissolved to give a pale violet colour with a strong red fluorescence in o-dichlorobenzene (1) and a very pale purple colour in concentrated sulphuric acid (2). Light absorption: (1) λ_{max} 565, 610 mμ (log ε 4.49,4.63. Fig. 4). (2) λ_{max} 940 mμ (log ε 4.98 Fig. 5). ν_{max} 1580 cm.$^{-1}$ (S), ·C:N· stretching.

The preparation of 1-aminopyrene

Preparation of 1-nitropyrene

Pyrene (20 g.) was dissolved in glacial acetic acid (160 c.c.) by heating and stirring and when all the pyrene was in solution, it was cooled to 50°. To the resulting slurry, a mixture of nitric acid (7 c.c., d = 1.42) and glacial acetic acid (10 c.c.) was added dropwise over 2-2½ hours. The yellow mixture was heated in 1 hour to 95°, and the yellow-brown solution kept at this temperature until crystals of 1-nitropyrene began to separate out (1½-2 hours). The mixture was cooled to room temperature, filtered, and washed with water and methanol to afford yellow needles (22.3 g., 91%), m.p. 150-154°. It was recrystallised from absolute ethanol (charcoal) to afford woolly yellow needles, m.p. 152-154°. (Found: N, 5.7. Calc. for $C_{16}H_9NO_2$:N, 5.7%).

Reduction to 1-aminopyrene.

3-Nitropyrene (21 g.), concentrated hydrochloric acid (25 c.c.) and 95% ethanol (500 c.c.), were refluxed with stirring on a steam-bath. Finely divided iron filings (21 g.) were added in four portions, 5 minutes being allowed between the addition of each portion, and the mixture refluxed for 2-2½ hours. The mixture was

made alkaline to Brilliant Yellow paper with 20% alcoholic potassium hydroxide solution, filtered hot, and the filter extracted with three portions (350 c.c.) of boiling 95% ethanol. The washings and the filtrate were combined, and the strong blue fluorescent solution concentrated under reduced pressure on a steam-bath to yield a dark coloured solid (17 g., 92%). On extraction with cyclohexane it afforded reddish yellow leaflets (11 g., 60% overall) on cooling, m.p. 113-114°. A sample was sublimed at 110°/0.002 m.m. and the pale yellow sublimate on recrystallisation from cyclohexane, deposited pale greenish yellow leaflets, m.p. 114-116°. (Found: N, 6.25. Calc. for $C_{16}H_{11}N$:N, 6.45%).

1-Aminopyrene (0.5 g., m.p. 113-114°) and 90% formic acid (10 c.c.) were shaken in a test-tube and heated in a water-bath for 15 minutes. The solution changed in colour from brown to olive-green. A few drops of water were added to the solution, which was allowed to cool to room temperature, and the pale green 1-formylaminopyrene filtered off and washed with a little water. It was recrystallised (charcoal) from 70% acetic acid to afford very pale green needles (0.15 g.), m.p. 228-230°. (Found: N, 5.7. Calc. for $C_{17}H_{11}NO$:N, 5.7%).

The preparation of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone

1-Aminopyrene (10 g., 0.046 mole.), anhydrous sodium acetate (4.6 g., 0.056 mole.) and chloranil (6.9 g., 0.028 mole.), were refluxed for 14 hours in absolute ethanol (190 c.c.), the mixture being kept under an atmosphere of nitrogen. The deep coloured mixture was filtered, washed with boiling water and boiling 95% ethanol, and dried to give 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone as a deep purple powder (9.6 g., 70%). It was very sparingly soluble in organic solvents and was purified by reduction and reoxidation as follows:-

The crude quinone (3.1 g.) and chlorobenzene (28 g.) were refluxed and stirred, whilst an excess of phenylhydrazine (1.5 g.) in chlorobenzene (3 g.) was added dropwise over 1 hour. The mixture gradually thickened and when all the phenylhydrazine had been added, the grey mixture was filtered off and well washed with acetone to yield light grey-green microcrystalline plates (2.7 g., 86%) of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-quinol, changing to the quinone on heating to 290°. (Found: C, 75.25; H, 3.6; N, 4.4. $C_{38}H_{22}N_2Cl_2O_2$ requires C, 75.5; H, 3.6; N, 4.6%). An attempt was made to measure the absorption spectrum in pyridine but

the colourless solution quickly changed to yellow-brown, even when cooled in ice. Absorption spectrum measurements compared directly to that of the quinone.

The quinol (2.5 g.) was stirred in nitrobenzene (32.5 g.) at 190° for 45 minutes, cooled and filtered, and washed free from nitrobenzene with hot ligroin (b.p. 100-120°) and alcohol to give purple-brown needles of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone (1.7 g., 68%), m.p. 348-351°. (Found: C, 74.7; H, 3.25; N, 4.85. $C_{38}H_{20}N_2Cl_2O_2$ requires C, 75.0; H, 3.3; N, 4.6%). It was sparingly soluble in concentrated sulphuric acid to give a dull blue colour but it was more soluble in 20% oleum to give a violet solution. It gave a yellow-brown colour in dioxan, λ_{max} 245,265,278,350,450 mμ (log ε 4.91,4.52,4.59, 4.51,3.93. Fig. 6).

The attempted cyclisation of 2,5-di(1-pyrenamino)-3,6-dichloro-1,4-benzoquinone

Method 1.

The quinone (3 g.), 2,4-dinitrophenol (1.5 g.) and nitrobenzene (60 g.), were refluxed with stirring for 4 hours. The brown mixture was allowed to cool, filtered, and washed with hot ligroin (b.p. 100-120°) and ethanol to give a brown powder (2.5 g.). This was found to be unchanged starting material. The experiment was repeated, but the time of reflux was 8 hours. Again there was little change in the starting material.

Method 2.

The quinone (3 g.), p-toluenesulphonyl chloride (1.5 g.) and 1-chloronaphthalene (60 c.c.), were refluxed with stirring for 30 minutes. The colour of the mixture quickly changed through violet to a deep blue. It was allowed to cool, filtered, and washed with hot 95% ethanol to give a deep navy-blue powder (2.1 g.).

The blue powder (0.128 g.) was dissolved with difficulty in hot (100°) o-dichlorobenzene (50 c.c.), and the blue solution columned on a steam heated alumina column (30 x 1.5 cm.). A deep blue band was formed from which a violet band could be completely detached by

eluting with o-dichlorobenzene containing 2% acetone. A very small amount of acetone soluble violet solid was eventually obtained but was insufficient in quantity for analysis or absorption spectrum measurements. The deep blue band was eluted with hot o-dichlorobenzene to yield a deep blue solution, from which a greenish blue microcrystalline solid (77mg.) was obtained on concentrating. The analysis indicated that it was 8,19-dichlorodiphenaleno [1,9-ab; 1',9'-lm] tripheno-dioxazine. (Found: N, 4.5; Cl, 11.75. $C_{38}H_{16}O_2N_2Cl_2$ requires N, 4.65; Cl, 11.8%). It dissolved with difficulty to give a pale green colour in concentrated sulphuric acid; it was more soluble in 20% oleum to give an olive-green colour. It gave a blue colour in o-dichlorobenzene, λ_{max} 570,615,670 mμ (log ε 4.29, 4.61,4.73. Fig. 7). ν_{max} 1580 cm.$^{-1}$ (s), ·C:N· stretching.

The preparation of 2,5-di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone.

4-Aminodiphenylamine (10 g., 0.054 mole.), anhydrous sodium acetate (4.6 g., 0.056 mole.) and chloranil (6.8 g., 0.028 mole.), were refluxed under an atmosphere of nitrogen in absolute ethanol (150 c.c.) for 8 hours. It was filtered hot, washed with water and 95% ethanol, to give a black crystalline powder (8.8 g., 60%). It was very sparingly soluble in most low boiling solvents but could be satisfactorily recrystallised from acetone to give lustrous black needles with a bronze reflectance, which did not melt below 360°. (Found: C, 66.55; H, 4.2; N, 10.2; Cl, 13.2. $C_{30}H_{22}N_4O_2Cl_2$ requires C, 66.5; H, 4.1; N, 10.05; Cl, 13.1%). 2,5-Di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone dissolved in dioxan to give a yellow-brown solution (1) and in concentrated sulphuric acid to give a deep majenta solution (2). Light absorption: (1) λ_{max} 288, 294,480 mμ (log ε 4.64,4.66,4.05. Fig. 8). (2) λ_{max} 545 mμ (log ε 4.44. Fig. 9). ν_{max} 1660 cm.$^{-1}$ (m), ·C:O· stretching; 3260 cm.$^{-1}$ (m), secondary amine stretching.

Attempted cyclisation of 2,5-di(4-aminodiphenylamino)-3,6-dichloro-1,4-benzoquinone.

The quinone (5 g.), phosphorus pentachloride (0.6 g.) and precipitated manganese dioxide (0.4 g.), were refluxed in dry nitrobenzene (50 c.c.) for 8 hours. The blue mixture was allowed to cool to 100°, filtered and washed with hot ligroin (b.p. 100-120°) and 95% ethanol to remove nitrobenzene, giving a greenish crystalline powder containing manganese dioxide (3.4 g.). A sample was recrystallised from o-dichlorobenzene to yield small bronze needles of no melting point. These dissolved in concentrated sulphuric acid to give a deep blue solution. (Found: N, 10.05; Cl, 6.45,6.85. $C_{30}H_{18}N_4O_2Cl_2$ requires N, 10.4; Cl, 13.2%). A sample in pyridine was examined by thin layer chromatography, eluting with o-dichlorobenzene to show the presence of at least three blue components, all showing very little separation.

The condensation of chloranil with aniline

Redistilled aniline (18.6 g., 0.20 mole.), anhydrous sodium acetate (16.4 g., 0.20 mole.) and chloranil (25 g., 0.102 mole.), were refluxed with stirring in 1,2,4-trichlorobenzene for 9 hours. The mixture was cooled to 100°, filtered, and washed with hot 95% ethanol and hot water to give a black crystalline powder (35 g., 98%). A sample was recrystallised from o-dichlorobenzene to yield black shining plates of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone, m.p. 330-333°. (Found: C, 60.1; H, 3.3; N, 7.7; Cl, 20.2. Calc. for $C_{18}H_{12}O_2N_2Cl_2$: C, 60.0; H, 3.4; N, 7.8; Cl, 19.8%). It dissolved with difficulty to give a yellow-brown solution in dioxan (1) and a violet-blue solution in concentrated sulphuric acid (2). Light absorption: (1) λ_{max} 268,390 mμ (log ε 4.25,4.20. Fig. 10). (2) λ_{max} 342.5,565 mμ (log ε 4.19,4.31. Fig. 11). ν_{max} 1660 cm.$^{-1}$ (s), ·C:O· stretching; 3270 cm.$^{-1}$ (s), secondary amine stretching.

The experiment was repeated but the time of condensation increased to 20 hours. No change in the final product was noticed. Continued heating of the quinone at its melting point caused decomposition with loss of hydrogen chloride.

The condensation of 2,6-dichloro-1,4-benzoquinone with aniline.

Preparation of 2,4,6-trichlorophenol

Method 1.

o-Chlorophenol (100 g.) was heated on a steam-bath, whilst a fast stream of chlorine was bubbled through the liquid until the contents had gained in weight by about 54 g. The liquid was cooled to room temperature and the resulting brownish white solid (153 g.) collected. It was recrystallised from aqueous acetic acid (charcoal) to give 2,4,6-trichlorophenol in long white needles (circa 60 g.), m.p. 58-61°.

Method 2.

Phenol-p-sulphonic acid (50 g., $C_6H_4 \cdot OH \cdot SO_3Na, 2H_2O$) in water (400 c.c.) was stirred whilst a stream of chlorine was bubbled through. Crystalline needles of 2,4,6-trichlorophenol were gradually precipitated and these were filtered off when the mixture became too thick to stir, and washed with water. A further stream of chlorine was passed into the mother liquor to yield more crystals of 2,4,6-trichlorophenol. This process was continued, until oxidation began to occur with the formation of halogenated 1,4-benzoquinones, giving an average yield of 35% of trichlorophenol. A sample was

recrystallised from aqueous acetic acid to give white needles, m.p. 65-67°.

Preparation of 2,6-dichloro-1,4-benzoquinone.

2,4,6-Trichlorophenol (25 g.) in absolute ethanol (100 c.c.) was cooled to between -5° and 0° whilst fuming nitric acid (50 g., d = 1.51) was added dropwise over 1½-2 hours with stirring. After about 1½ hours yellow crystals began to separate from the orange-red solution. When all the nitric acid had been added, the mixture was stirred a further ½ hour and then filtered cold, washed with water and a little aqueous methanol, to give on drying, yellow prisms (6.5 g.), m.p. 117-119°. A sample was sublimed at 95°/0.002 mm. and the yellow sublimate recrystallised from ligroin (b.p. 80-100°) to afford beautiful yellow prismatic needles of 2,6-dichloro-1,4-benzoquinone, m.p. 120-121°. (Found: Cl, 40.5. Calc. for $C_6H_2Cl_2O_2$:Cl, 40.1%).

Condensation of 2,6-dichloro-1,4-benzoquinone with aniline.

2,6-Dichloro-1,4-benzoquinone (20 g.) and anhydrous sodium acetate (9.5 g.) were stirred at room temperature in absolute ethanol (300 c.c.). Redistilled aniline (11 g.) was run in over 15 minutes and the whole mixture refluxed on a steam-bath for 5 hours. It was filtered

hot, washed with hot methanol and hot water, and dried to give a yellow-brown powder (18 g., 69%). A sample on recrystallisation from benzene gave purple-brown hair like needles of 2,5-dianilino-3-chloro-1,4-benzoquinone, m.p. 269-270°. A sample was sublimed at 185°/0.002 mm. (Found: C, 66.25; H, 4.2; N, 9.0. Calc. for $C_{18}H_{13}N_2O_2Cl$:C, 66.6; H, 4.0; N, 8.65%). It was soluble in most organic solvents, i.e., readily soluble in dioxan to give a yellow-brown solution (1) and in concentrated sulphuric acid to give a deep red-violet solution (2). Light absorption: (1) λ_{max} 268,383 mμ (log ε 4.27,4.24. Fig. 12). (2) λ_{max} 325,535 mμ (log ε 4.13,4.27, Fig. 13).

The condensation of 1,4-benzoquinone with aniline

1,4-Benzoquinone (10 g., 0.094 mole.) was stirred in absolute ethanol (100 c.c.) whilst aniline (5.8 g., 0.063 mole.) was run in over 15 minutes. The mixture was refluxed for 5 hours, filtered hot, and well washed with hot 95% ethanol to yield a reddish brown crystalline powder (7.5 g., 82%). A sample was recrystallised from o-dichlorobenzene to give purple glistening plates of 2,5-dianilino-1,4-benzoquinone, m.p. 354-356°, (lit., 345°). (Found: C, 74.8; H, 4.8; N, 9.95. Calc. for $C_{18}H_{14}N_2O_2$:C, 74.5; H, 4.8; N, 9.7%). It was very sparingly soluble in most organic solvents but would dissolve in dioxan to give a yellow-brown solution (1) and in concentrated sulphuric acid to give a deep red solution (2). Light absorption: (1) λ_{max} 268,375 mμ (log ε 4.29,4.28 Fig. 14). (2) λ_{max} 314,520 mμ (log ε 4.08,4.37. Fig. 15). ν_{max} 1643 cm.$^{-1}$ (s), ·C:O· stretching; 3260 cm.$^{-1}$ (m), secondary amine stretching.

The preparation of 6,13-dichlorotriphenodioxazine

Condensation of o anisidine-with chloranil

Chloranil (25 g., 0.102 mole.) and anhydrous sodium acetate (20 g., 0.24 mole.) were suspended with stirring in o-dichlorobenzene (125 c.c.) at room temperature. Redistilled o-anisidine (29 g., 0.225 mole.) was run in over 40 minutes and the mixture refluxed for 3 hours. It was allowed to cool to room temperature, stood 12 hours, and then filtered. The filter was washed with hot 95% ethanol and hot water and dried to give a lustrous black powder (33 g., 70%). A sample was recrystallised from 95% ethanol to afford small green-black plates of 2,5-di(o-anisidine)-3,6-dichloro-1,4-benzoquinone, m.p. 257-259°. (Found: C, 57.3; H, 3.65; N, 6.85. $C_{20}H_{16}N_2O_4Cl_2$ requires C, 57.5; H, 3.8; N, 6.7%). It dissolved in concentrated sulphuric acid to give a bright blue-violet solution which dulled on standing to give a pale blue. It dissolved readily in dioxan to give a yellow-brown solution. λ_{max} 278.5, 385 mμ (log ε 4.15,4.08. Fig. 16).

Cyclisation of 2,5-di(o-anisidino)-3,6-dichloro-1,4-benzoquinone.

Fresh anhydrous aluminium chloride (62.5 g., 0.47

mole.) was added with stirring, in small portions, to anhydrous pyridine (325 g.). When all the aluminium chloride was added, the temperature was raised to 80-90° and 2,5-di(o-anisidine)-3,6-dichloro-1,4-benzoquinone (25 g., 0.06 mole.) was added in small portions. The red-brown mixture was raised to reflux temperature, when it changed to royal blue, and then refluxed for 20 hours. It was allowed to cool and the solid mass added to 2N hydrochloric acid (500 c.c.) with stirring. Concentrated hydrochloric acid (250 c.c.) was then added to this mixture and the whole diluted with hot water (1250 c.c.) and allowed to stand for 48 hours. The deep brownish red mixture was filtered and well washed with ethanol and hot water to give a dull brown solid (15 g., 71%). A sample was twice recrystallised from o-dichlorobenzene to give purple needles of 6,13-dichlorotriphenodioxazine. (Found: N, 7.95; Cl, 20.0. Calc. for $C_{18}H_8O_2N_2Cl_2$:N, 7.9; Cl, 20.0%). A sample of the mother liquor, examined by thin plate chromatography, showed the presence of two orange components, one being extremely faint. This was later found to be 6-chlorotriphenodioxazine (see page 176). 6,13-Dichlorotriphenodioxazine was soluble in most high boiling solvents and in dioxan, in which it gave an orange solution with a green fluorescence(1).

It dissolved in concentrated sulphuric acid to give a pure blue solution (2). Light absorption: (1) λ_{max} 259,266,445,471,506.5 mμ (log ε 4.46,4.47,4.35,4.66, 4.79. Fig. 21). (2) λ_{max} 655 mμ (log ε 4.84. Fig. 22). ν_{max} 1585 cm.$^{-1}$ (s), ·C:N· stretching.

6,13-Dichlorotriphenodioxazine (1 g.) was well powdered in a mortar and added to boiling xylene (40 c.c.) in an atmosphere of nitrogen. An excess of phenylhydrazine (circa. 6 c.c.) in xylene (10 c.c.) was added dropwise over 20 minutes, or until the solution had lost its orange colour. The mixture was filtered when cool, and washed with a little 95% ethanol to yield a dirty white powder (0.49 g.). A sample was recrystallised twice from pyridine containing a little phenylhydrazine, to give small white leaflets of 7,14-dihydro-6,13-dichlorotriphenodioxazine. (Found: C, 60.55; H, 2.85. $C_{18}H_{10}N_2O_2Cl_2$ requires C, 60.5; H, 2.8%). It gradually oxidized to the red 6,13-dichlorotriphenodioxazine if left standing in air or if it was warmed.

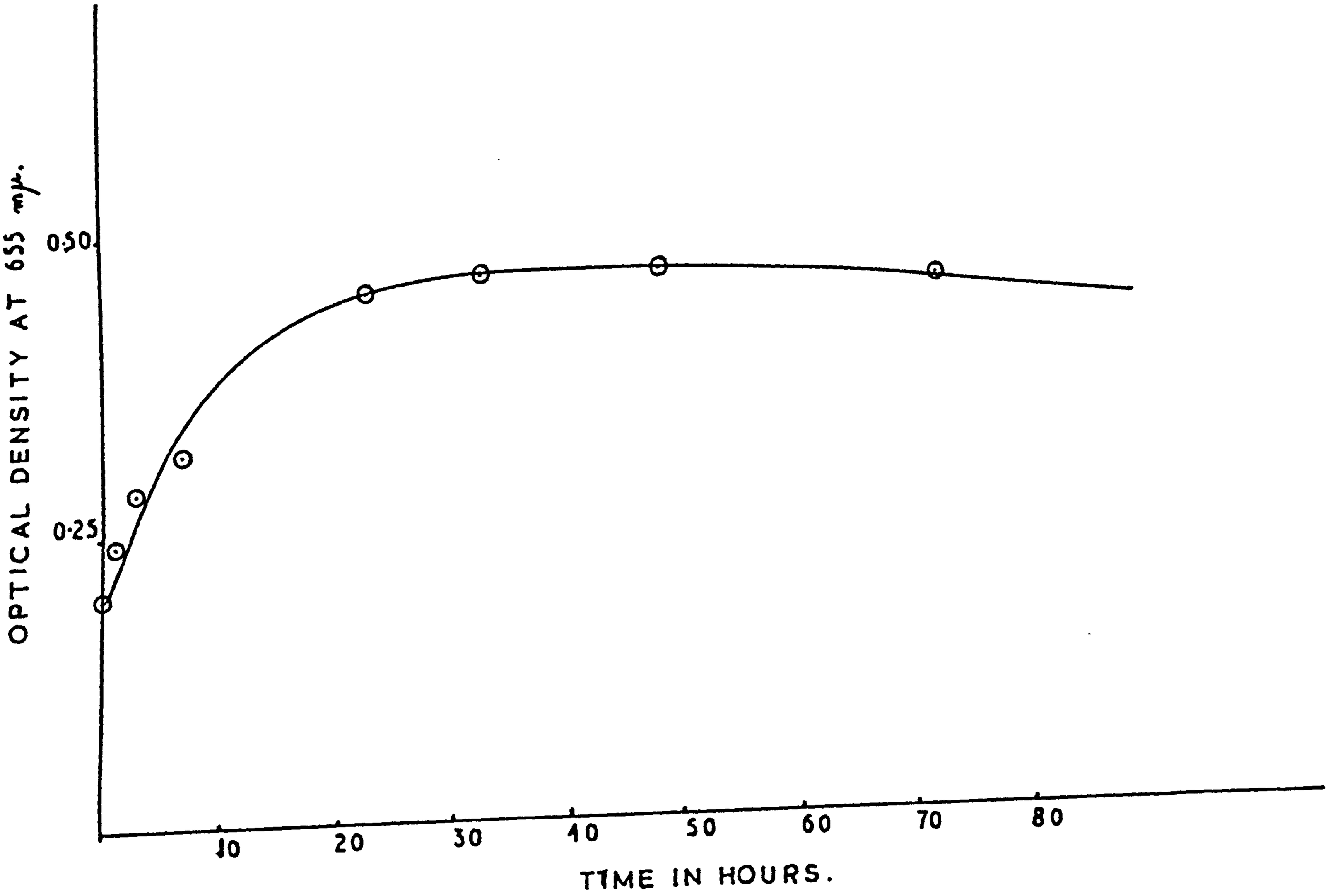
The condensation of chloranil with o-phenetidine

Chloranil (15 g., 0.062 mole.) and anhydrous sodium acetate (12 g., 0.146 mole.) were suspended with stirring in o-dichlorobenzene (75 c.c.) at room temperature. Redistilled o-phenetidine (20 g., 0.146 mole.) was run in over 40 minutes and the navy blue mixture was refluxed for 3 hours. It was allowed to cool, stood 12 hours, and then filtered and washed with hot methanol and hot water to give a black crystalline powder (21.5 g., 73%). It was recrystallised from acetone to give black lustrous plates of 2,5-di(o-phenetidino)-3,6-dichloro-1,4-benzoquinone, m.p. 211-213°. (Found: N, 5.9; Cl, 15.6. $C_{22}H_{20}O_4N_2Cl_2$ requires N, 6.25; Cl, 15.9%). It was soluble in concentrated sulphuric acid to give a violet solution which soon changed to a pale dull blue on standing. It gave a yellow-brown solution in dioxan, λ_{max} 280,290 mμ (log ε 4.25, 4.14. Fig. 19).

