

AN EXAMINATION OF THE EFFECTS OF
EXTENDED CONJUGATION THROUGH POLYCYCLIC
SYSTEMS INCORPORATED INTO MONOAZO DYES

Thesis

Submitted in fulfilment of the requirements
for the degree of
DOCTOR OF PHILOSOPHY

by

BONIFACE TYOTSUWE WADA

. - D e p t . of Colour Chemistry,
University of Leeds,
January, 1978.

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks for the guidance and encouragement given by Dr. G. Hallas throughout the course of this work.

He is equally grateful to Professor I.D. Rattee, in whose department the work was carried out, to Dr. K. D. Bartle for his assistance in interpreting the n.m.r. spectra, to all the technical staff in the department of Colour Chemistry for their assistance and co-operation and to my wife for her incalculable help and great patience throughout the period of this work.

A grant from the Benue/Plateau State governments as well as a study fellowship from Ahmadu Bello University Zaria is highly acknowledged.

To

My Wife

CONTENTS

Title Page	i
Acknowledgements	ii
Contents	iii
Summary	vii

GENERAL INTRODUCTION

1.	Diazo and Azo Compounds	1
(a)	Historical Developments	1
(b)	Diazo Compounds	1
(c)	Azo Compounds	3
(d)	Methods of Preparing Aromatic Azo Compounds	3
(e)	Diazotisation, Mechanism and Techniques	9
(f)	Azo Coupling and the Significance of Couplers	12
2.	Classification of Azo Dyes	16
(a)	According to Structure	16
(b)	According to Usage	20
3.	Link between Colour and Constitution of Azo Dyes	21
(a)	Early Theories	21
(b)	Stereoisomerism and Tautomerism	22
(c)	Protonation	26
(i)	Substituents Effects	28
(ii)	Steric Hindrance	33
(d)	Extension of Conjugation	37
(e)	Recent Developments	40

DISCUSSION OF RESULTS

	<u>Part A</u>	<u>Spectroscopic Investigations</u>	42
1.		<u>N,N</u> -Diethylaniline dyes	42
	(a)	Overall comparison of phenylazo dyes with polycyclicazo dyes	43
	(b)	Behaviour of <u>N,N</u> -diethylaniline dyes in acid media	44
	(c)	Naphthalene dyes	48
	(d)	9,10-Dihydrophenanthrene and phenanthrene dyes	52
2.		<u>N</u> -2-Cyanoethyl-1,2,3,4-tetrahydroquinoline dyes	56
3.		Kairoline dyes	59
4.		Julolidine dyes	64
5.		Comparison between the different couplers	72
6.		Solvatochromism	73
	<u>Part B</u>	<u>Dyeing and Fastness Properties</u>	76
1.		Dyeing procedure	76
2.		Light fastness properties	76
	<u>Part C</u>	<u>Conclusions</u>	80
		<u>PREDICTIVE METHODS IN ORGANIC CHEMISTRY</u>	83
1.		Introduction	83
	(a)	The Valence Bond Method	85
	(b)	The Free Electron Molecular Orbital method	85
	(c)	The Hückel Molecular Orbital (HMO) method	87
	(i)	Short-comings of the HMO method	91
	(ii)	The ω -technique	91

(d)	The Antisymmetrized Molecular Orbital method and ASMO CI	92
(e)	The Self-Consistent-Field method	92
(f)	The Pariser-Parr-Popple (PPP) method	93
2.	Application of the PPP method	93
(a)	Choice of parameters in the PPP method	93
(b)	Bond order	96
(c)	Configuration interaction (CI)	97
(d)	Oscillator strength (OS or f)	98
3.	Further application of the PPP method	101
(a)	Naphthalene intermediate	101
(b)	Azo dyes derived from naphthalene	108
(c)	Azo dyes derived from 9,10-dihydrophenanthrene and from phenanthrene	117
4.	Conclusions	124
	<u>DISCUSSION OF EXPERIMENTAL</u>	
I	Intermediates	127
1.	2,7-Disubstituted phenanthrenes	130
2.	3,9-Disubstituted phenanthrenes	142
3.	3,6-Disubstituted phenanthrenes	150
4.	Naphthalene Derivatives	154
II	Preparation of Couplers	158
III	Preparation of Dyes	160
1.	Diazotization	160
2.	Coupling	162
3.	Purification	162