The pyrolysis of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone in diphenyl ether

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (1.0 g.) was dissolved in diphenyl ether (100.0 g.) under an atmosphere of nitrogen, and refluxed and stirred. A series of pipettes were made from glass test-tubes and these were roughly calibrated to hold 0.1 c.c. of liquid. After the required time interval a sample of the solution was drawn off, pipetted into a tared beaker, weighed, and then dissolved in concentrated sulphuric acid (100.0 c.c.). The optical density of this solution was measured at 655 mμ, and corrected to a concentration of 1 mg. per 100 c.c. of sulphuric acid from the weight found. This gave a rough indication of the rate of cyclisation.

Time (hr.)	Corrected optical density
0	0.20
1	0.24
3	0.29
7	0.32
23	0.46
33	0.47
48	0.47
72	0.46


OPTICAL DENSITY AT 655 mμ.
0·50
0·25
10
20
30
40
50
60
70
80
TIME IN HOURS.

The preparation of Triphenodioxazine

Preparation of 2-amino-3-phenoxazone

o-Aminophenol (8 g.) was dissolved in thiophene-free benzene (550 c.c.) and absolute ethanol (4 c.c.) by stirring and refluxing. Yellow, well powdered mercuric oxide (48 g.) was added over 1½ hours and the reddish brown mixture refluxed for 7 hours. It was filtered hot, and the black mercurous oxide on the filter extracted with benzene (250 c.c.) in a Soxhlet apparatus until the extract was colourless, and then the original filtrate and extracts were combined. This was evaporated nearly to dryness on a steam-bath to give a brown powder (2.7 g.). A sample on recrystallisation from 95% ethanol gave small dark red microcrystalline needles of 2-amino-3-phenoxazone, m.p. 250-252°.

Condensation to triphenodioxazine

o-Aminophenol (5 g.) was dissolved in boiling 95% ethanol (75 c.c.) and made acid to Congo Red paper by the addition of concentrated hydrochloric acid. It was boiled 1 minute (charcoal), to afford o-aminophenol hydrochloride as a grey crystalline powder (2.1 g.).

o-Aminophenol hydrochloride (1.4 g.) was intimately

mixed in a mortar with 2-amino-3-phenoxazone (2 g.) and placed in a Pyrex test-tube. This was heated to 180° in an aluminium block and kept at this temperature for 5 minutes. Water vapour was given off and the mass coagulates. It was cooled, well powdered in a mortar, and extracted with three portions of boiling water (200 c.c.) and finally in a Soxhlet apparatus with methanol, to remove resinous impurities, leaving a red-brown-powder (1.5 g.).

This crude triphenodioxazine (0.67 g.) was dissolved in o-dichlorobenzene (1.50 c.c.) at 80-100° and chromatographed on a steam heated alumina column (40 x 2.5 cm.). A dark immobile band was formed at the top of the column whilst a strong orange-red band and a faint red band, moved down the column. The orange-red band was completely eluted with hot o-dichlorobenzene and the elute was concentrated to give red-violet plates (0.30 g.). A sample was recrystallised from o-dichlorobenzene to give glistening red plates of triphenodioxazine. (Found: C, 75.25; H, 3.7; N, 9.7. Calc. for $C_{18}H_{10}N_2O_2$:C, 75.5; H, 3.5; N, 9.8%). It was sparingly soluble in most organic solvents but dissolved in dioxan to give a yellow solution with a strong green fluorescence (1). It

dissolved to give a blue solution in concentrated sulphuric acid (2). Light absorption: (1) λ_{max} 240.5, 257,440,467.5,502.5 mμ (log ε 4.44,4.66,4.38,4.71, 4.84. Fig. 25). (2) λ_{max} 592,642.5 mμ (log ε 4.67, 4.94. Fig. 26). ν_{max} 1580 cm.$^{-1}$ (s), ·C:N· stretching.

A NEW SYNTHESIS OF TRIPHENODIOXAZINE

Condensation of o-anisidine with 1,4-benzoquinone

1,4-Benzoquinone (32 g., 0.296 mole.) was stirred in absolute ethanol (350 c.c.). Freshly redistilled o-anisidine (25 g., 0.201 mole.) was added dropwise over 20 minutes and the deep coloured mixture was refluxed for 5 hours. It was cooled to room temperature, filtered, and washed with hot ligroin (b.p. 60-80°) to yield a chocolate-brown crystalline powder (16 g., 45%). A sample was recrystallised from absolute ethanol to give purple needles of 2,5-di(o-anisidino)-1,4-benzoquinone, m.p. 249-250°. (Found: C,68.65; H,5.4; N,8.35. $C_{20}H_{18}N_2O_4$ requires C,68.6; H,5.15; N,8.0%). It was soluble in concentrated sulphuric acid to give a violet-blue colour which quickly changed to a dull blue, and in dioxan it gave a yellow-brown. For dioxan, light absorbtion: λ_{max} 268,275,405 mμ (log ε 4.28,4.27,4.24. Fig.18).

Cyclisation of 2,5-di(o-ansidino)-1,4-benzoquinone to triphenodioxazine

Anhydrous aluminium chloride (30 g., 0.215 mole.) was added in small portions with stirring to redistilled

pyridine (160 g.). After it had all been added, the temperature was adjusted to 60-80° and 2,5-di(o-anisidino)-1,4-benzoquinone (10 g., 0.028 mole.) added in small portions. The blue-violet mixture was refluxed for 18 hours, turning to a dull purple colour after 1 hour, and when cooled, it was mixed with 2N hydrochloric acid (240 c.c.). The purple mixture was stirred with concentrated hydrochloric acid (120 c.c.) and then diluted with hot water (600 c.c.) and allowed to stand for 12 hours. It was filtered, washed with boiling methanol and boiling water until the washings were nearly colourless, and then dried to give a dull brown powder (9 g.).

This brown powder (0.7 g.) was dissolved in o-dichlorobenzene (300 c.c.) by extraction and chromatographed on a steam heated alumina column (3 x 55 c.m.). A dark diffuse band was formed at the top of the column from which an orange-red band could be completely eluted with o-dichlorobenzene leaving behind dark impurities on the top of the column. The resulting orange yellow-solution, which exhibited a strong green fluorescence, was concentrated on a steam-bath under reduced pressure to give a red crystalline powder (0.19 g.).

This was recrystallised from o-dichlorobenzene to afford reddish purple glistening plates of triphenodioxazine. (Found: C,75.5; H,3.55; N,9.8. Calc. for $C_{18}H_{10}N_2O_2$: C,75.5; H,3.5; N,9.8%). Comparison by use of thin layer chromatography indicated that this product was identical to that obtained from the condensation of o-aminophenol hydrochloride with 2-amino-3-phenoxazone.

The effect of heating 2,5-dianilino-3,6-dichloro-1,4-benzoquinone at its melting point.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (1.0 g.) was placed in a Pyrex test-tube which was attached to an apparatus for absorbing hydrogen chloride. The tube was immersed for 4 minutes in a bath of boiling di-n-butyl phthalate (b.p. 340°), whilst a slow stream of nitrogen was swept through the contents, and the resulting gases being passed through 25 ml. of $\frac{N}{5}$ sodium hydroxide solution. 10 ml. of this solution was back titrated against 1.2 x $\frac{N}{5}$ hydrochloric acid using phenolphthalein as an indicator. This was equivalent to 0.1168 g. HCL per 1.0 g. of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone. The product (0.82 g.) was ground up to a homogeneous powder in a mortar, and a sample was dissolved in o-dichlorobenzene and examined by thin layer chromatography to show the presence of three orange-red components and one yellow component.

The product (1.5 g.) was dissolved in boiling o-dichlorobenzene (300 c.c.) and chromatographed on a steam heated alumina column (80 x 3.8 cm.). A strong red diffuse band was formed which was eluted with

o-dichlorobenzene into three fractions, B, C, and D; leaving behind a diffuse dark band, A, at the top of the column and showing no separation.

Band A.

The top part (circa top 5 cm.) of this band was exhaustively extracted with o-dichlorobenzene containing a little phenol. This also dissolved some solid, which had crystallised from the original liquor, together with the absorbed material. It was rechromatographed from o-dichlorobenzene on a steam heated alumina column (30 x 1 cm.) to give a purple, slightly mobile, band at the top of the column, and a lower mobile violet band. The lower band was completely eluted with o-dichlorobenzene to give a violet solution with a green fluorescence. Evaporation of this solution yielded a very small amount of violet solid, which contained several violet components as was shown by thin layer chromatography, and so it was discarded. The top band was extracted with difficulty with o-dichlorobenzene containing a little phenol to give a brown solution, which afforded purple plates (0.01 g.) on concentrating. These were recrystallised from o-dichlorobenzene to give shining purple plates, m.p. 350-353°. (Found: C,73.6; H,4.65;

N,9.7. Calc. for $C_{18}H_{14}N_2O_2$: C,74.5; H,4.83; N,9.65%). A solution in o-dichlorobenzene and a sample examined by thin layer chromatography gave a yellow band which compared directly with 2,5-dianilino-1,4-benzoquinone. It dissolved in concentrated sulphuric acid to give a red solution whose absorption spectrum was the same as the absorption spectrum of 2,5-dianilino-1,4-benzoquinone.

Fraction B.

This fraction contained only one orange component when examined by thin layer chromatography and was about 400 c.c. in volume. It was concentrated to low bulk on a steam-bath under reduced pressure, and the resulting solid recrystallised from o-dichlorobenzene to give purple-red needles (0.083 g.). (Found: C,60.45; H,2.45; N,7.95; Cl, 20.4. Calc. for $C_{18}H_8N_2O_2Cl_2$: C,60.8; H,2.25; N,7.9; Cl,20.0%). A sample compared directly with a sample of 6,13-dichlorotriphenodioxazine prepared by demethylation of 2,5-di(o-anisidino)-3,6-dichloro-1,4-benzoquinone, when examined by thin layer chromatography.

Fraction C.

Examination by thin layer chromatography showed this fraction to consist of two orange components, one of

which was 6,13-dichlorotriphenodioxazine. The liquor (circa 1L) was concentrated to 150 c.c. under reduced pressure on a steam-bath. This was chromatographed on a steam heated alumina column (80 x 3.8 cm.) and eluted with o-dichlorobenzene. The column formed two very diffuse bands, working from a purple-red colour at the top of the column to a red colour at the bottom. The lower band was eluted until about 400 c.c. of orange liquid had been collected or until a mixture of the two orange components began to form in the eluted liquor. Constant testing by thin layer chromatography was required in order to check the purity of the eluted material. The first fraction was concentrated to yield purple-red needles of 6,13-dichlorotriphenodioxazine (0.06 g.). The column was drained and the remaining red band divided mechanically into five equal portions. The top three portions were found to consist of the unknown orange component together with a little 6,13-dichlorotriphenodioxazine, whilst the remaining two portions were mixtures and were discarded. The three portions were extracted with o-dichlorobenzene (100 c.c.) and rechromatographed on a steam heated alumina column (29 x 2 cm.). The column was eluted until about 20 c.c. of liquor had run through, which contained most of the 6,13-dichlorotriphenodioxazine. The column was drained, and extracted with

o-dichlorobenzene, to yield an orange extract which on concentrating gave a red solid. This solid was recrystallised from o-dichlorobenzene to give small bright majenta needles (0.01 g.) which appeared to be 6-chlorotriphenodioxazine. (Found: C,66.75; H,3.1. $C_{18}H_9N_2O_2Cl$ requires C,67.4; H,2.8%). It dissolved in dioxan to give an orange-yellow solution with a green fluorescence (1) and in concentrated sulphuric acid to give a pure blue coloured solution (2). Light absorption: (1) λ_{max} 260,445,470,503 mμ (log ε 4.59,4.37,4.70,4.83. Fig. 23). (2) λ_{max} 605,650 mμ (log ε 4.51,4.82. Fig. 24).

Fraction D.

Thin layer chromatography showed the presence of three orange components,,the main one being 6,13-dichloro-triphenodioxazine with a very little 6-chlorotripheno-dioxazine, and a small quantity of unknown product. The liquor (1L.) was reduced to low volume (100 c.c.) and chromatographed on a steam heated alumina column (80 x 3.8 cm.). A deep red diffuse band was formed and it was eluted with o-dichlorobenzeneuntil most of 6,13-dichloro- and 6-chlorotriphenodioxazine was run off. This was checked by testing the purity of the eluted material by

use of thin layer chromatography. The column was drained and divided into four equal parts. On extraction of the parts with o-dichlorobenzene, the bottom fourth portion was discarded as examination by thin layer chromatography showed it to contain the least quantity of the unknown component. The remaining extract from the other three portions was concentrated (20 c.c.) and rechromatographed on a steam heated alumina column (30 x 1 cm.) to form a further diffuse red band. About the first 20 c.c. which were eluted were collected and concentrated to yield small purple crystals (0.005 g.). (Found : C,73.6; H,3.55; N,9.3; Cl, circa 1.0; ash,1.4. $C_{18}H_{10}N_2O_2$ requires C,75.5; H,3.5; N,9.8%). A sample examined by thin layer chromatography showed the presence of two orange components, the strongest comparing with triphenodioxazine and the other with 6,13-dichlorotripheno-dioxazine. Further attempts at purification appeared impracticable.

THE SYNTHESIS OF 6-CHLOROTRIPHENODIOXAZINE

Condensation of o-anisidine with 2,6-dichloro-1,4-benzoquinone.

2,6-Dichloro-1,4-benzoquinone (10 g., 0.067 mole.) and anhydrous sodium acetate (2.3 g., 0.028 mole) were stirred in absolute ethanol (50 c.c.). Freshly redistilled o-anisidine (7.5 g., 0.061 mole) was added over 10 minutes and then the mixture was refluxed on a steam-bath for 5 hours. The resulting dark coloured mixture was allowed to cool, filtered, and washed with ligroin (b.p. 60-80°, 300 c.c.) and hot water (250 c.c.) to give a dark brown crystalline powder (8.5 g.). A sample was recrystallised from methanol to give chocolate-brown microplates of 2,5-di(o-anisidino)-3-chloro-1,4-benzoquinone, m.p. 189-190°. A sample was sublimed at 175°/0.002 mm. to give a brown crystalline powder, m.p. 189-190°. (Found: C,62.6; H,4.45; N,7.65. $C_{20}H_{17}N_2O_4Cl$ requires C,62.5; H,4.4; N,7.9%). It dissolved in concentrated sulphuric acid to give an indigo-blue colour which changed to a dull purple on standing. It was readily soluble in organic solvents, e.g., in dioxan it was yellow-brown, light absorption: λ_{max} 268, 278,400 mμ (log ε 4.20,4.22,4.18. Fig. 17).

Cyclisation to the triphenodioxazine

Anhydrous aluminium chloride (16 g., 0.120 mole) was added in small portions to anhydrous pyridine (30 g.) with stirring. When all had been added, 2,5-di(o-anisidino)-3-chloro-1,4-benzoquinone (5 g., 0.013 mole.) was added gradually and then the mixture was refluxed for 20 hours. The mixture changed to a deep violet-blue colour after refluxing for 1 hour.

It was allowed to cool to room temperature and then mixed with 2N. hydrochloric acid (125 c.c.). To this mixture, concentrated hydrochloric acid (63 c.c.) was added with stirring, and then the whole mass diluted with hot water (312 c.c.) and allowed to stand for at least 12 hours. It was filtered and well washed with boiling water until the filtrate was only slightly coloured, to leave a reddish brown powder (4 g.). A sample examined by thin layer chromatography showed there to be two orange components, the lowest one comparing with triphenodioxazine, and the other with the suspected sample of 6-chloro-triphenodioxazine obtained by the pyrolysis of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

A sample was ground up in a mortar, dissolved in boiling o-dichlorobenzene and a strip of solution estimated

quantitatively as outlined on page 132. From the known absorption spectra, the relative concentrations could be estimated.

1. 6-Chlorotriphenodioxazine, λ_{max}(dioxan) @ 503 mμ ($E^{0.001\%}_{1\ cm.}$ = 2.13).

O.D./10 ml. = 0.26 C = 0.0122 R_c = 1.000

2. Triphenodioxazine, λ_{max}(dioxan) @ 502.5 mμ ($E^{0.001\%}_{1\ cm.}$ = 2.41)

O.D./5 ml. = 0.12 C = 0.0025 R_c = 0.205

O.D. = The optical density for a 1 cm. layer of the component dissolved in 5 or 10 ml. of dioxan.

C = Concentration of component in mg./100 ml. as calculated from O.D. and $E^{0.001\%}_{1\ cm.}$

R = Relative concentration.

The product (0.35 g.) was dissolved in o-dichlorobenzene (150 c.c.) by extraction and chromatographed on a steam heated alumina column (75 x 1.5 cm.). A diffuse red band was formed on eluting with o-dichlorobenzene, and

detached itself from the immobile black band at the top of the column, which would contain the impurities. About 150 c.c. were eluted from the column, or until a sample examined by thin layer chromatography showed the presence of more than one component, and the resulting orange-yellow, green fluorescent liquid, concentrated on a steam-bath under reduced pressure to yield a red crystalline powder (0.050 g.). This was recrystallised from o-dichlorobenzene to give purple-red microcrystalline needles of 6-chloro-triphenodioxazine. (Found: C,66.8; H,2.75; N,8.4. $C_{18}H_9N_2O_2Cl$ requires C,67.4; H,2.8; N,8.75%).

<u>The effect of heating 2,5-dianilino-1,4-benzoquinone at its melting point.</u>

2,5-Dianilino-1,4-benzoquinone (1.0 g.) was placed in a Pyrex test-tube and heated at 360-362° in an aluminium block for 5 minutes whilst a slow stream of nitrogen was circulating through the test-tube. It was cooled, and the solid mass (0.8 g.) well pulverised in a mortar. A sample dissolved in o-dichlorobenzene and examined by thin layer chromatography, showed the presence of only one yellow component, which compared to the starting material. A sample was recrystallised from o-dichlorobenzene, to give purple plates of 2,5-dianilino-1,4-benzoquinone, m.p. 354-356°.

The effect of a boiling solvent on 2,5-dianilino-1,4-benzoquinone.

Nitrobenzene

2,5-Dianilino-1,4-benzoquinone (1.0 g.) was refluxed with stirring in dry nitrobenzene (35 c.c.) for 24 hours. The mixture was cooled, filtered, washed with hot ligroin (b.p. 80-100°, 100 c.c.) and hot 95% ethanol (100 c.c.) and then dried at 100° to give a brown crystalline mass (1.81 g.). This was pulverised in a mortar and a sample in o-dichlorobenzene examined by thin layer chromatography. This showed the presence of only one yellow component which compared with the starting material. A sample was recrystallised from o-dichlorobenzene to give purple plates of 2,5-dianilino-1,4-benzoquinone, m.p. 354-356°.

The experiment was repeated, but the time of reflux changed to 48 hours. Unchanged starting material was again recovered.

Diphenyl Ether

2,5-Dianilino-1,4-benzoquinone (1.0 g.) was refluxed in diphenyl ether (b.p. 258°, 35 c.c.) with stirring for 24 hours. It was cooled, filtered, and well washed with boiling 95% ethanol to remove diphenyl ether, to leave a crystalline powder (1.5 g.). This was again found to be unchanged starting material on examination by thin layer chromatography.

The effect of condensing agents on 2,5-dianilino-1,4-benzoquinone.

p-Toluenesulphonyl chloride

Method 1.

2,5-Dianilino-1,4-benzoquinone (1 g., 0.0035 mole.), anhydrous sodium acetate (0.6 g., 0.0073 mole.) and p-toluenesulphonyl chloride (1.32 g., 0.0071 mole.), were refluxed for 24 hours with stirring in dry benzene (35 c.c.). The product was cooled, filtered, and washed with 95% ethanol to give back unchanged starting material (0.8 g.).

Method 2.

2,5-Dianilino-1,4-benzoquinone (2 g.), p-toluene-sulphonyl chloride (1.3 g.) and diphenyl ether (35 c.c.), were refluxed for 2 hours. Considerable spitting and evolution of water occurred and the resulting deep blue mixture filtered, leaving a dark mass on the filter (circa 0.3 g.) which appeared to be charcoal. No further work was carried out on the filtrate in view of the considerable decomposition which appeared to take place.

Method 3.

2,5-Dianilino-1,4-benzoquinone (1 g.) was refluxed in 1,2,4-trichlorobenzene (35 c.c.) containing

p-toluenesulphonyl chloride (1.32 g.) for 24 hours. The deep red-violet mixture was filtered leaving a negligible amount of solid on the filter. The filtrate was examined by thin layer chromatography and showed the presence of at least thirteen components, ranging in colour from orange to blue. The orange component compared with triphenodioxazine and the red-violet solution could be decolourised by boiling with alkaline sodium dithionite, the colour returning on standing. It was felt in view of the large number of products present, that it would be impracticable to attempt to separate further these components and it was thus abandoned.

Anhydrous aluminium chloride

Anhydrous aluminium chloride (3.1 g.) was added gradually to anhydrous pyridine (35 c.c.) with stirring. When all had been added, 2,5-dianilino-1,4-benzoquinone (1 g.) was added in small portions and then the mixture was refluxed for 24 hours. The mixture turned a bright orange colour after refluxing for about 1 hour. It was cooled, added to concentrated hydrochloric acid (20 c.c.) with stirring, and then diluted with hot water (100 c.c.). After standing, it was filtered and washed to give a brown powder (circa 0.9 g.), which when examined by thin layer chromatography showed the presence of only one

yellow component. A sample was recrystallised from o-dichlorobenzene to give purple plates of 2,5-dianilino-1,4-benzoquinone, m.p. 353-355°.

A similar experiment employing o-dichlorobenzene as the solvent again resulted in unchanged starting material.

The effect of diphenyl ether (b.p. 258°) as a solvent on 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (2.0 g.) and diphenyl ether (35 c.c., prepared by melting the solid at 50°) were refluxed with stirring under a slow stream of nitrogen. Any hydrogen chloride which was evolved was absorbed in 35 ml. $\frac{N}{5}$ sodium hydroxide and determined by back titration with $\frac{N}{5}$ hydrochloric acid. After the required time interval, the mixture was allowed to cool to 50°, filtered, and washed with 95% ethanol to remove diphenyl ether. The resulting crystalline mass was weighed, powdered in a mortar, and a sample dissolved in o-dichlorobenzene and quantitatively examined by thin layer chromatography by the procedure already outlined (see page 182.).

The following components were identified by use of

thin layer chromatography over a total time interval of 24 hours. Working from the top to the bottom of the chromatoplate (see chromatoplate 2, page 201) the following components were identified as set out in Table 1.

TABLE 1.

Reference number of component.	Colour of Chromatogram.	Identified components.	λ_{max} (mμ) in dioxan.	$E_{1\ cm.}^{0.001\%}$
1.	Orange-red	6,13-Di-chloro-tripheno-dioxazine	506.5	1.725
2.	Yellow	2,5-Dianil-ino-3,6-dichloro-1,4-benzoquinone.	390	0.44
3.	Orange-red	6-Chlorotri-phenodioxa-zine	503	2.13
	Orange-yellow			
4.	Yellow	2,5-Dianil-ino-3-chloro-1,4-benzo-quinone.	383	0.54
5.	Yellow	2,5-Dianil-ino-1,4-benzoquinone.	375	0.67

A faint trace of triphenodioxazine was also observed but it was assumed to be in a negligible proportion compared to the other components. Components 3 and 4 were in most

cases incompletely separated on the chromatoplate, as their R_f values were very similar under these conditions, so the absorption of the mixture was measured at the wavelength maximum of 3 and 4. The results obtained are tabulated in Table 2.

TABLE 2.

Time of heating. (hr.)	Yield. (g.)	g.HCl/2g. starting product.	Components obtained.	O.D.	C.	R_c.
3	1.66	0.0399	1.	0.058	0.0034	1.000
			2.	0.297	0.0675	19.850
			4.	0.002	0.0004	0.118
6	1.18	-	1.	0.290	0.0168	1.000
			2.	0.143	0.0325	1.935
			(3.	0.080	0.0037	0.220
			(4.	0.138	0.0256	1.520
10	1.22	0.2603	1.	0.360	0.0209	1.000
			3.	0.260	0.0122	0.585
			5.	0.135	0.0202	0.967
24	0.85	-	1.	0.285	0.0165	1.000
			3.	0.195	0.0092	0.557
			5.	0.125	0.0186	1.130

O.D. = The optical density for a 1 cm. layer of the component dissolved in 5 or 10 ml. of dioxan at λ_{max}.

C = Concentration of component in mg./100 ml. as calculated from O.D. and $E_{1\ cm.}^{0.001\%}$

R_c = Relative concentration.

The effect of nitrobenzene (b.p. 211°) as a solvent on 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (2.0 g.) and dry A.R. nitrobenzene (35 c.c.) were refluxed with stirring under a slow stream of nitrogen. Any hydrogen chloride evolved was absorbed in 30 ml. $\frac{N}{5}$ sodium hydroxide and determined by back titration with $\frac{N}{5}$ hydrochloric acid using phenolphthalein as indicator. After the required time interval, the mixture was cooled to room temperature, filtered, and washed with 95% ethanol and ligroin (b.p. 80-100°) to remove nitrobenzene. The resulting crystalline mass was powdered in a mortar, weighed and a sample dissolved in o-dichlorobenzene and examined quantitatively by thin layer chromatography (see page 132).

The following components were identified over a total time interval of 72 hours. Working from top to bottom of the chromatoplate (see chromatoplate 1, page 201), they are tabulated in Table 3.

TABLE 3.

Reference number of component.	Colour of chromatogram.	Identified components.	λ_{max} (mμ) in dioxan.	$E_{1\ cm.}^{0.001\%}$
1.	Orange-red	6,13-Dichl-orotripheno-dioxazine.	506.5	1.725
2.	Yellow.	2,5-Dianil-ino-3,6-dichloro-1,4-benzo-quinone.	390	0.44
3.	Orange-red	6-Chloro-tripheno-dioxazine.	503	2.13
	Orange-yellow			
4.	Yellow.	2,5-Dianil-ino-3-chloro-1,4-benzo-quinone.	383	0.54
5.	Orange-red	Tripheno-dioxazine	502.5	2.41
6.	Yellow	2,5-Dianil-ino-1,4-benzoquinone.	375	0.67

The results obtained are tabulated in Table 4.

TABLE 4.

Time of heating. (hr.)	Yield (g.)	g.HCl/2g. starting product.	Components obtained.	O.D.	C.	R_c.
9	1.60	-	Negligible change in the starting product.			
24	1.43	0.1040	1.	0.800	0.0464	1.000
			2.	0.220	0.0500	1.079
			3.)	0.060	0.0028	0.061
			4.)	0.207	0.0383	0.825
48	1.36	0.1860	1.	1.590	0.0923	1.000
			3.)	0.480	0.0225	0.244
			4.)	0.284	0.0526	0.570
			5.	0.174	0.0072	0.078
			6.	0.175	0.0261	0.283
72	1.37	0.2190	1.	1.980	0.1148	1.000
			3.)	0.730	0.0343	0.299
			4.)	0.275	0.0509	0.444
			5.	0.215	0.0089	0.078
			6.	0.315	0.0470	0.410

O.D. = The optical density for a 1 cm. layer of the component dissolved in 5 or 10 ml. of dioxan.

C = Concentration of component in mg./100 ml. as calculated from O.D. and $E_{1\ cm.}^{0.001\%}$

R_c = Relative concentration.

A similar experiment was carried out by using 1,2,4-trichlorobenzene (b.p. 213°) as the solvent. Negligible change occurred in the starting material after refluxing it in trichlorobenzene for 72 hours.

The effect of p-toluenesulphonyl chloride on the cyclisation of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone in different solvents.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (2.0 g.) was refluxed with p-toluenesulphonyl chloride (0.5 g.) in the solvent (35 c.c.) for 6 hours. When cool, the product was filtered and washed with two portions of boiling 95% ethanol (125 c.c.) and then dried at 100°. The resulting crystalline mass was weighed, pulverised in a mortar, and a sample dissolved in o-dichlorobenzene and examined quantitatively by thin layer chromatography by the procedure already outlined (see page 132).

The products identified over the range of the experiment are, working from top to bottom of the chromatoplate (see chromatoplate 3, page 201), tabulated in Table 5.

TABLE 5.

Reference number of component.	Colour of chromatogram.	Identified components.	λ_{max}(mμ) in dioxan.	$E_{1\ cm.}^{0.001\%}$
1.	Orange-red	6,13-Dichloro-tripheno-dioxazine.	506.5	1.725
2.	Yellow	2,5-Dianil-ino-3,6-dichloro-1,4-benzo-quinone.	390	0.44
3.	Orange-red	6-Chlorotri-pheno-dioxazine	503	2.13
	Orange-yellow			
4.	Yellow	2,5-Dianil-ino-3-chloro-1,4-benzo-quinone	383	0.54
5.	Orange-red	Tripheno-dioxazine	502.5	2.41
6.	Yellow	2,5-Dianil-ino-1,4-benzoquinone	375	0.67

The results obtained are tabulated in Table 6.

TABLE 6.

Solvent employed.	Yield (g.)	Components Obtained.	O.D.	C.	R_c.
o-Dichloro-benzene (b.p.180°)	No measurable change occurred over the required time interval.				
Nitro-benzene (b.p.211°)	1.14	1.	0.820	0.0475	1.000
		2.	0.133	0.0152	0.320
		3.)	0.160	0.0038	0.079
		4.)	0.220	0.0204	0.430
1,2,4-Tri-chloro-benzene (b.p.213°)	1.09	1.	0.690	0.0400	1.000
		2.	0.050	0.0057	0.143
		3.)	0.100	0.0024	0.060
		4.)	0.080	0.0074	0.185
Diphenyl ether (b.p.258°)	1.02	1.	0.175	0.0101	1.000
		3.	0.220	0.0103	1.020
		5.	0.113	0.0047	0.465
		6.	0.085	0.0063	0.627

O.D. = The optical density for a 1 cm. layer of the component dissolved in 5 or 10 ml. of dioxan.

C. = Concentration of component in mg./100 ml. as calculated from O.D. and $E_{1\ cm.}^{0.001\%}$

R_c = Relative concentration.

The effect of diphenyl ether on 2,5-dianilino-3-chloro-1,4-benzoquinone.

2,5-Dianilino-3-chloro-1,4-benzoquinone (2.0 g.) was refluxed in diphenyl ether (35 c.c.) with stirring under an atmosphere of nitrogen for 24 hours. The hydrogen chloride evolved was absorbed in 25 ml. $\frac{N}{5}$ sodium hydroxide and determined by back titration with $\frac{N}{5}$ hydrochloric acid. The mixture was allowed to cool, filtered, and washed with 95% ethanol to remove diphenyl ether. The resulting crystalline mass was weighed, powdered in a mortar, and a sample dissolved in o-dichloro-benzene and examined quantitatively by thin layer chromatography (see page 132). The products identified are tabulated in Table 7.

TABLE 7.

Reference number of component.	Colour of chromatogram.	Identified components.	λ_{max} (mμ) in dioxan.	$E^{0.001\%}_{1\ cm.}$
1.	Orange-red	6-chloro-tripheno-dioxazine	503	2.13
2.	Yellow	2,5-Dianil-ino-1,4-benzo-quinone	375	0.67

The results obtained are tabulated below.

Yield. (g.)	g.HCl/2g. starting product.	Components obtained.	O.D.	C.	R_c.
0.85	0.1660	1.	0.135	0.0032	1.000
		2.	0.415	0.0310	9.700

O.D. = The optical density for a 1 cm. layer of the component dissolved in 5 or 10 ml. of dioxan.

C. = Concentration of component in mg./100 ml. as calculated from O.D. and $E_{1\ cm.}^{0.001\%}$

R_c. = Relative concentration.

A sample of the product (0.20 g.) was dissolved in boiling o-dichlorobenzene (130 c.c.) and chromatographed on a steam heated alumina column (35 x 1.5 cm.). It was eluted with o-dichlorobenzene forming two bands. The upper was a dark purple slow moving band, whilst the lower was a red mobile band, which was completely eluted from the column. The orange, green fluorescent eluate was concentrated to give a red crystalline powder (circa 0.005 g.). This was sublimed at 200°/0.2 mm. to give a red sublimate.

(Found: N,8.6. $C_{18}H_9N_2O_2Cl$ requires N,8.75%).

The purple band at the top of the column was extracted with o-dichlorobenzene and the extract concentrated to give a crystalline solid (0.015 g.). This was recrystallised from o-dichlorobenzene to give purple plates, m.p. 355°, of 2,5-dianilino-1,4-benzoquinone. (Found: C,73.9; H,4.75. Calc. for $C_{18}H_{14}N_2O_2$: C,74.5; H,4.8%).

The experiment was repeated under the same conditions but using nitrobenzene as the solvent. Unchanged starting material was recovered.

The hydrogenation of 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

2,5-Dianilino-3,6-dichloro-1,4-benzoquinone (0.2 g.) was dissolved in boiling toluene (200 c.c., A.R.). To this, Raney nickel (circa 1 g., British Drug Houses stabilised brand) was introduced with stirring. The mixture was then refluxed for 8 hours whilst a steady stream of hydrogen was bubbled through it. It was filtered hot, and the colourless solution concentrated, turning brown during the process. It gave on cooling, a dark crystalline powder (0.11 g.). (Found: Cl,15.2. Calc. for $C_{18}H_{12}N_2O_2Cl_2$: Cl,19.8%). This was well powdered in a mortar and a sample dissolved in o-dichloro-benzene and examined quantitatively by thin layer chromatography (see page 132). 2,5-Dianilino-3,6-dichloro-1,4-benzoquinone, 2,5-dianilino-3-chloro-1,4-benzoquinone, and a trace of 2,5-dianilino-1,4-benzoquinone were identified (see chromatoplate 1, page 201). From previous data obtained in tables 3 and 5 (see pages 190, 194) on their absorption spectra, the following results were obtained.

Identified component	O.D.	C.	R_c
2,5-Dianilino-3,6-dichloro-1,4-benzoquinone	0.405	0.0920	1.000
2,5-Dianilino-3-chloro-1,4-benzoquinone	0.405	0.0750	0.816

O.D. = The optical density for a 1 cm. layer of the component dissolved in 10 ml. of dioxan.

C. = Concentration of component in mg./100 ml. as calculated from O.D. and $E_{1\ cm.}^{0.001\%}$ obtained in tables 3,5.

R_c. = Relative concentration.

1. Triphenodioxazine.
2. 6-Chlorotriphenodioxazine.
3. 6,13-Dichlorotriphenodioxazine.
4. 2,5-Dianilino-1,4-benzoquinone.
5. 2,5-Dianilino-3-chloro-1,4-benzoquinone.
6. 2,5-Dianilino-3,6-dichloro-1,4-benzoquinone.

7.	Effect of nitrobenzene on 6.	24 hours.
8.		48 hours.
9.		72 hours.

10. Product from the hydrogenation of 6.

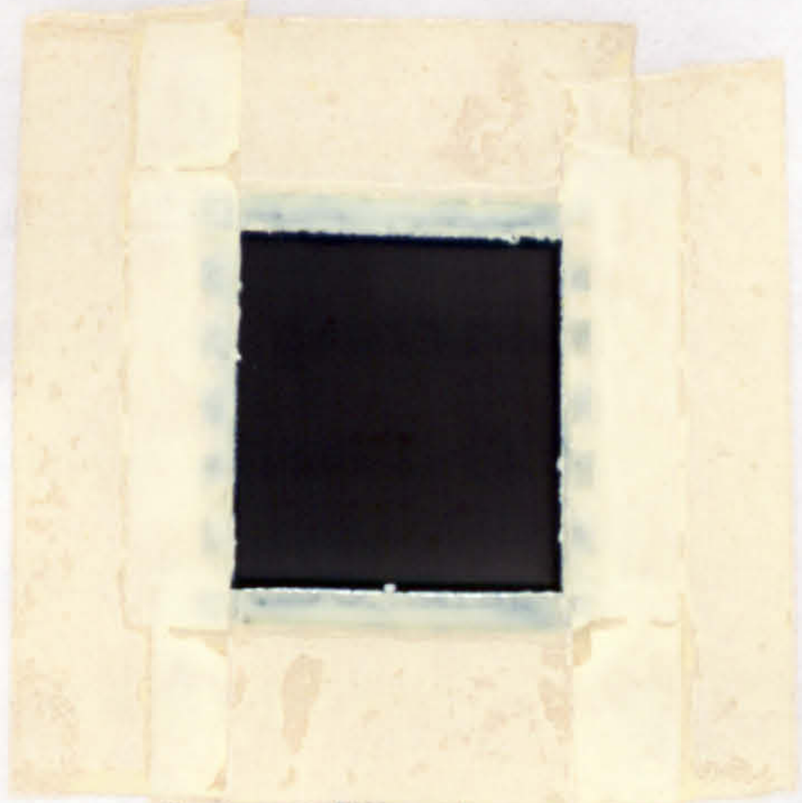
11.	Effect of diphenyl ether on 6.	3 hours.
12.		10 hours.
13.		24 hours.

14.	Effect of solvent and p-toluenesulphonyl chloride on 6.	Nitrobenzene.
15.		Trichlorobenzene.
16.		Diphenyl ether.

Concentrations in o-dichlorobenzene.

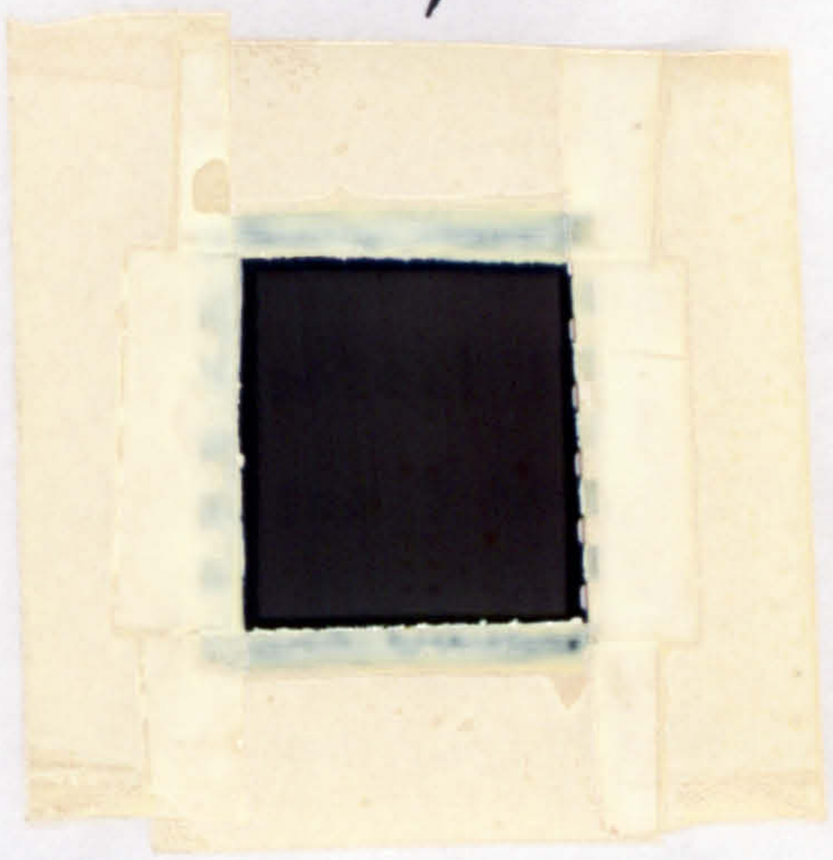
5 mg./30 c.c.	1,4.
5 mg./10 c.c.	2,3,5,6.
10 mg./10 c.c.	7 - 16.

Chromatoplate. 1.



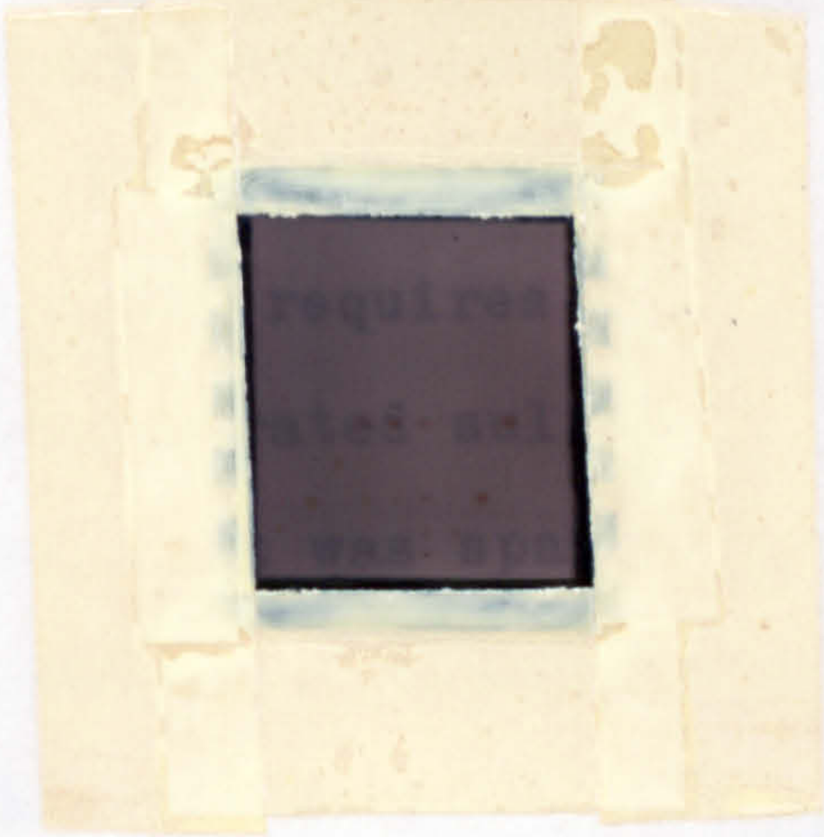
4. 5. 6. 10. 7. 8. 9. 1. 2. 3.

Chromatoplate. 2.



4. 5. 6. 11. 12. 13. 1. 2. 3.

Chromatoplate. 3.



4. 5. 6. 14. 15. 16. 1. 2. 3.

Chromatogram developed by eluting 2× with A.R. Toluene.