IV	Miscellaneous	163
1.	Dyes Derived from Benzo[c]cinnoline	163
2.	Routes to Benzo[c]cinnoline	164
3.	Preparation of Benzo[c]cinnoline Intermediates	165
	<u>EXPERIMENTAL DETAILS</u>	
	Notes	170
	General Procedures	171
	<u>Part A</u> <u>General Intermediates</u>	173
I	Naphthalene Derivatives	173
II	9,10-Dihydrophenanthrene and Derivatives	181
III	Phenanthrene Derivatives	189
1.	2,7-Disubstituted phenanthrenes	189
2.	Attempted synthesis of 3,6-disubstituted phenanthrene derivatives	193
3.	3,9-Disubstituted phenanthrenes	196
	<u>Part B</u> <u>Dyes</u>	203
I	<u>N,N</u> -Diethylaniline Dyes	203
II	<u>N</u> -2-Cyanoethyl-1,2,3,4-tetrahydroquinoline Dyes	211
III	Kairolone(<u>N</u> -Methyl-1,2,3,4-tetrahydroquinoline) Dyes	216
IV	Julolidine(2,3,6,7-Tetrahydro-1 <u>H</u> ,5 <u>H</u> -benzo[<i>ij</i>]-quinolizine) Dyes	220
	<u>Part C</u> <u>Miscellaneous</u>	224
	<u>REFERENCES</u>	227

Summary

A systematic investigation has been carried out into the spectroscopic behaviour of some monoazo dyes derived from polycyclic systems. Hallas and his students have previously examined various phenylazo dyes derived from terminally bridged systems, viz. kairoline (N-methyl-1,2,3,4-tetrahydroquinoline), N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline, lilolidine(1,2,5,6-tetrahydro-4H-pyrrolo[3,2,1-i]quinoline) and julolidine (2,3,6,7-tetrahydro-1H,5H-benzo[i,j]quinolizine). The present work is a continuation of these researches and includes dyes derived from more complex molecules based on naphthalene and phenanthrene. Novel azo dyes have also been prepared by coupling polycyclic systems to N,N-diethylaniline in order to compare their characteristics with the well-documented properties of simple dialkylamino compounds.

Several useful intermediates have been prepared for the first time and improved routes to others have been developed. Thus, 1-amino-2-nitronaphthalene was obtained by direct amination of 2-nitronaphthalene and was found to be identical with samples obtained by other routes. A pure sample of 7-nitrotetral-1-one has been prepared and its oxime has been shown to melt at 170°C in contrast to the reported value of 150°C. A useful route has been devised for the preparation of several unsymmetrically disubstituted

9,10-dihydrophenanthrene derivatives and the corresponding phenanthrene analogues. The dinitration of 9,10-dihydrophenanthrene affords largely 2,7-dinitro-9,10-dihydrophenanthrene from which 2-amino-7-nitro-9,10-dihydrophenanthrene is obtained through selective reduction. The analogous phenanthrene compound is best obtained by aromatisation of the dinitro-9,10-dihydro compound followed by selective reduction.

The electron-donating abilities of four different couplers have been examined by monitoring the spectral changes of appropriate dyes in ethanol and in ethanolic hydrogen chloride. The terminally bridged systems are in general better electron donors than a simple dialkylamino group, although dyes derived from N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline show hypsochromic shifts in ethanol with respect to the corresponding dialkylamino dyes owing to the strong electron withdrawing influence of the cyano group.

Spectral data have also shed light on the complex question of colour chemical constitution relationships as well as establishing the halochromism of some of the dyes in various solvents.