The condensation of m-nitroaniline with chloranil

Chloranil (9 g., 0.037 mole.) and anhydrous sodium acetate (6 g., 0.073 mole.) were added with stirring to a solution of m-nitroaniline (10 g., 0.072 mole.) in absolute ethanol (175 c.c.) and refluxed for 3 hours. The resulting deep violet coloured mixture was filtered hot, and washed with boiling 95% ethanol and water until the washings were no longer violet coloured, to leave a yellow-brown powder (7.1 g., 43%). A sample was recrystallised from o-dichlorobenzene to give bronze plates of 2,5-di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone, m.p. 322-324°. (Found: C,48.55; H,2.55; N,12.6. $C_{18}H_{10}N_4O_6Cl_2$ requires C,48.1; H,2.25; N,12.45%). It dissolved in concentrated sulphuric acid to give a red-brown solution. It was sparingly soluble in most organic solvents but would dissolve in dioxan to give a yellow-brown. Light absorption: λ_{max} 268,380 mμ (log ε 4.52,4.23. Fig. 20).

The attempted cyclisation of 2,5-di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone.

2,5-Di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone (2 g.) and p-toluenesulphonyl chloride (0.5 g.) were

refluxed with stirring in dry nitrobenzene (35 c.c.) for 8 hours. On cooling, the blue-black mixture was filtered and well washed with boiling 95% ethanol to give a dark powder (1.5 g.). Examination of a sample of this powder dissolved in o-dichlorobenzene and examined by thin layer chromatography showed the presence of a large amount of impurity together with a small amount of orange component. On continual development of the chromatogram, the orange component separated into two barely definable orange components. In view of the apparent decomposition and small amount of product it was considered impracticable to pursue further with the investigation.

ABSORPTION SPECTRA

Absorption spectra were carried out using a Unicam S.P. 600 spectrophotometer employing fused silica 1 cm. cells. The absorption coefficient was recorded as optical density (O.D.) for 1 mg. substance in 100 c.c. solvent, i.e., $E_{1\ cm.}^{0.001\%}$. The relationship between $E_{1\ cm.}^{0.001\%}$ and the molar extinction coefficient ε, is given by the following equation:-

$$\varepsilon = 100.\ M.\ E_{1\ cm.}^{0.001\%}$$

where M is the molecular weight of the substance to be measured.

The dioxan was purified and dried according to Vogel.[99]

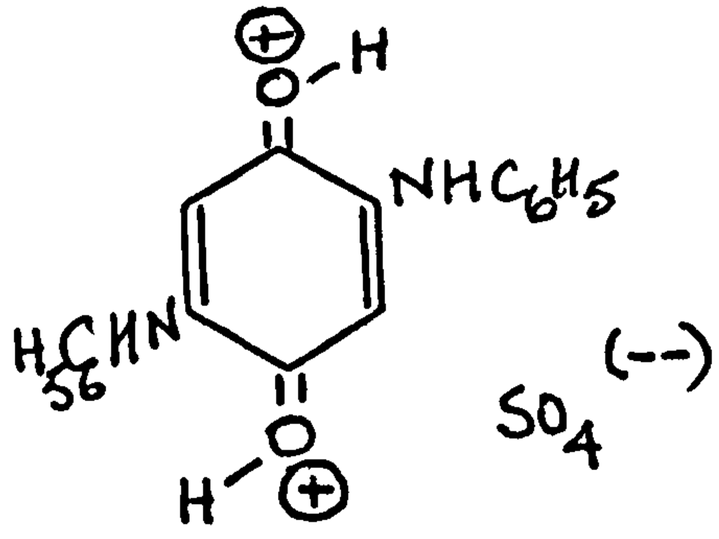
The sulphuric acid used was of A.R. Quality.

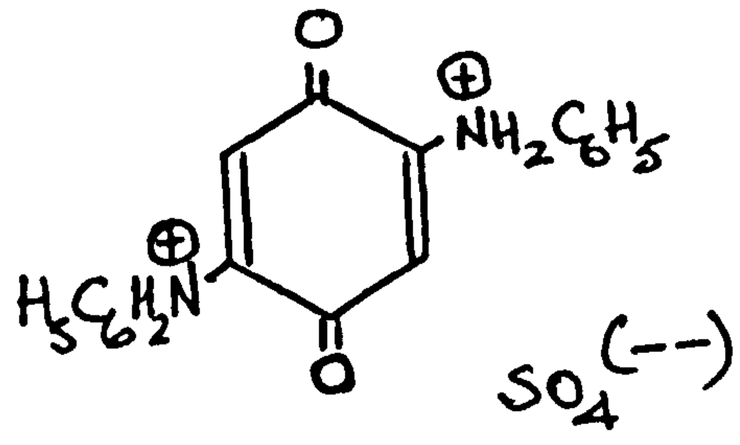
The o-dichlorobenzene used was twice distilled over calcium chloride.

The pyridine was distilled over potassium hydroxide and used immediately.

All the arylaminoquinones dissolved in concentrated

sulphuric acid with the formation of characteristic colours, the colour disappearing on dilution with water with the precipitation of the original arylaminoquinone. The colour was much deeper than in neutral solvents although the general shape of the curve was similar. The main absorption peak was shifted to a longer wavelength than in neutral solvents. This shift could be attributed to the increase in unsaturation brought about by the formation of onium salts.





The extinction coefficient, at the main peak in sulphuric acid, is a measure of the readiness of the arylaminoquinone to be protonated. Steric considerations apart, this readiness will be greatest in those molecules which have the most nucleophilic substituents, since these will give rise to the maximum availability of electrons at the -O- and -N- atoms. This was observed in that 2,5-dianilino-1,4-benzoquinone had a higher extinction than 2,5-dianilino-3,6-dichloro-1,4-benzoquinone.

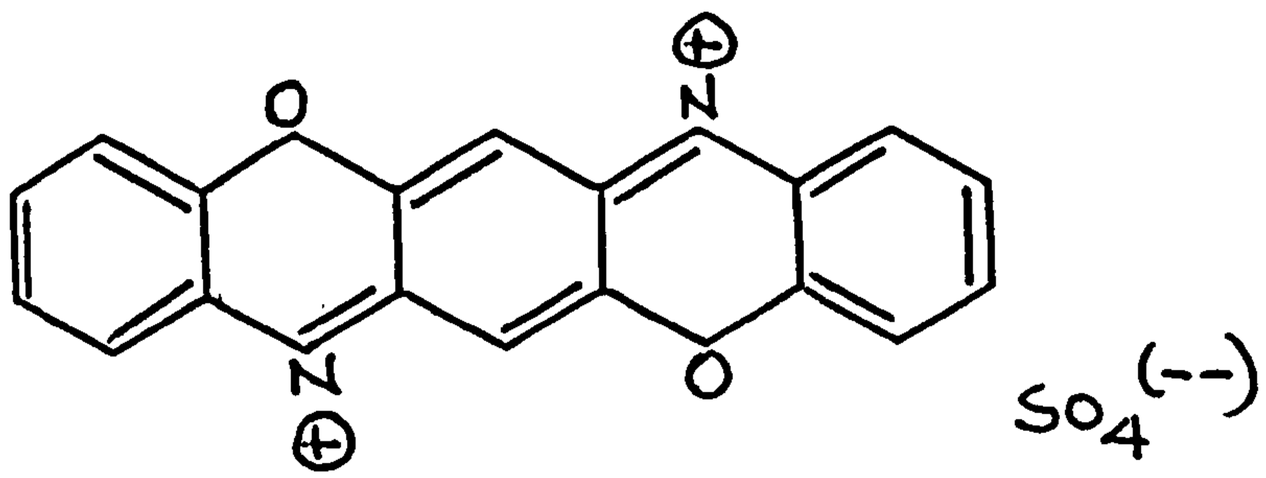
The introduction of chlorine into the molecule caused a bathochromic shift and a hypochromic effect, e.g., colours in sulphuric acid:-

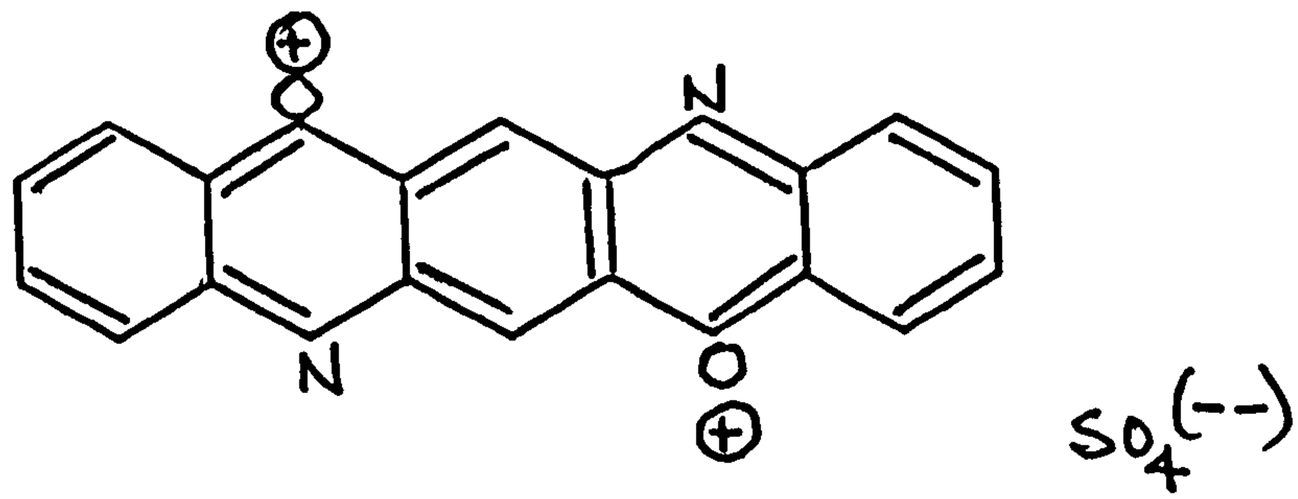
2,5-Dianilino-1,4-benzoquinone.	Red.
2,5-Dianilino-3-chloro-1,4-benzoquinone.	Red-violet.
2,5-Dianilino-3,6-dichloro-1,4-benzoquinone.	Blue-violet.

The chlorine atoms donate electrons to the system causing an increase in conjugation with a resulting bathochromic shift.

The same effect was noticed in neutral solvents although the reverse effect was noticed when chlorine was introduced into 2,5-di(o-anisidino)-1,4-benzoquinone, a hypsochromic shift occurring. This is rather difficult to explain in view of the fact that there are further electron donating groups which are added to the system, all of which would cause a bathochromic shift. Chlorine could withdraw electrons due to its inductive properties and the presence of it in addition to the $-OCH_3$ groups, which also contribute electrons, may cause the electron donating groups to donate less electrons than if they had not been together.

The triphenodioxazine derivatives all dissolve in concentrated sulphuric acid with the formation of quaternary nitrogen and oxonium salts.





The quaternary nitrogen salt is the most likely form as it owes its stability to the p-quinonoid nitrogen structure, while the oxonium salt requires a rearrangement of the bonds in the middle ring to form a benzenoid structure which would presumably be unstable in the presence of an oxidizing agent such as sulphuric acid. The spectra usually contains one large peak which is shifted towards the longer wavelengths with the increase of

molecular weight of the triphenodioxazine. Both in sulphuric acid and in neutral solvents, there is a bathochromic shift on the introduction of chlorine into the molecule.

INDEX TO ABSORPTION SPECTRA

Fig. 11. 2,5-Dianilino-3,6-dichloro-1,4-benzoquinone in sulphuric acid.

Fig. 12. 2,5-Dianilino-3-chloro-1,4-benzoquinone in dioxan.

Fig. 13. 2,5-Dianilino-3-chloro-1,4-benzoquinone in sulphuric acid.

Fig. 14. 2,5-Dianilino-1,4-benzoquinone in dioxan.

Fig. 15. 2,5-Dianilino-1,4-benzoquinone in sulphuric acid.

Fig. 16. 2,5-Di(o-anisidino)-3,6-dichloro-1,4-benzoquinone in dioxan.

Fig. 17. 2,5-Di(o-anisidino)-3-chloro-1,4-benzoquinone in dioxan.

Fig. 18. 2,5-Di(o-anisidino)-1,4-benzoquinone in dioxan.

Fig. 19. 2,5-Di(o-phenetidino)-3,6-dichloro-1,4-benzoquinone in dioxan.

Fig. 20. 2,5-Di(3-nitroanilino)-3,6-dichloro-1,4-benzoquinone in dioxan.

Fig. 21. 6,13-Dichlorotriphenodioxazine in dioxan.

Fig. 22. 6,13-Dichlorotriphenodioxazine in sulphuric acid.

Fig. 23. 6-Chlorotriphenodioxazine in dioxan.

Fig. 24. 6-Chlorotriphenodioxazine in sulphuric acid.

Fig. 25. Triphenodioxazine in dioxan.

Fig. 26. Triphenodioxazine in sulphuric acid.

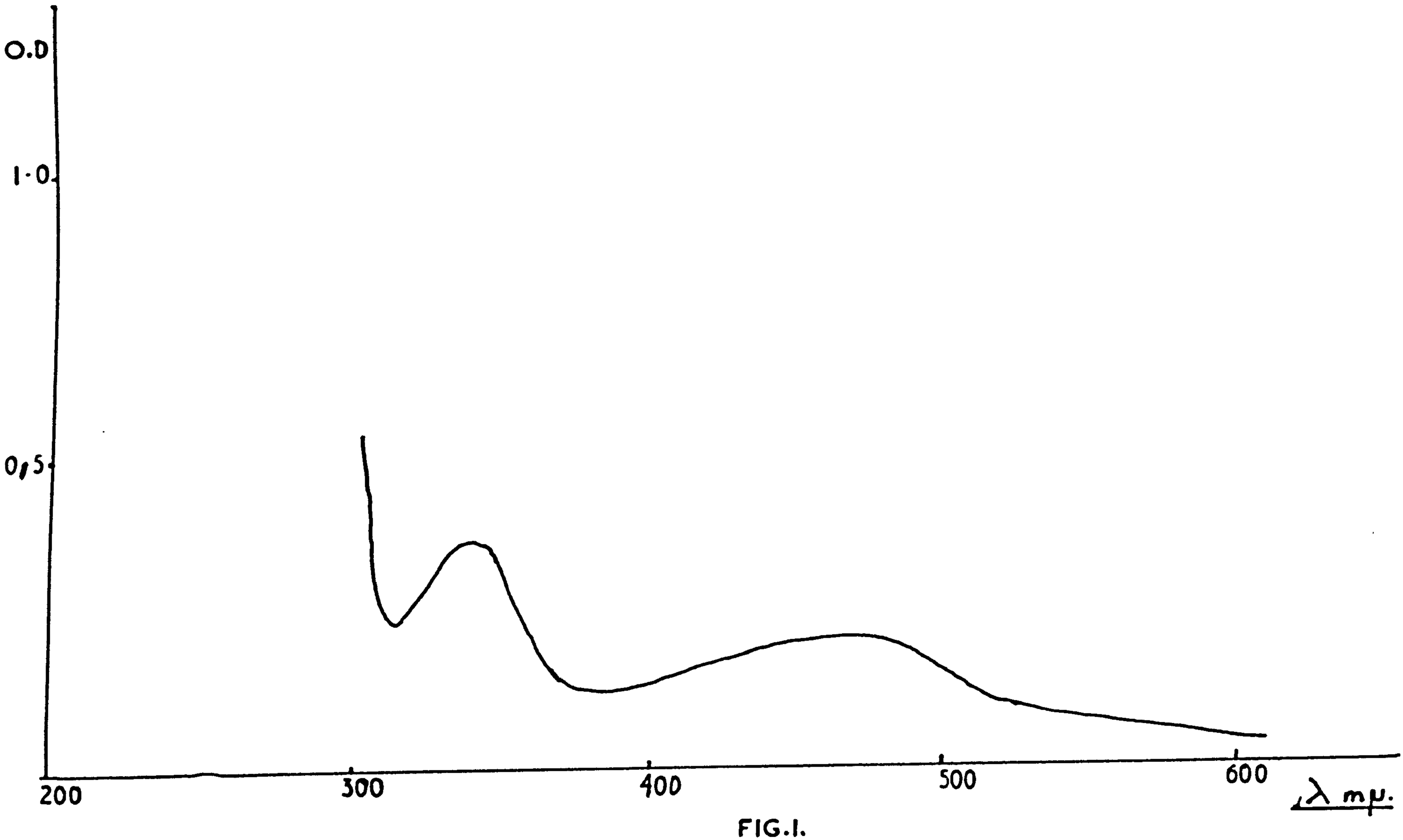


FIG.I.

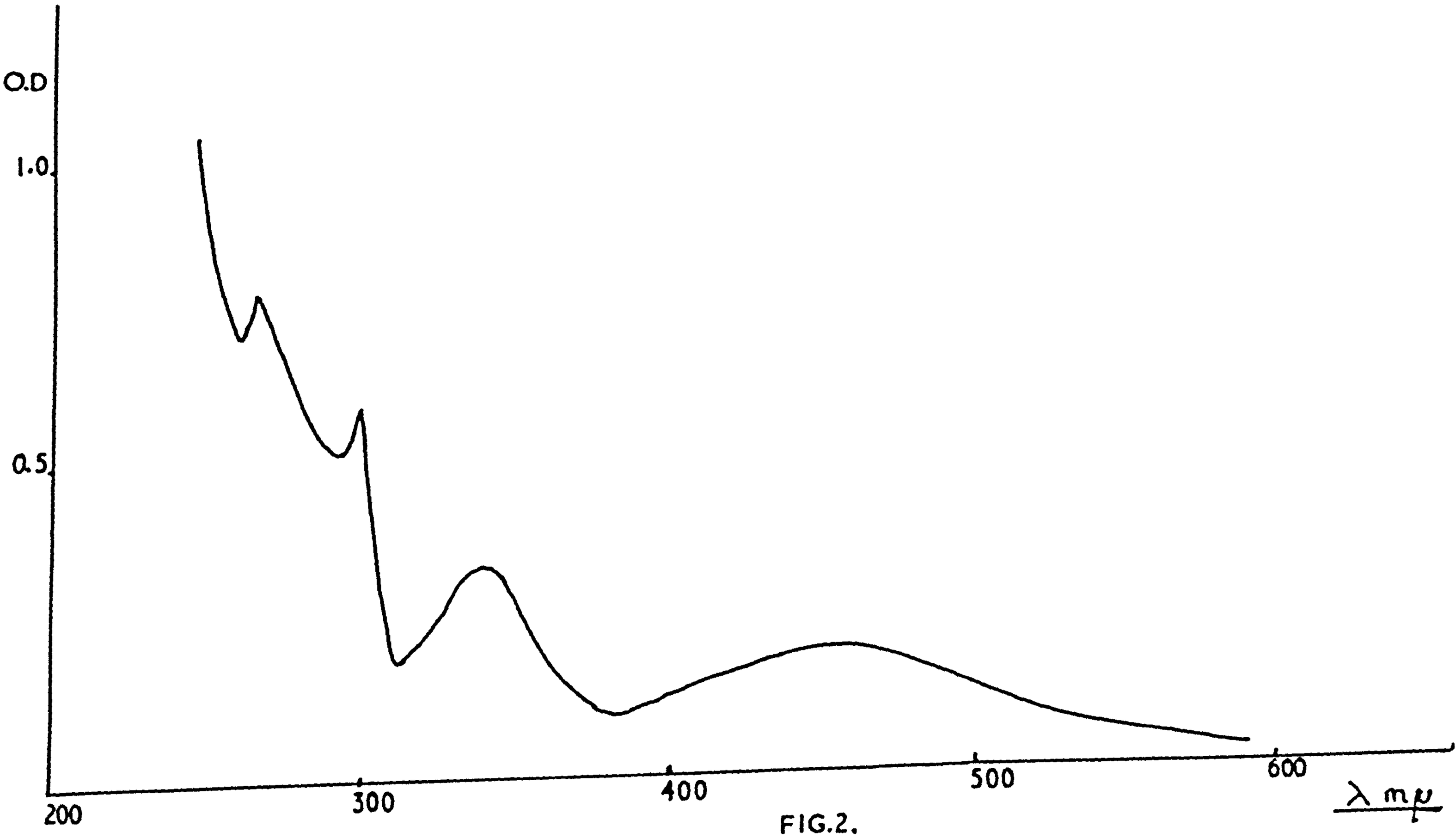


FIG.2.

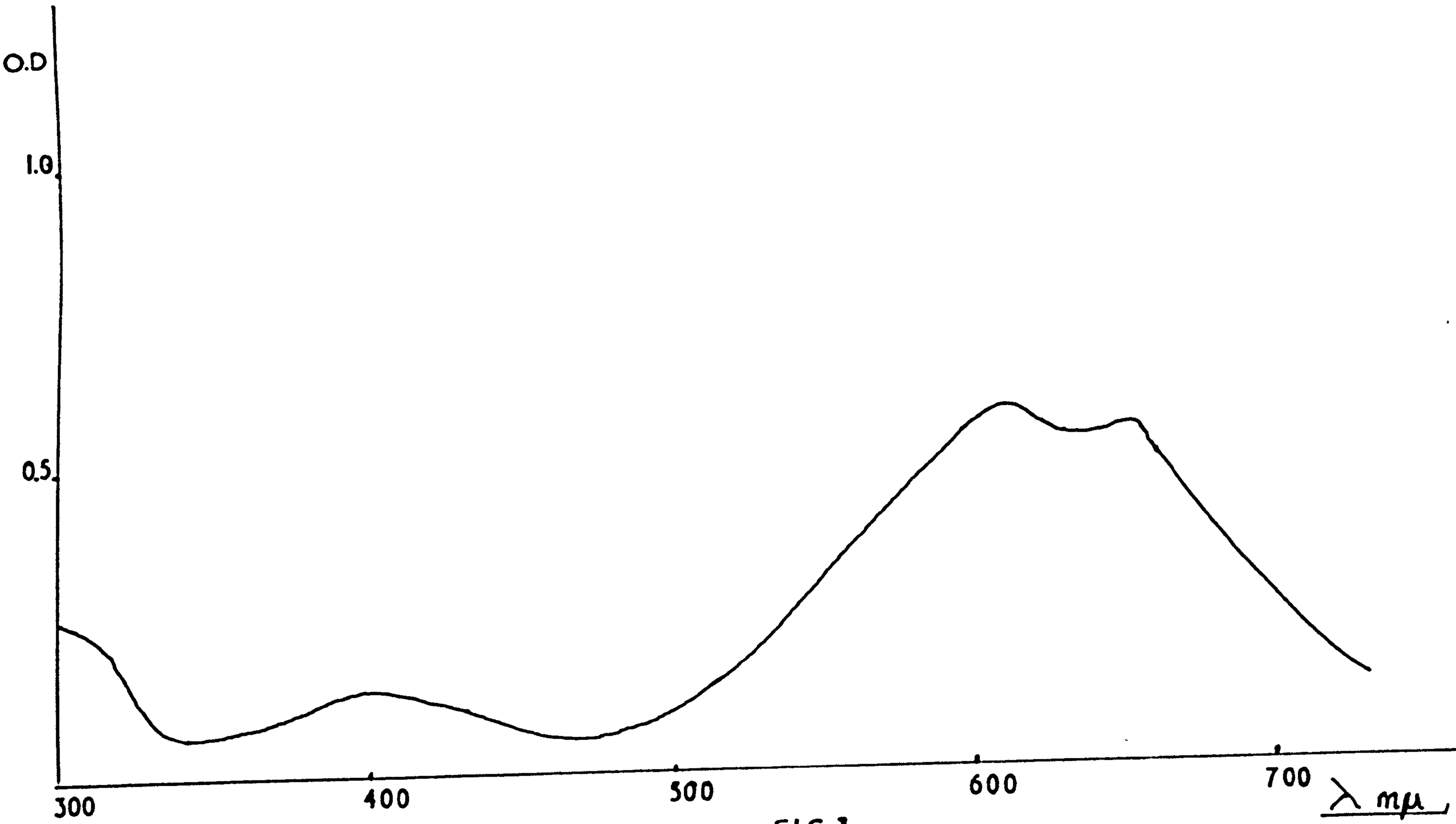


FIG.3.

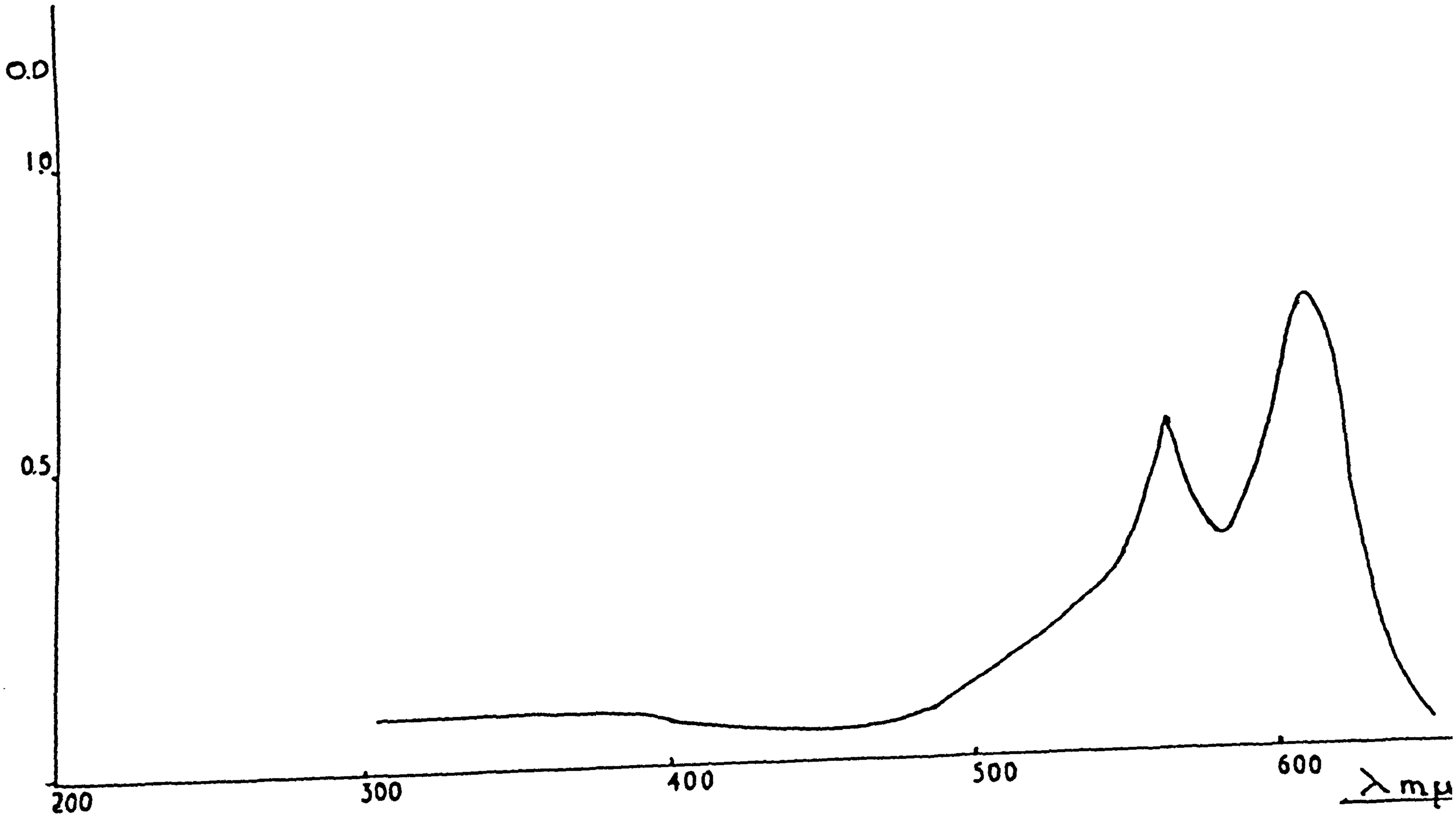


FIG.4.

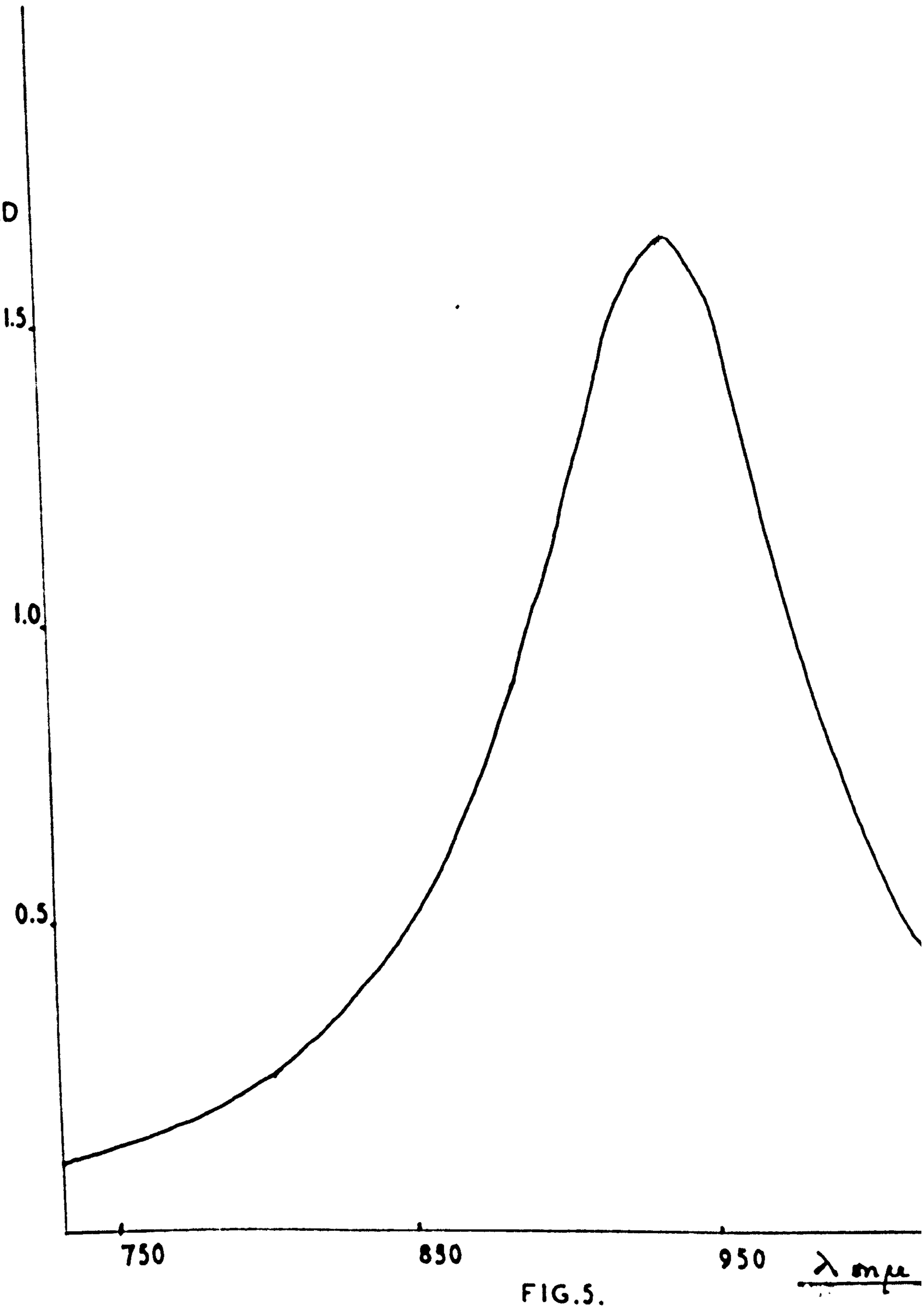


FIG.5.

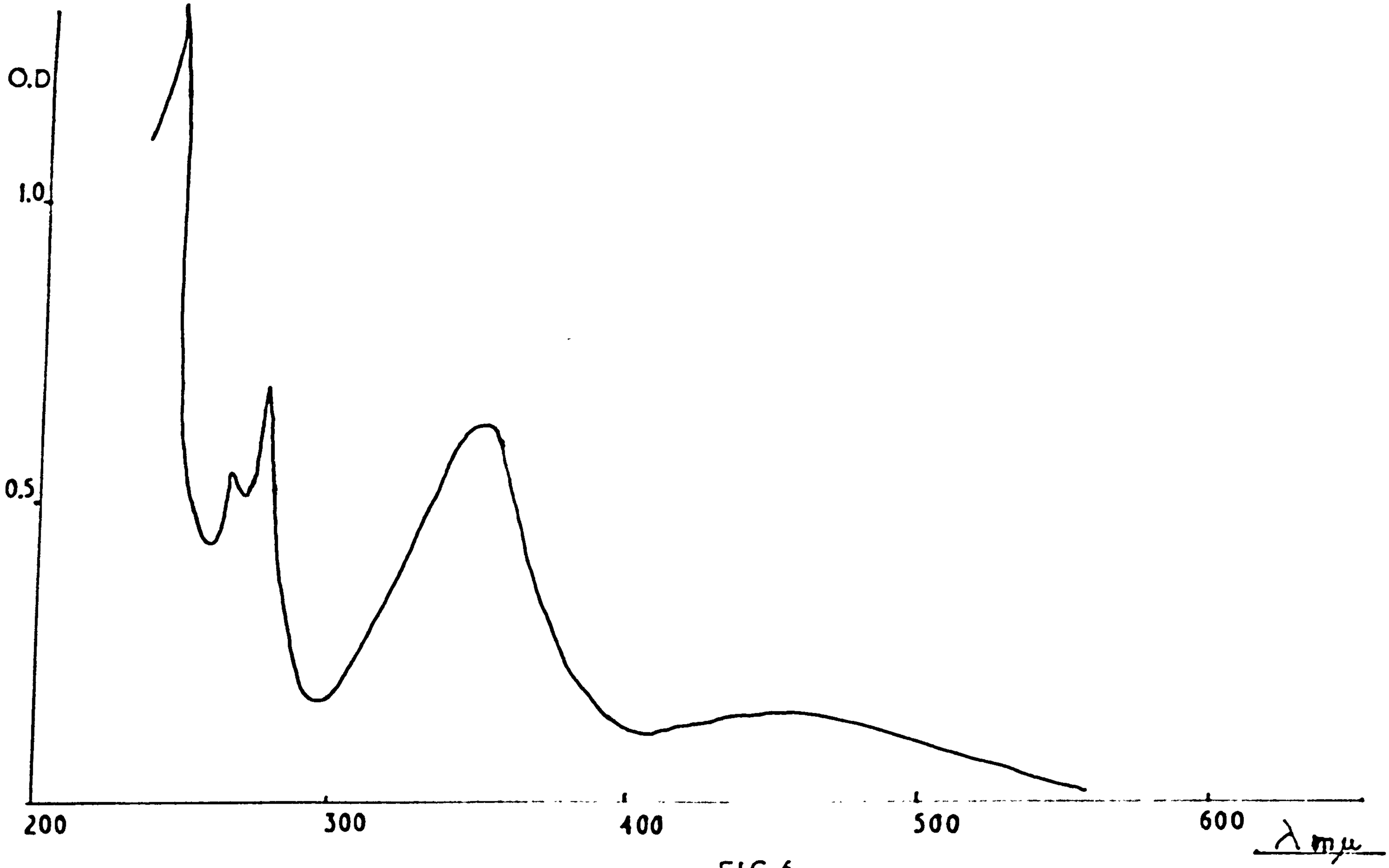


FIG.6.

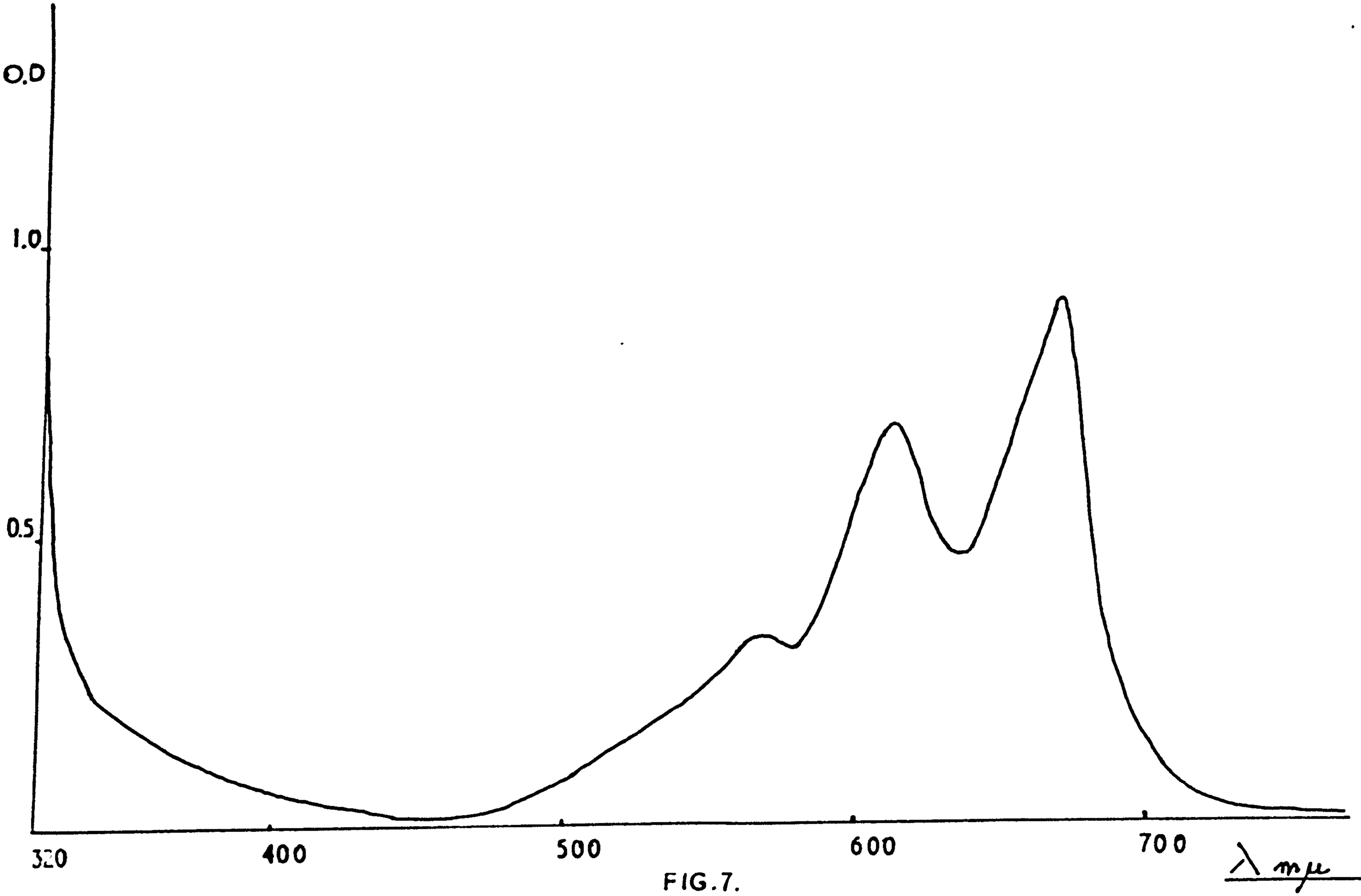


FIG. 7.

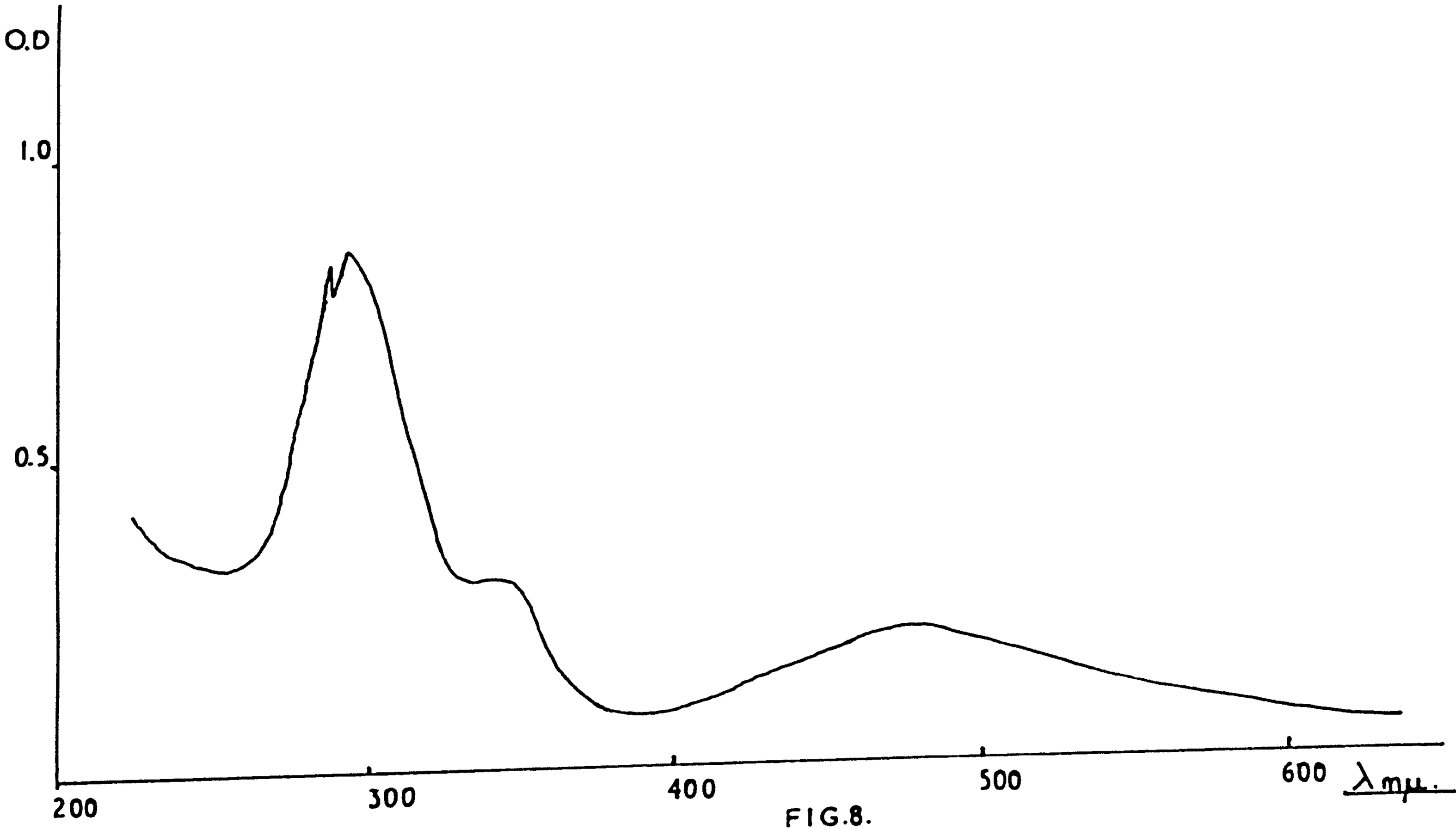


FIG.8.