The Pariser-Parr-Pople Molecular Orbital method with limited configuration interaction (PPP-MO CI) has been applied to most of the intermediates and the corresponding dyes for the prediction of molecular properties in the ground state and in the first singly excited state.

The applicability of these dyes to synthetic fibres has been tested by means of disperse dyeing on polyester and assessment of the light fastness properties.

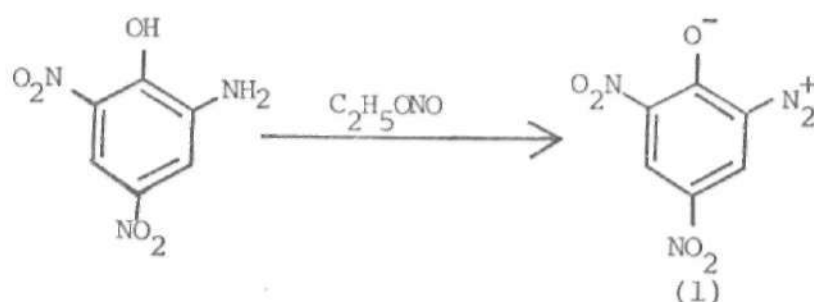
Unsuccessful attempts have been made to prepare 2,7-disubstituted benzo[c]cinnolines.

GENERAL INTRODUCTION

1. Diazo and Azo Compounds

(a) Historical Developments

The history of azo chemistry dates back to 1858 following the discovery by Johann Peter Griess.¹ Griess set out to prepare dihydroxydinitrobenzene by passing nitrous fumes into a cold ethanolic solution of picramic acid (2-amino-4,6-dinitrophenol), but obtained instead a precipitate of 4,6-dinitrobenzene-2-diazo-1-oxide (1).

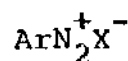


Griess's conviction that the nitrogen atoms had in fact replaced two hydrogen atoms in the benzene nucleus led to the erroneous name 'diazodinitrophenol'. Detailed investigations by Griess² in the following years brought to light this misconception, but the name 'diazo compounds' has been retained for purely historical reasons.

(b) Diazo Compounds

Diazo compounds are most commonly prepared by the process of diazotisation which usually involves the treatment of an arylamine (aliphatic amines as a class form rather unstable diazonium compounds) in an aqueous acidic medium

with 'nitrous acid'. Generally speaking, diazonium salts (2) play only the role of an intermediary in the dyestuff industry.



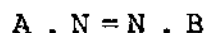
(2)

The difficulty of handling diazonium salts owing to their often explosive nature, particularly the nitrates, makes their isolation undesirable. This hazardous tendency notwithstanding, many stabilised diazo compounds in the form of chlorides, sulphates, zinc chloride double salts and fluoroborates are marketed on a large commercial scale.

Several methods of preparing diazo compounds which do not involve diazotisation have been reported.³ These various methods are classified under oxidation, reduction and scission reactions. An example of an oxidative method is the reaction between arylhydrazines⁴ and mercury(II) oxide in acid medium. Other suitable oxidising agents include mercury(II) acetate, bromine, silver salts in exposed photographic emulsion and nitrogen trioxide. Nitrous acid is known to reduce many nitroso compounds⁵ to the corresponding diazo compounds. Most of these techniques are, however, only of academic interest and with the exception of perhaps the silver salts find little technical application. The direct introduction of the diazonium group into the aromatic nucleus has also been reported.⁶

(c) Azo Compounds

The term 'azo compounds' applies to all compounds of the general form shown (3),



(3)