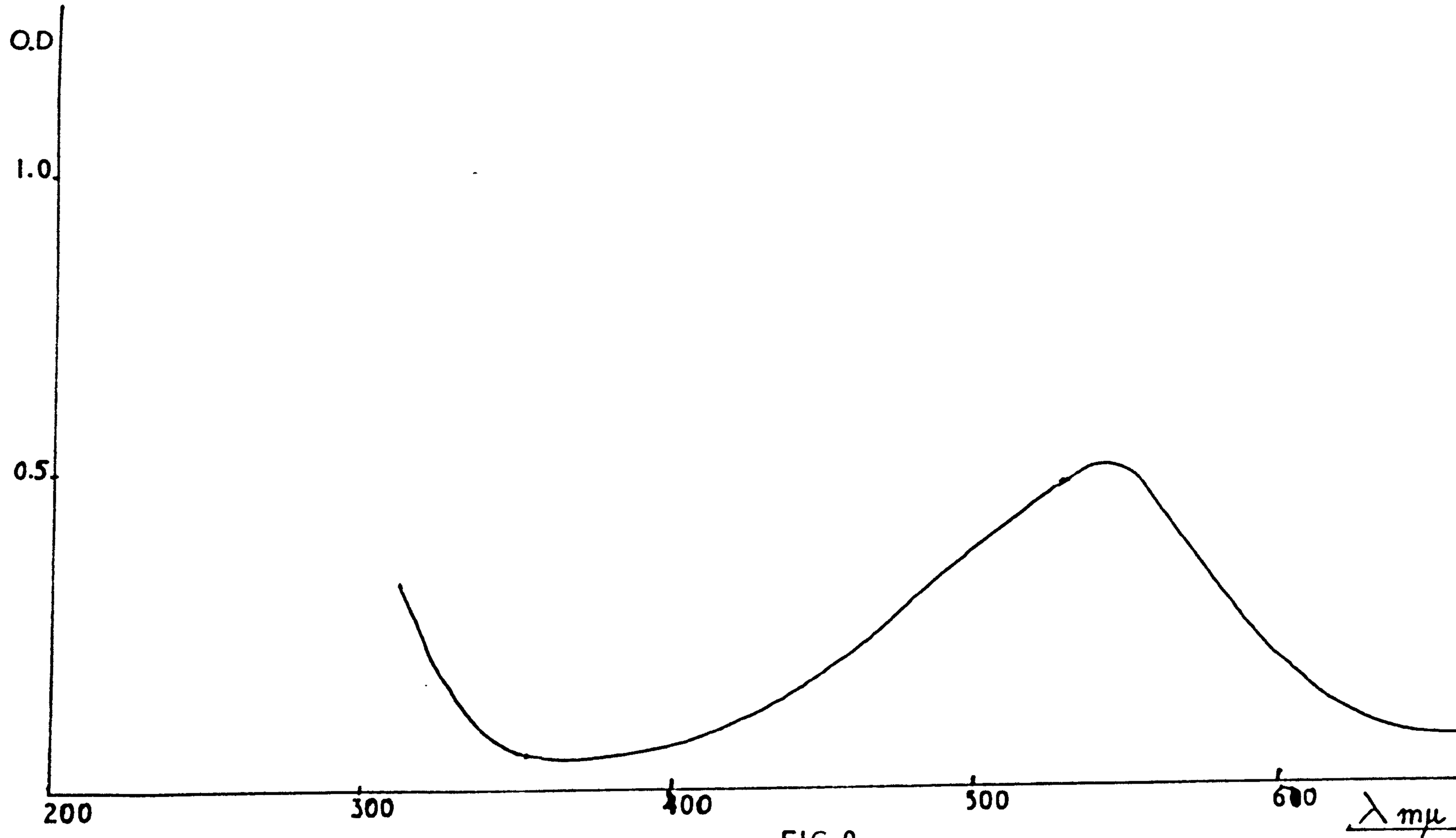
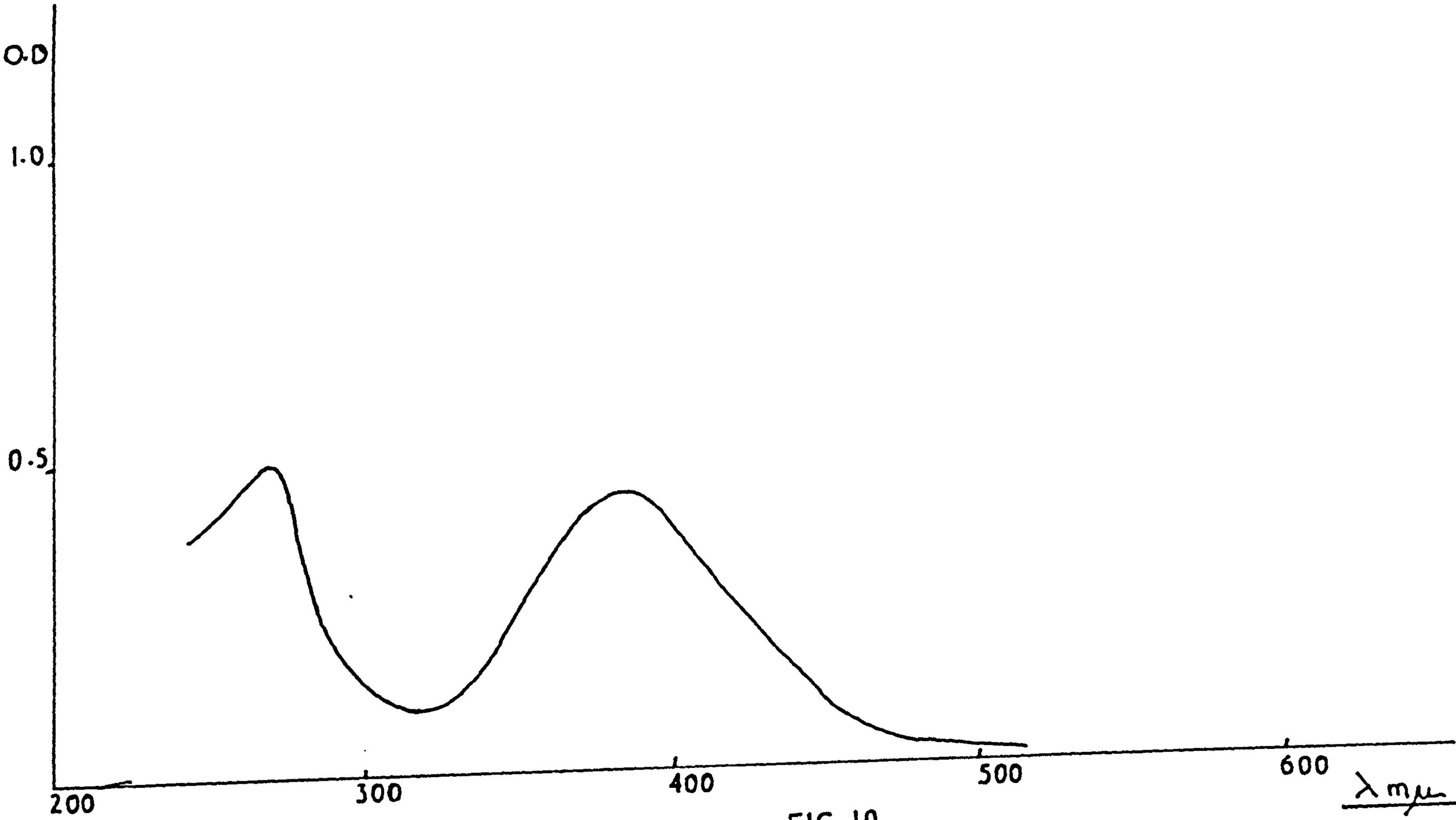


FIG. 9.



FIG·10·

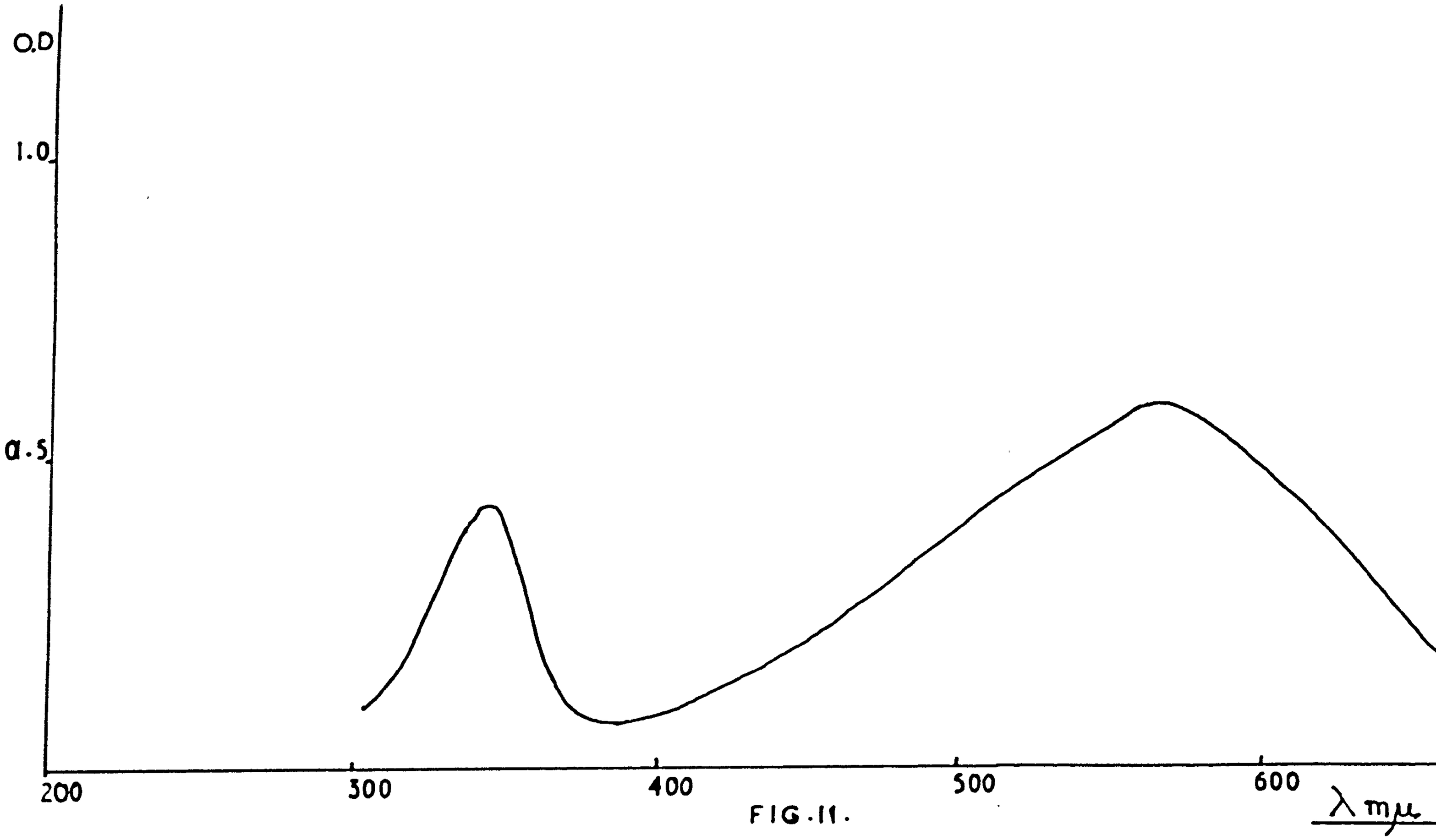
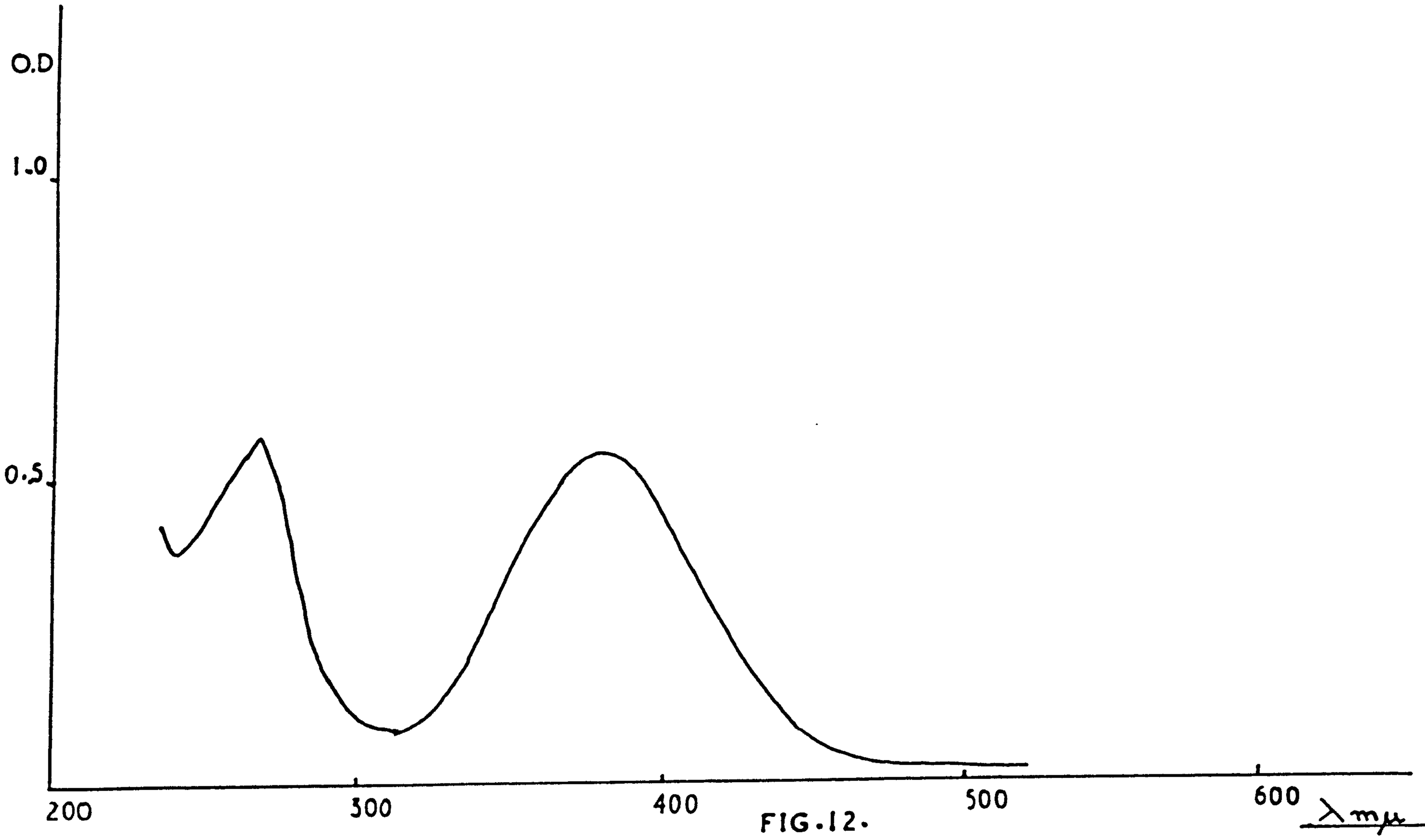


FIG. 11.



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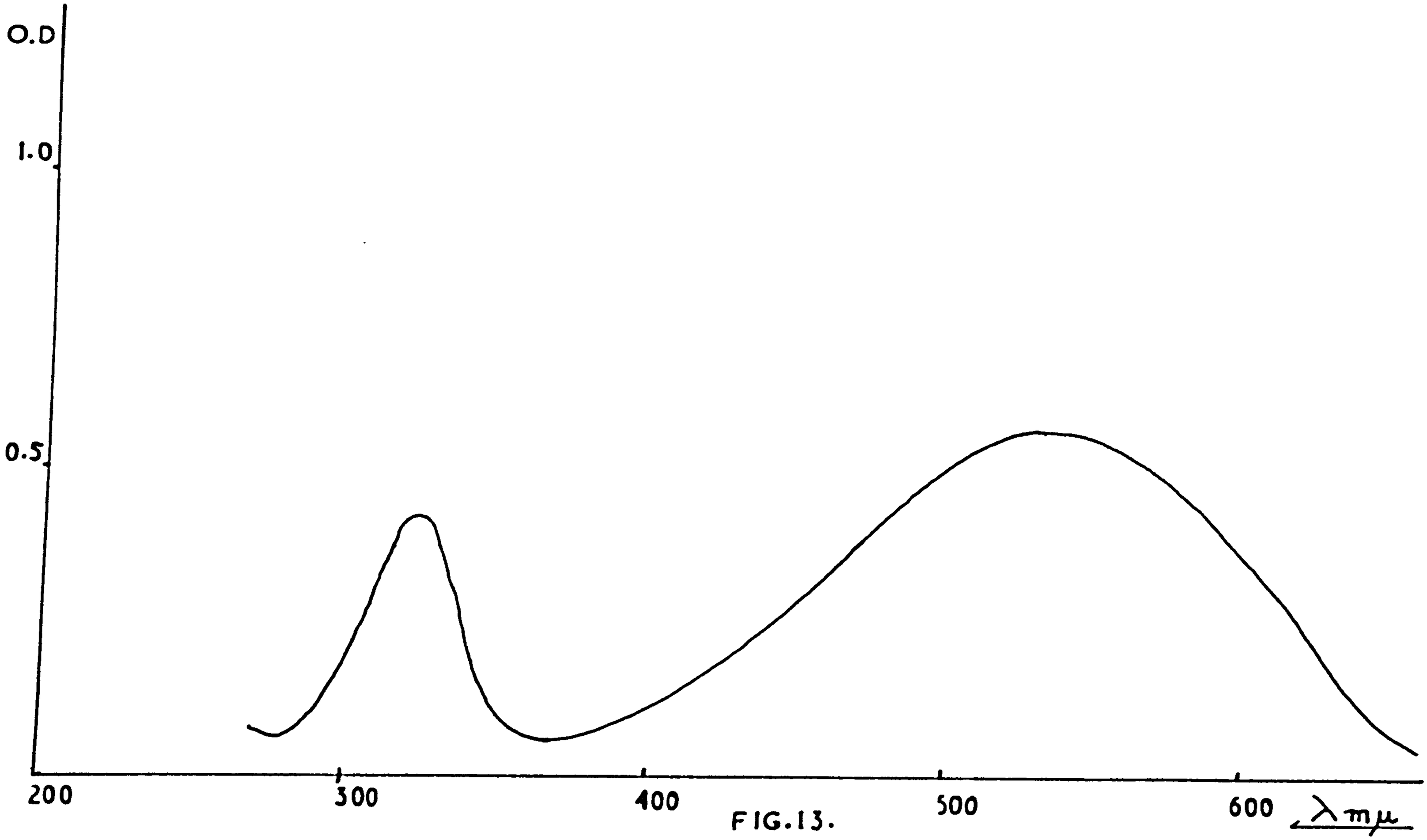

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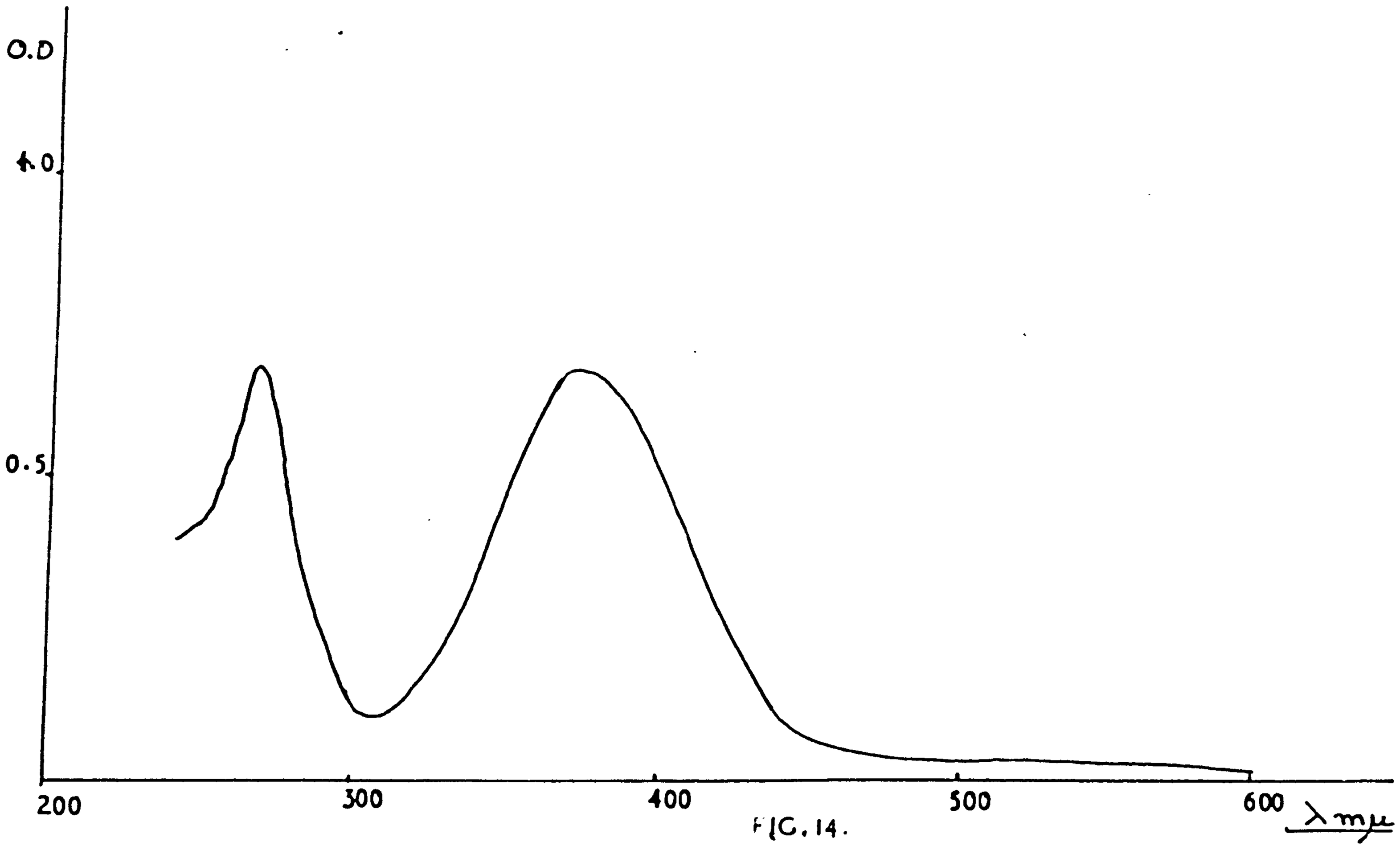
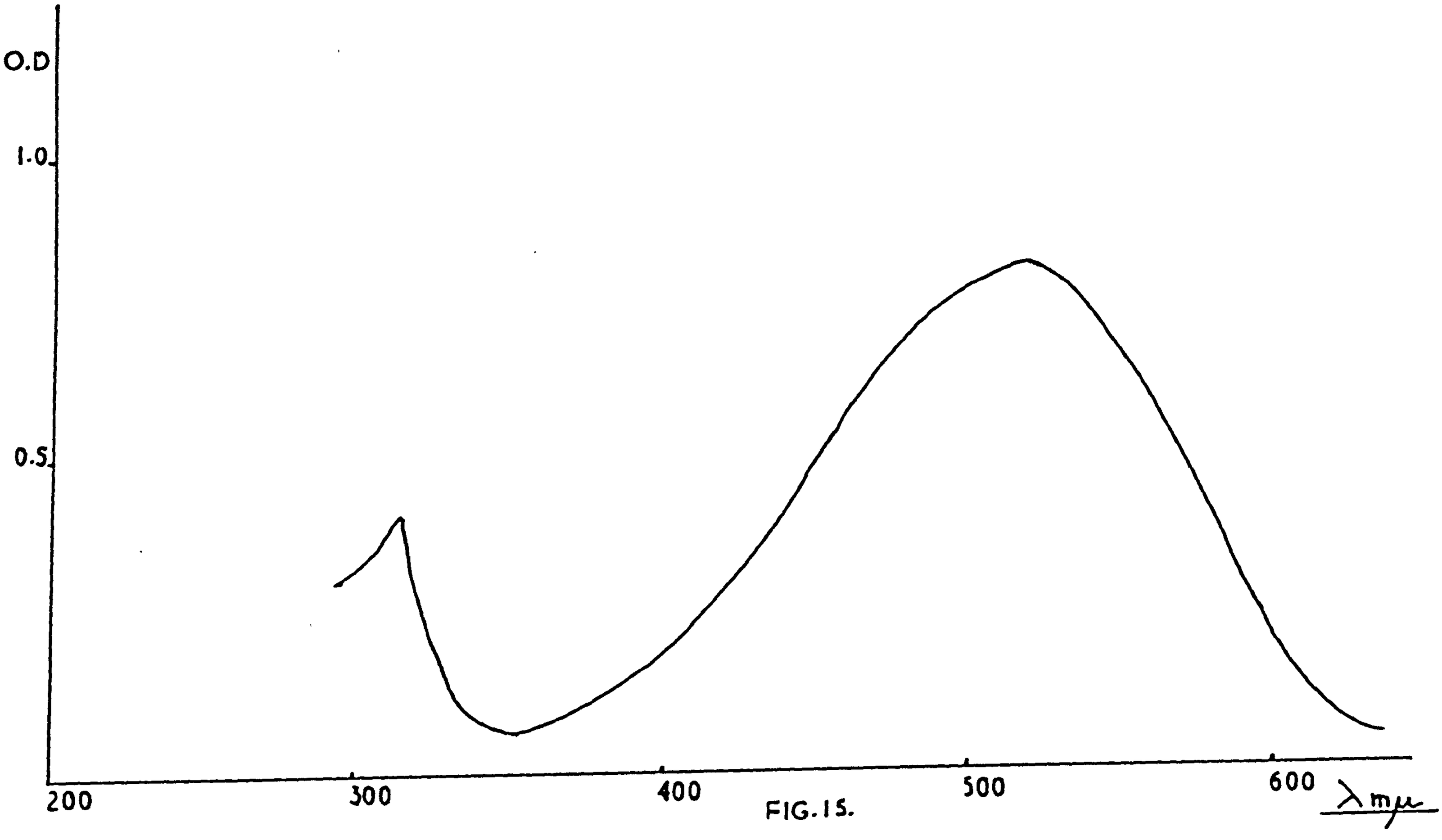


FIG. 14.