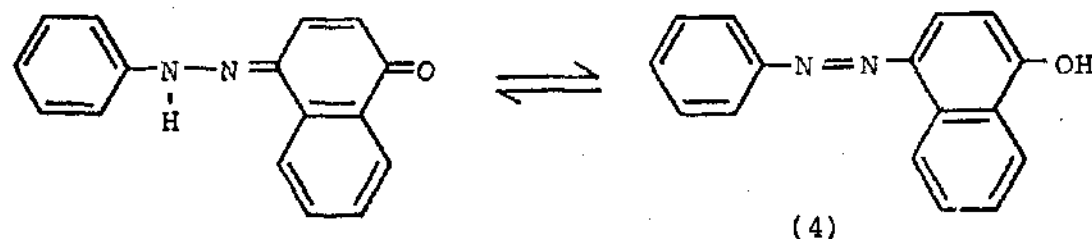
characterized by the presence of an azo group in which A and B are either aromatic or quasi-aromatic nuclei. Even though an azo dye can be designated by the same general structure, it differs significantly from a weakly coloured simple azo compound. Azo dyes belong to the very large group of coloured compounds classified under the general term 'Donor-Acceptor Chromogens'.⁷ In addition to the characteristic azo group, azo dyes carry an electron donating substituent and owe their intense colour to an electronic transition usually associated with the migration of electrons from the donor group into the rest of the chromogen.

(d) Methods of Preparing Aromatic Azo Compounds

By far the most important route to azo compounds is the coupling reaction between a diazo compound and a coupling component (coupler). This method of synthesis has been used throughout the present work. Nevertheless, in order to handle the topic in its entirety, non-coupling methods used in obtaining azo compounds will be dealt with briefly.

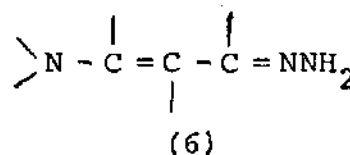
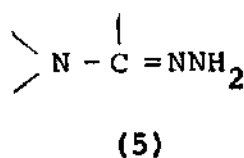
In 1834, Mitscherlich⁸ prepared azobenzene by the action of ethanolic potassium hydroxide on nitrobenzene.

Some modifications⁹ of this method are to be found in the literature, but the process has not found wide technical application. Zincke and Bindewald¹⁰ prepared 4-phenylazo-1-naphthol (4) by condensing phenylhydrazine with 1,4-naphthoquinone.



In fact, this tautomeric equilibrium is now known to be possible for all hydroxyazo aromatic compounds with a hydroxyl group ortho or para to the azo linkage (see section 3(b)).

The synthetic difficulties normally accompanying the diazotisation of heterocyclic amines are circumvented through the so-called oxidative coupling technique discovered by Hünig and his co-workers.¹¹ The azo dye is formed from an amidrazone (5) or its vinylogue (6).



The reaction takes place in the presence of an oxidising agent and is illustrated by the interaction between 1-methyl-carbostyryl hydrazone (7) and dimethylaniline to give (8).

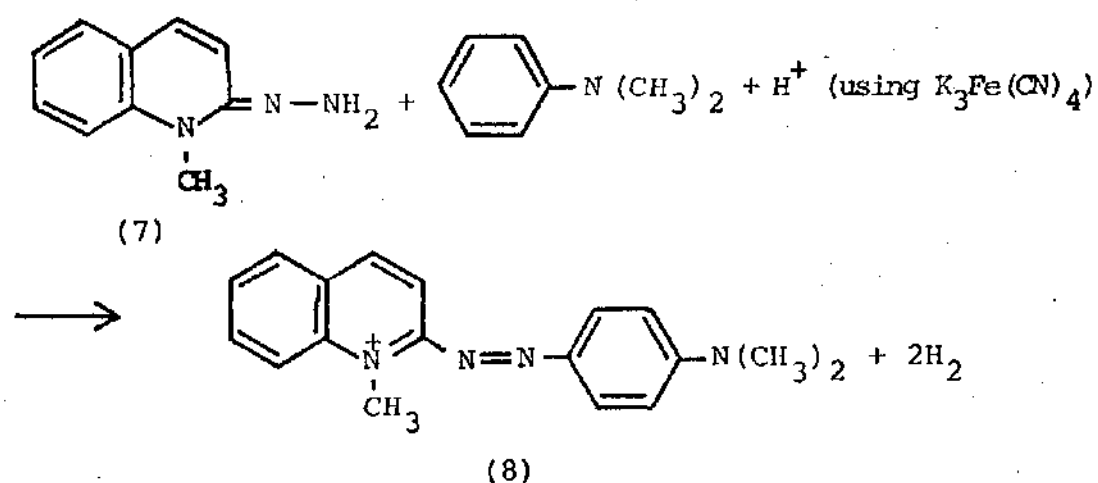


Chart 1. Oxidative coupling of 1-methylcarbostryl hydrazone.