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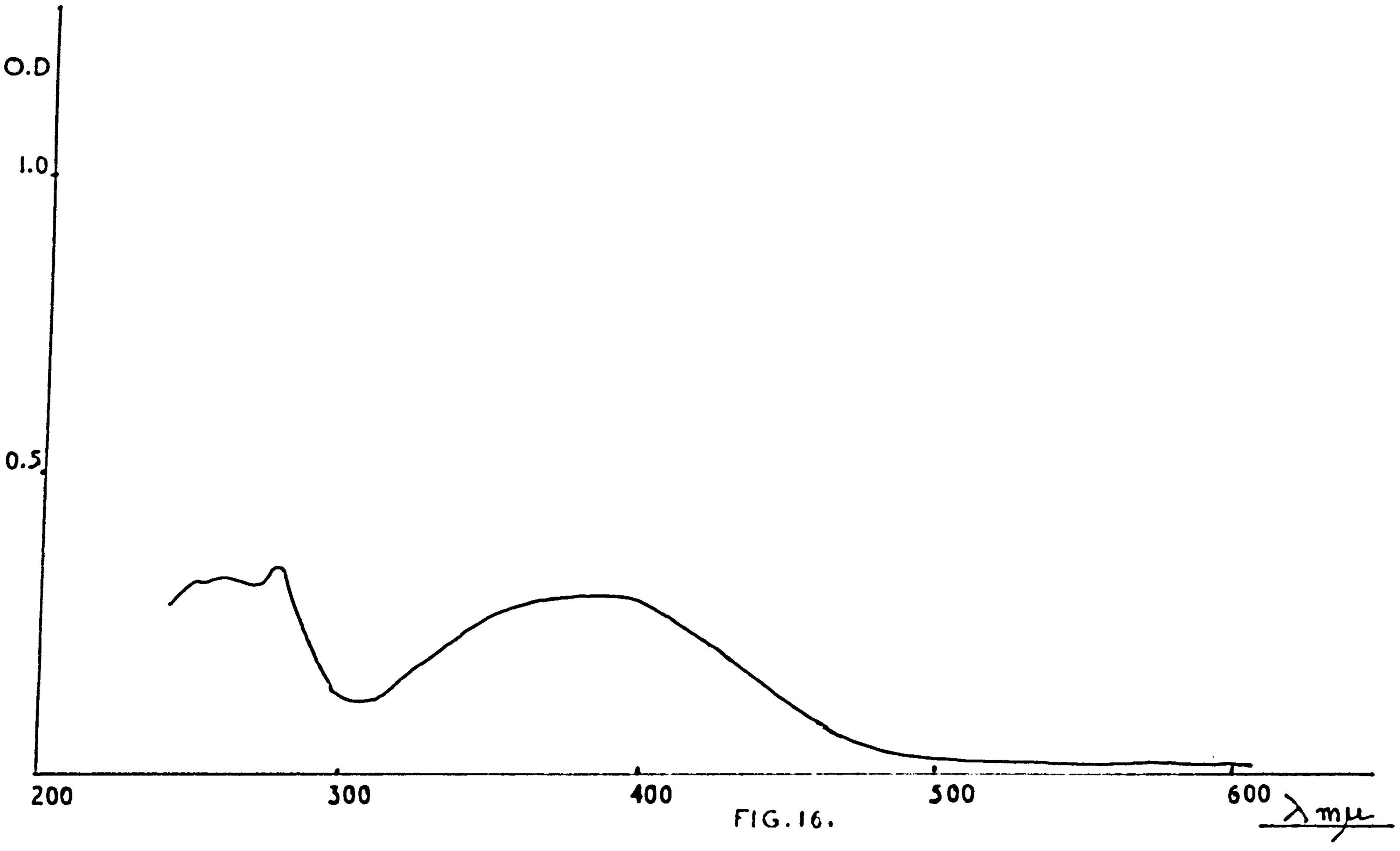

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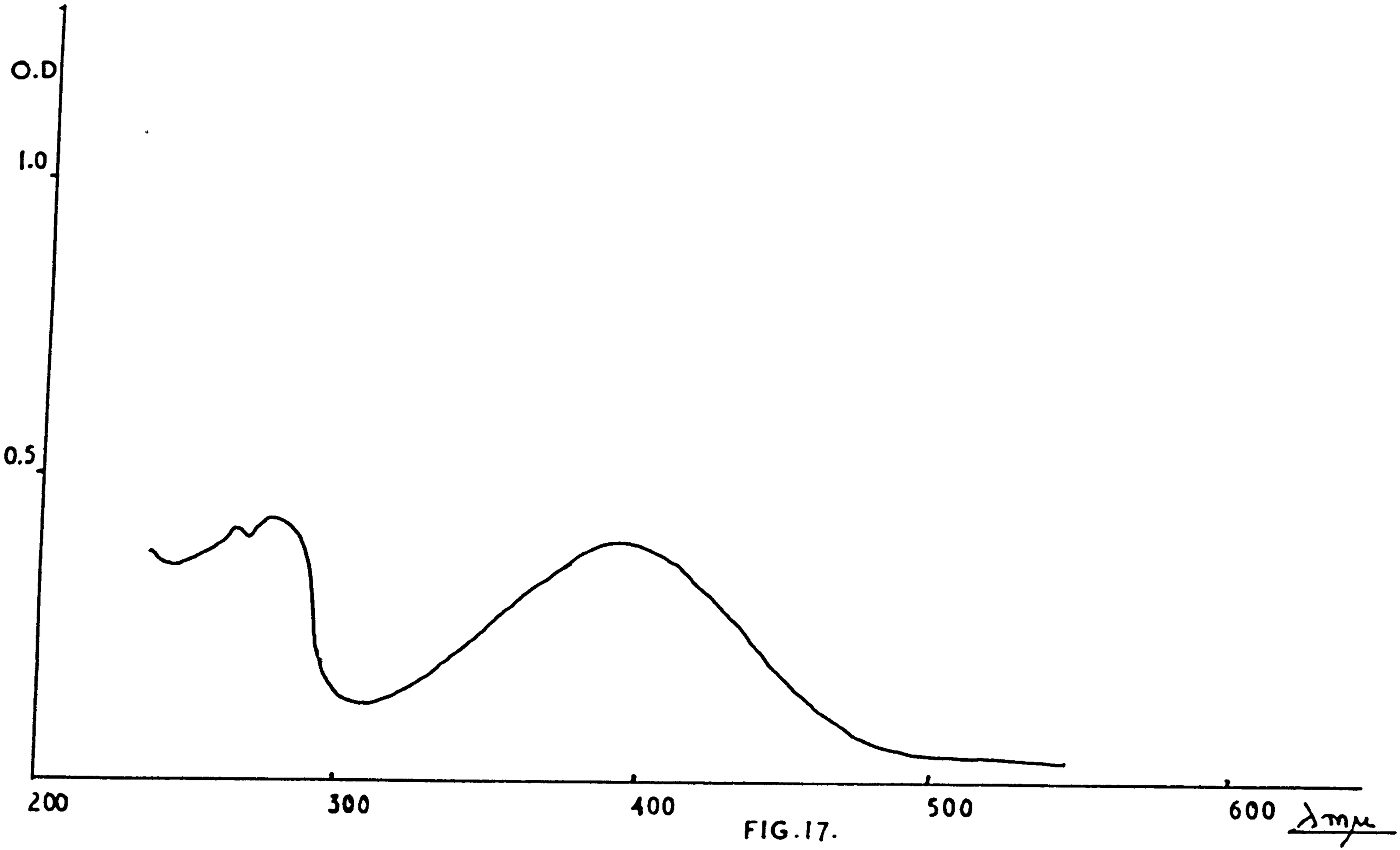

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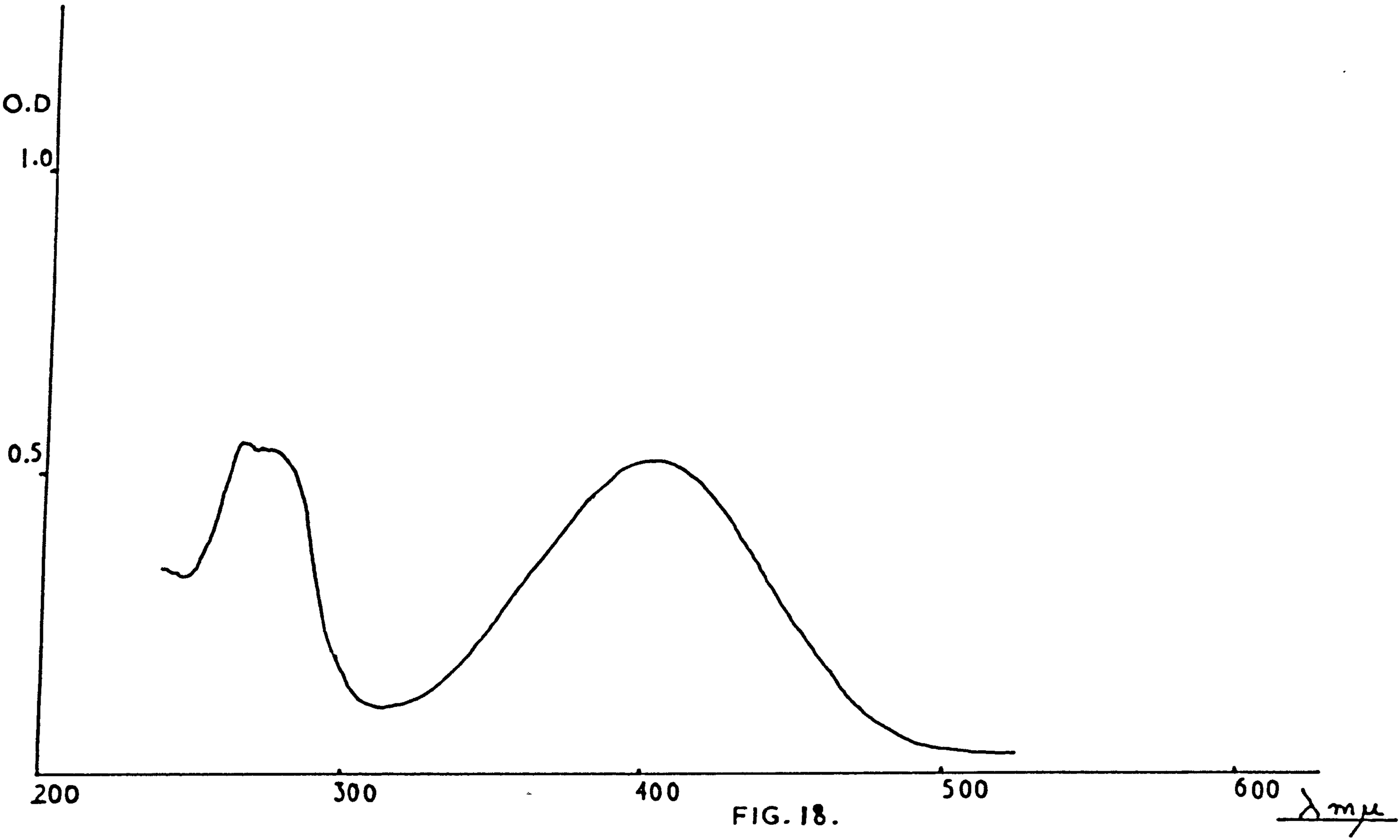

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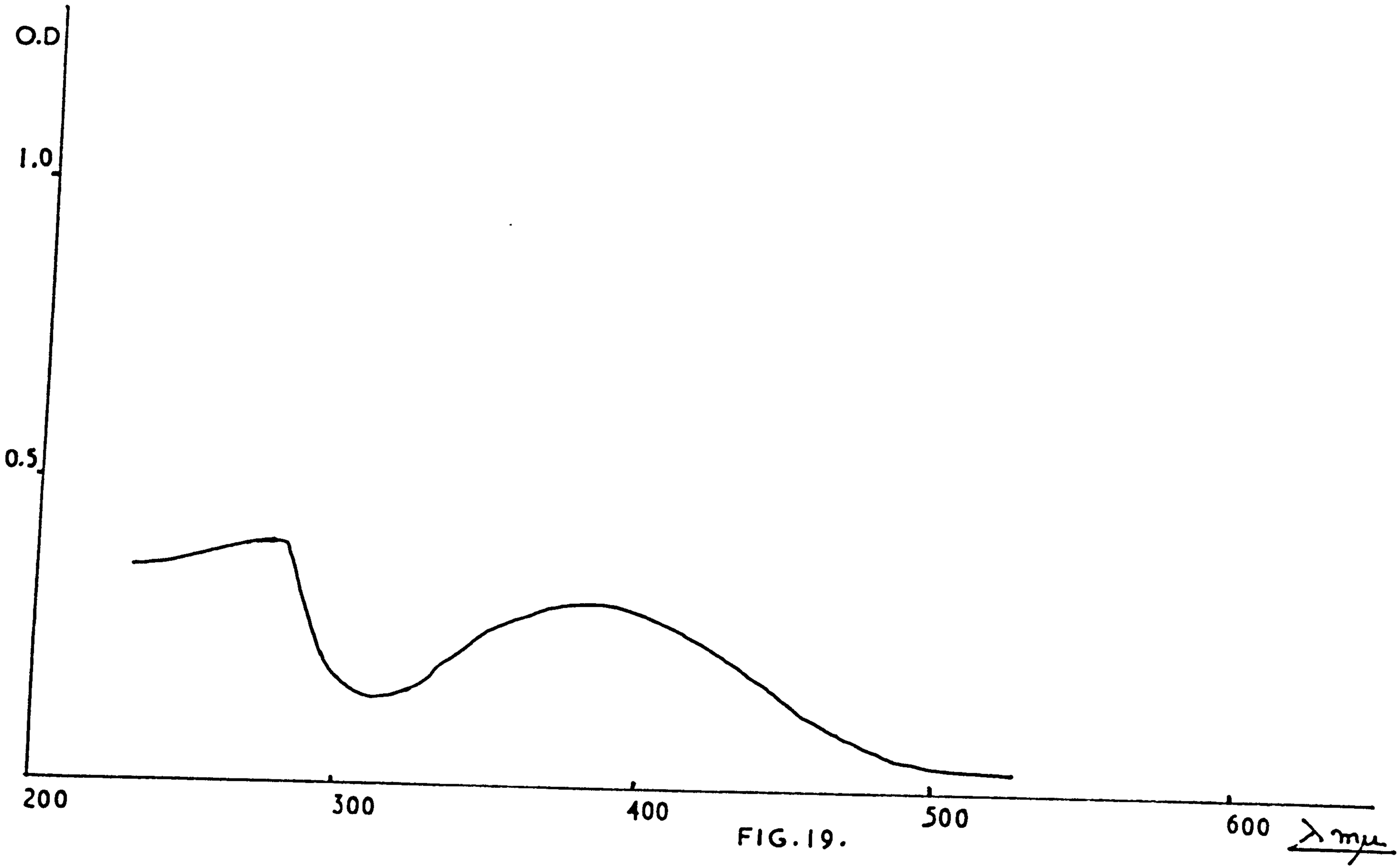

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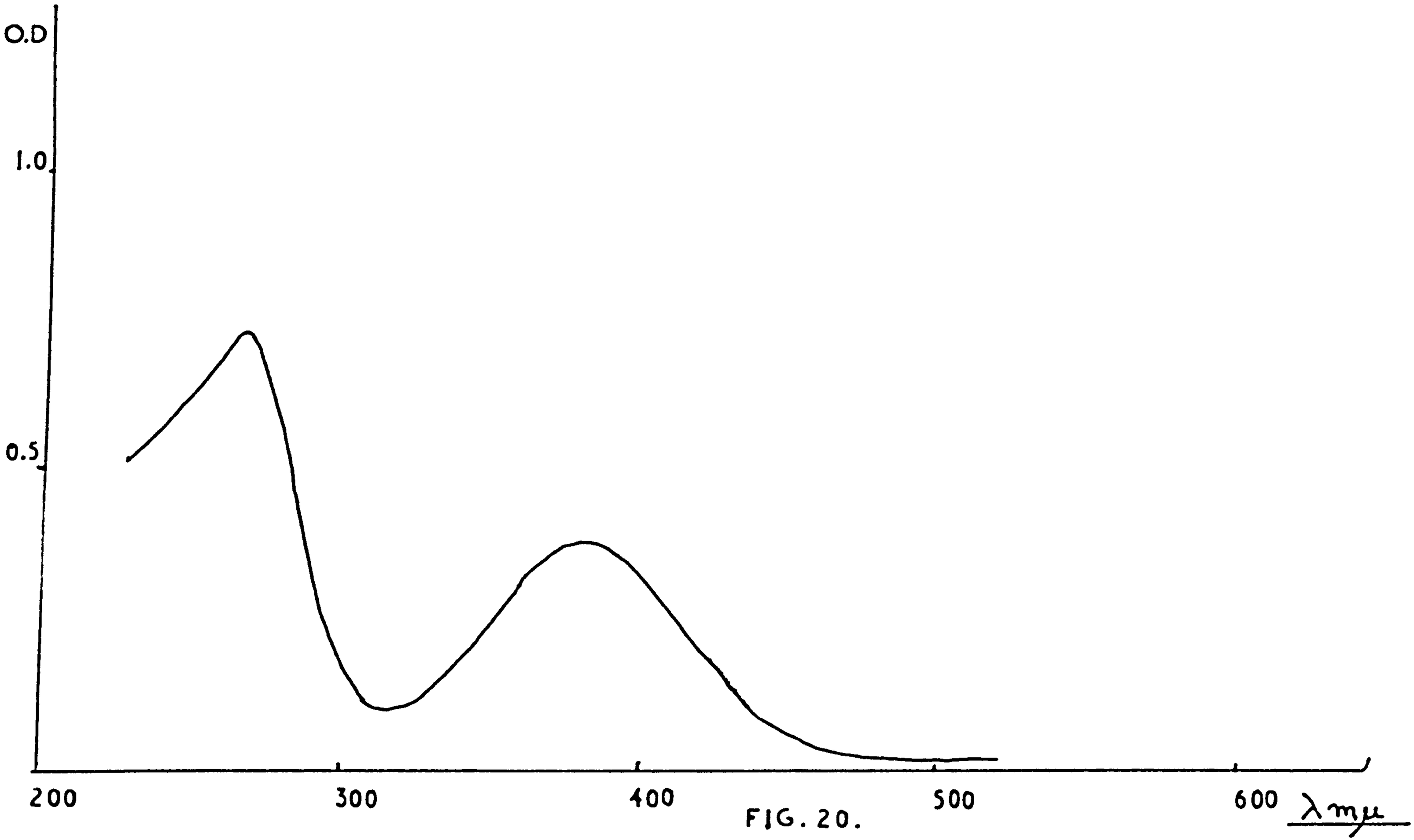


FIG. 20.

FIG. 21.

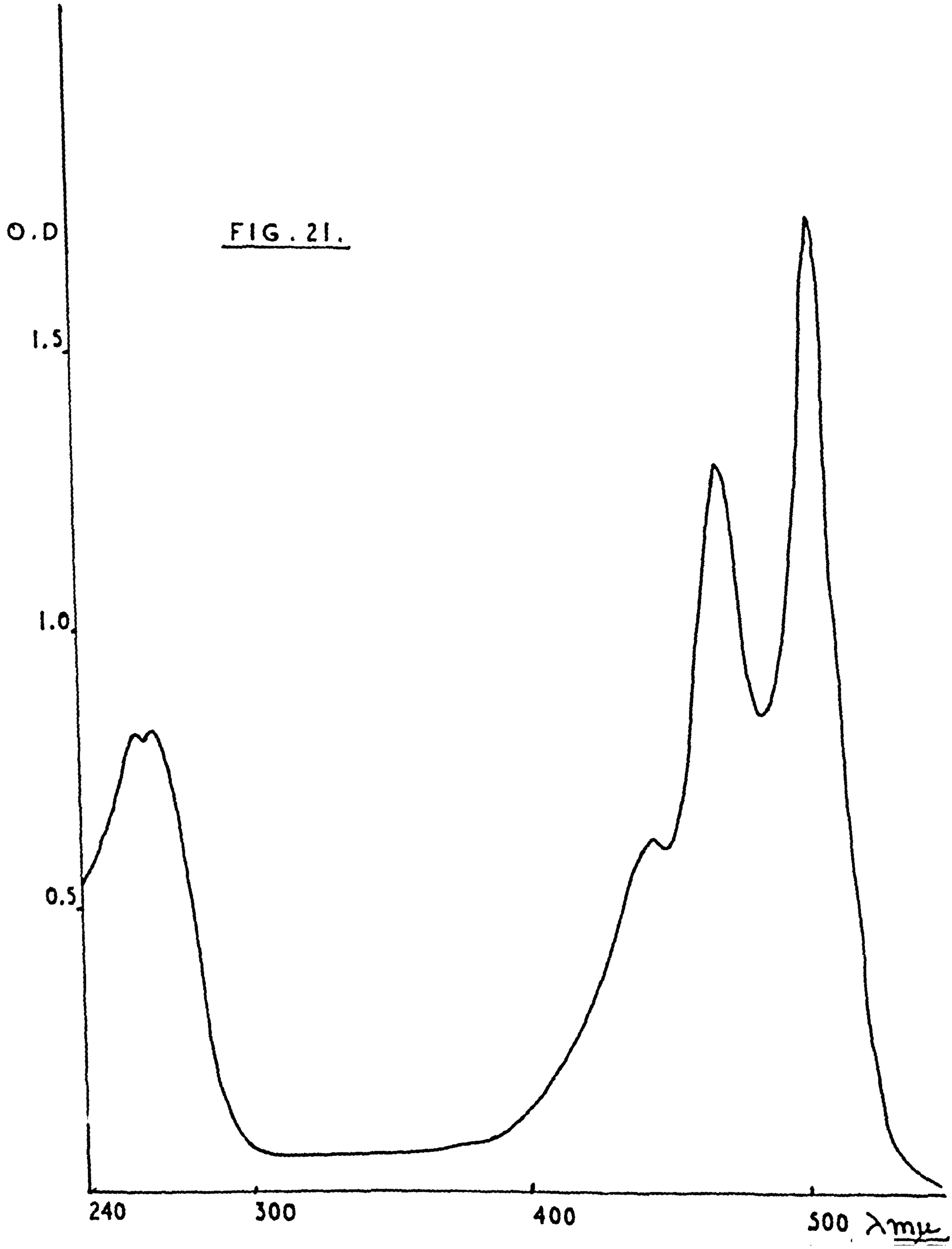
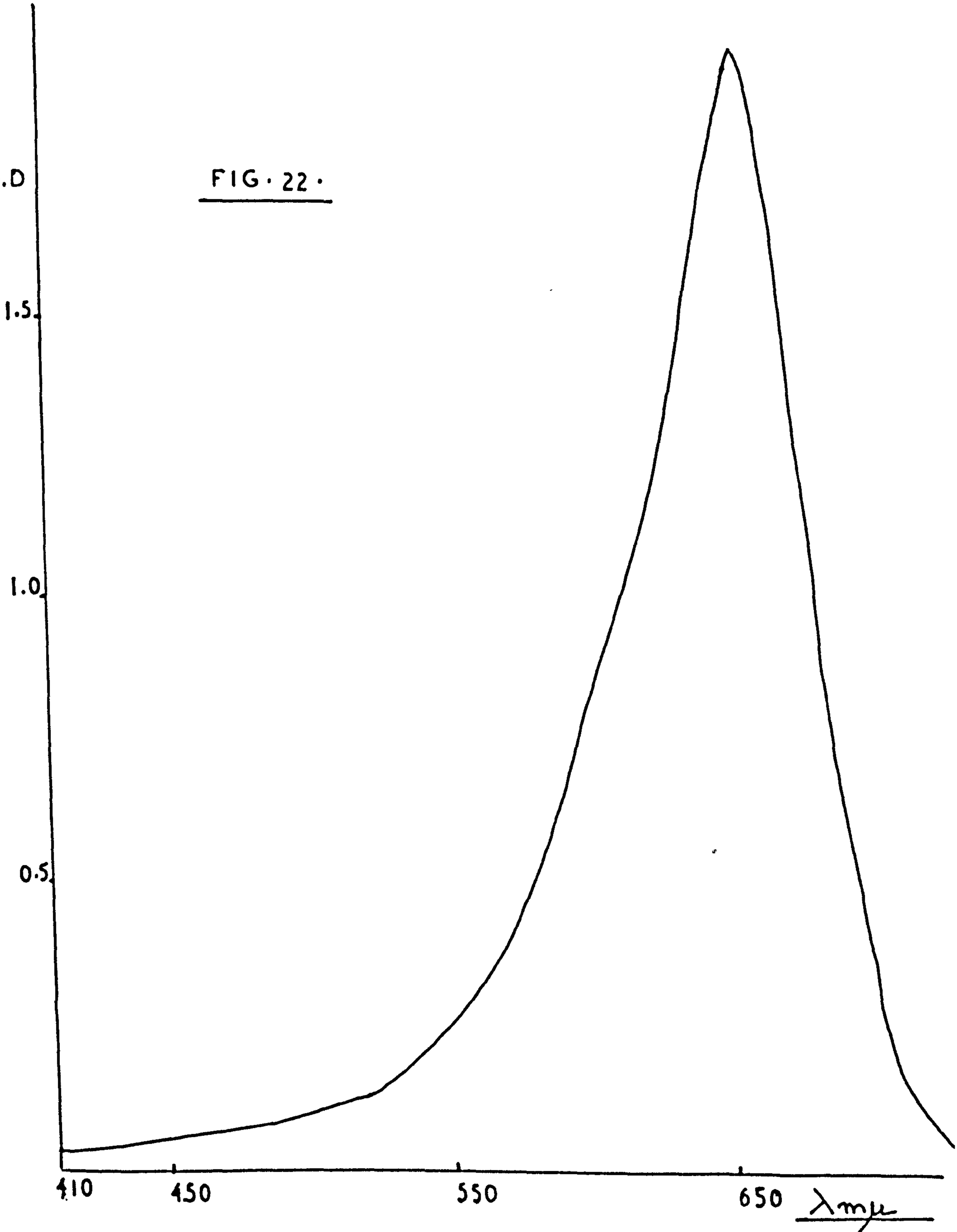


FIG · 22 ·



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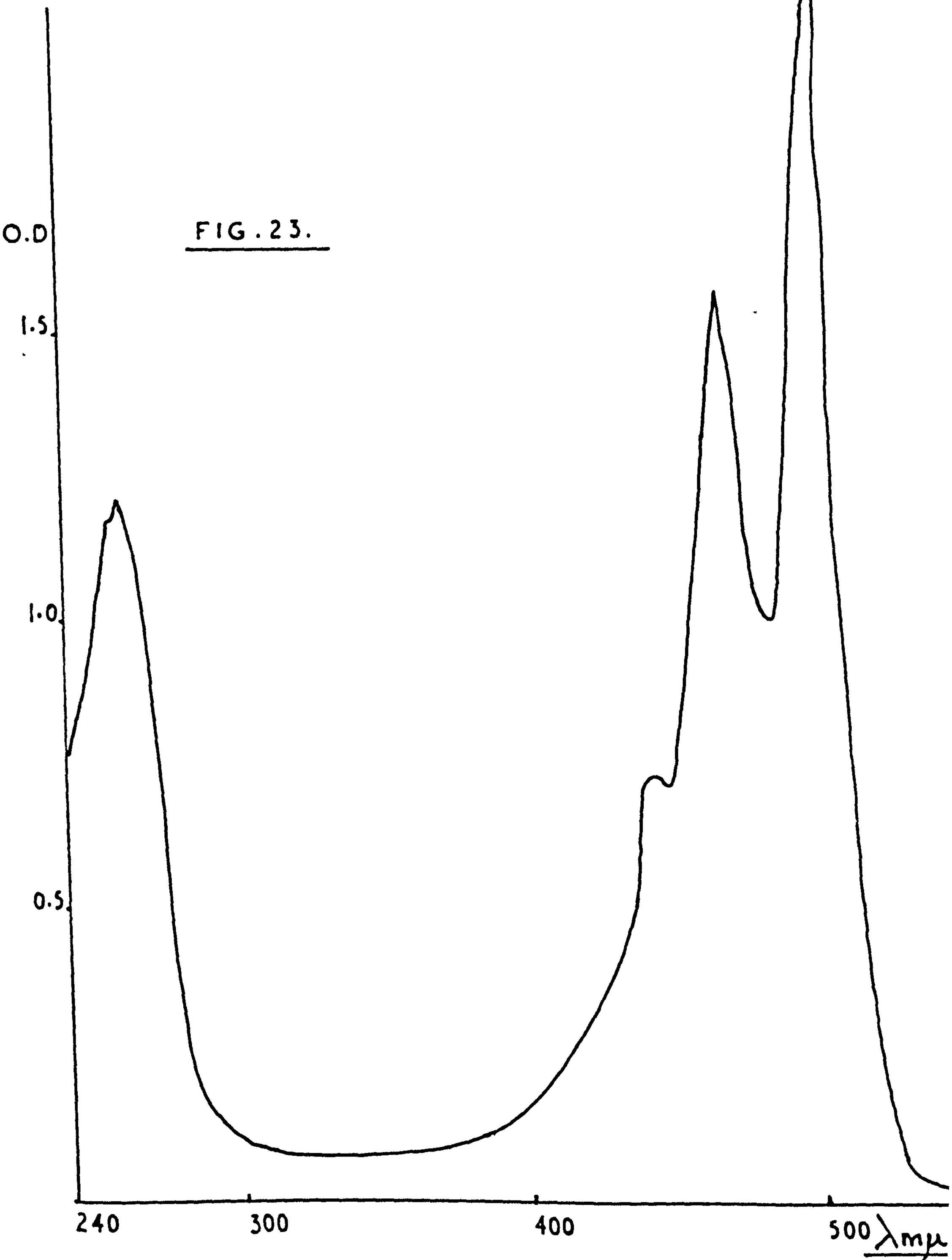

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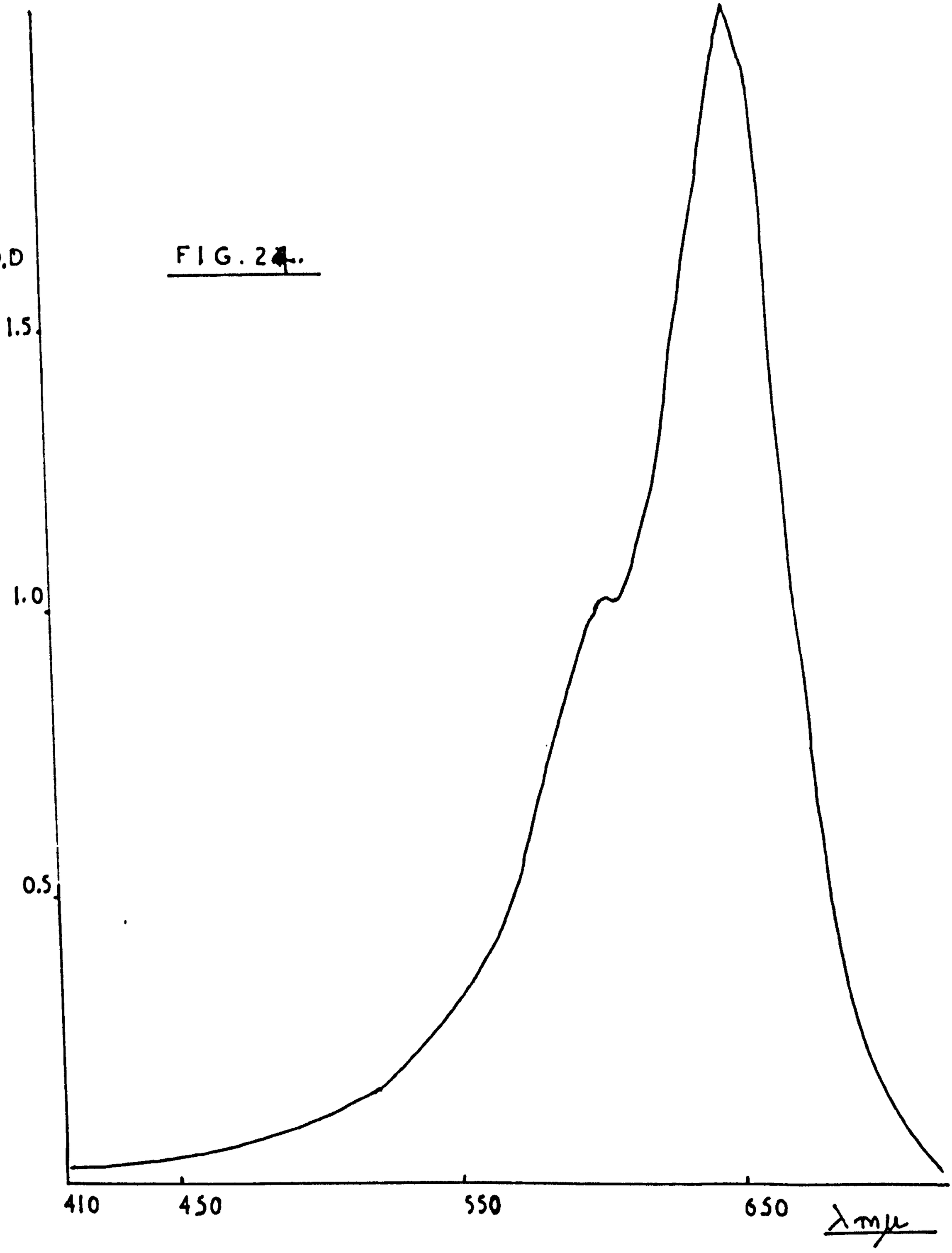

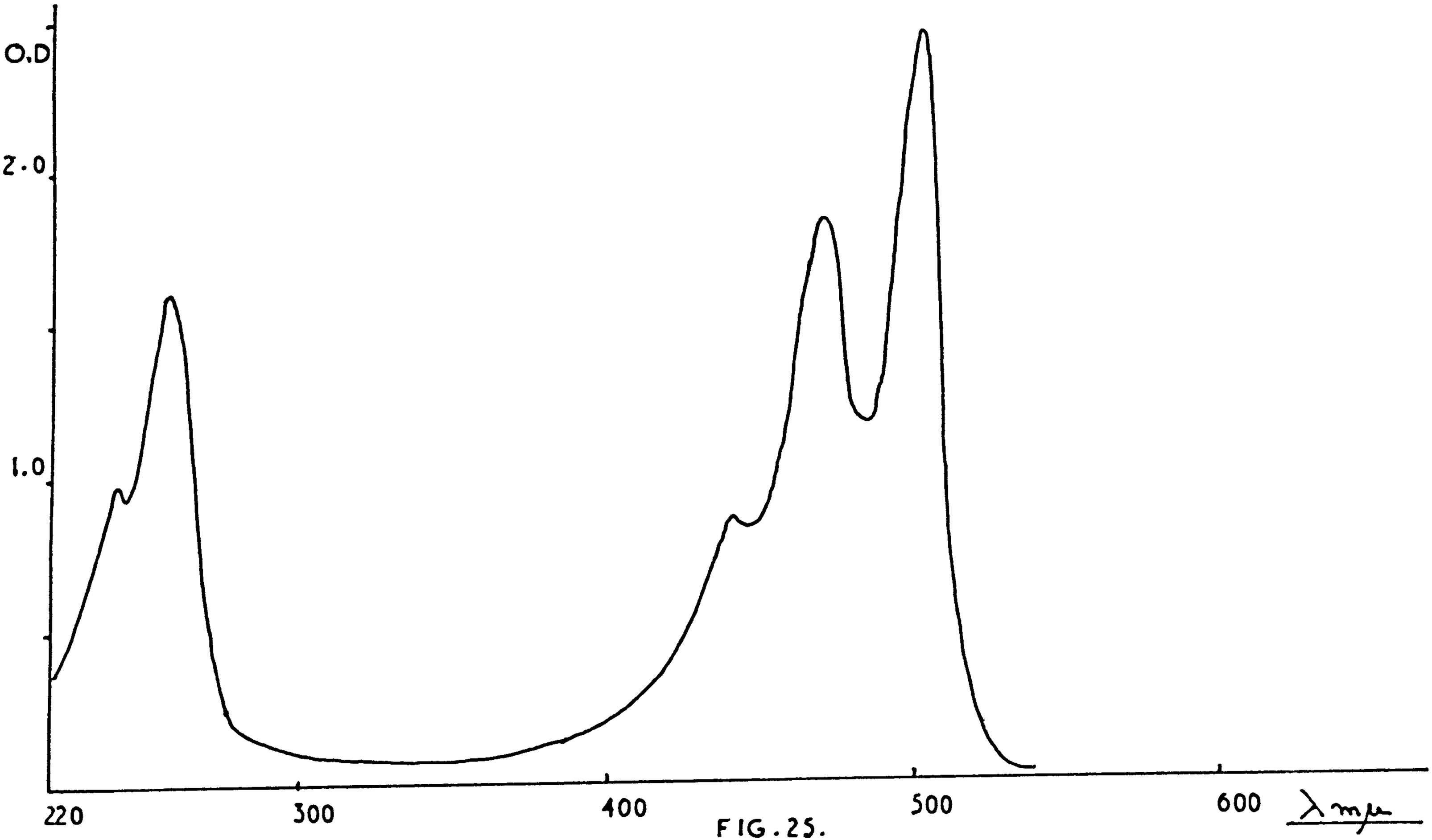

FIG. 25.

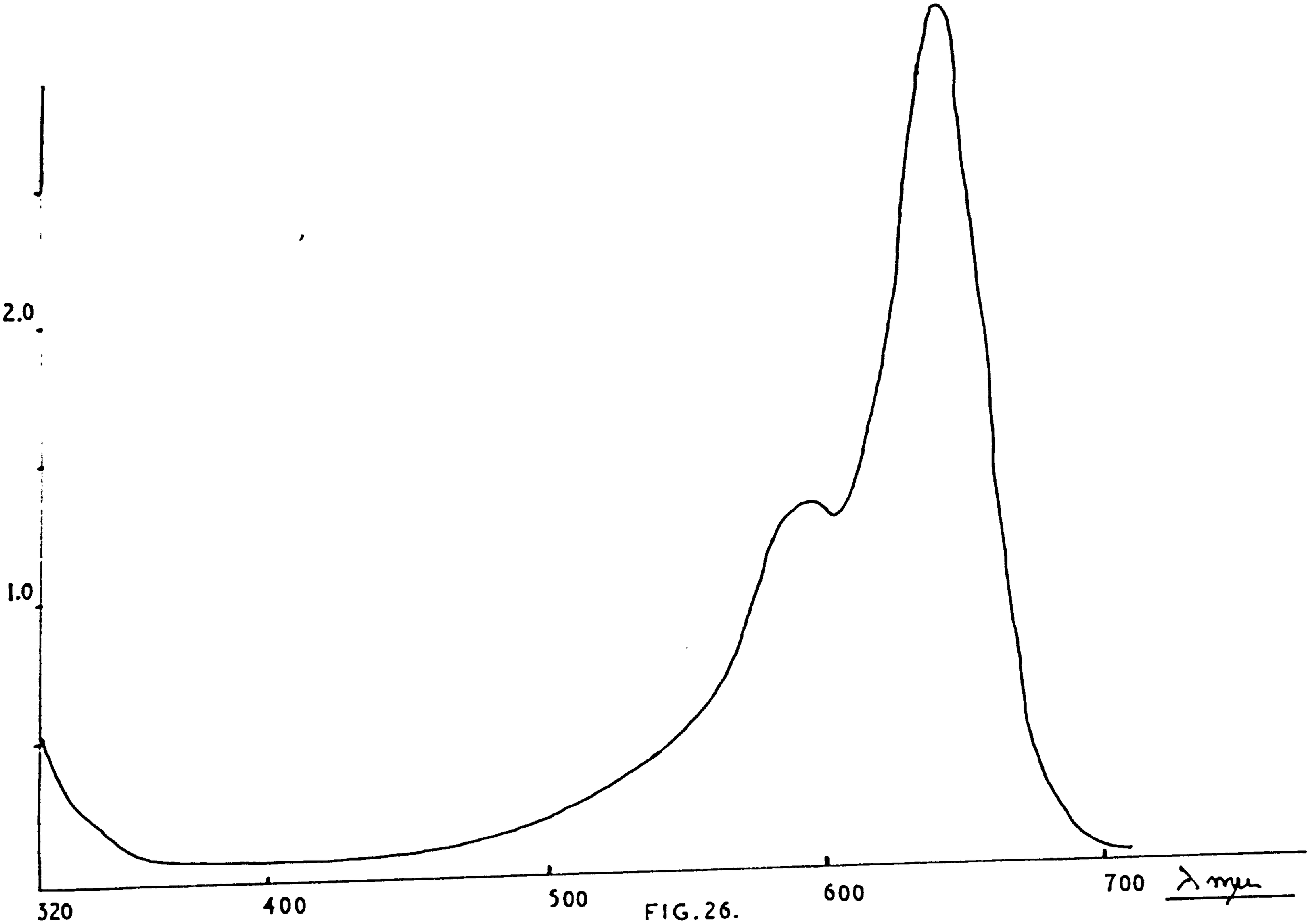

FIG. 26.

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