The versatility of the method has been demonstrated by the wide range of diazo components and couplers that have been used by Hünig and his collaborators. Another example is the reaction of N-alkylpyridonehydrazones (9) with phenol to form (10), but very low yields of the azo compounds are obtained.¹¹

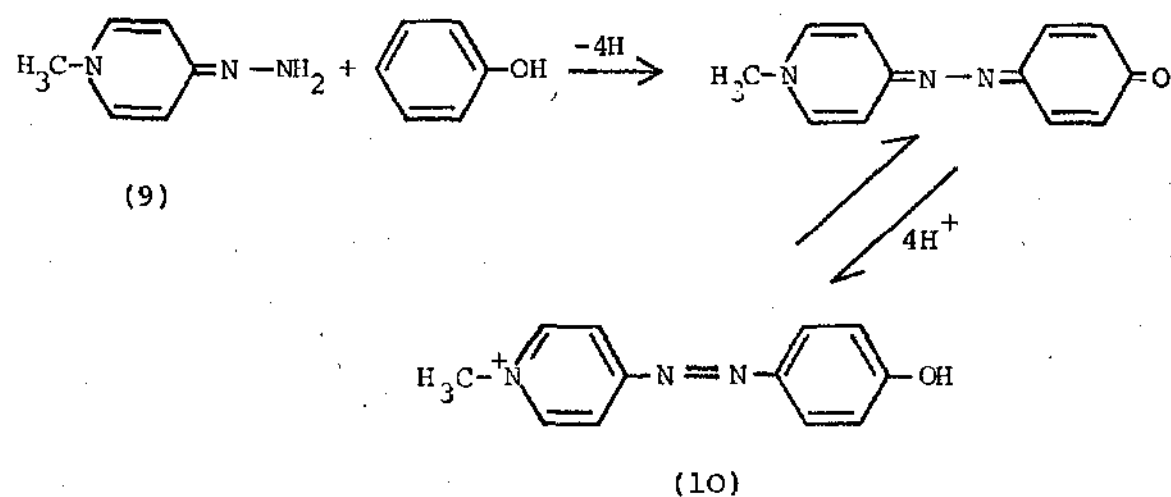
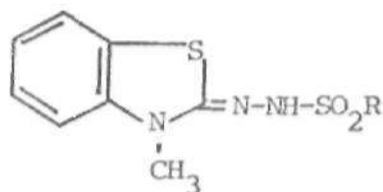


Chart 2. Oxidative coupling of N-alkylpyridonehydrazones with phenol.

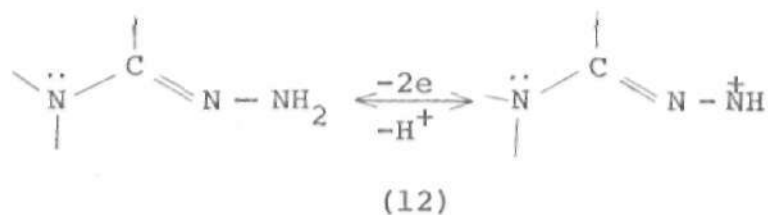
The oxidising agent commonly used is potassium hexacyanoferrate(III), although many other reagents such as iron(III) chloride, hydrogen peroxide in the presence of iron(II) salts and lead(IV) oxide are as effective. The acidity or basicity of the reaction medium is governed by the same rules as in classic coupling reactions, namely acid buffers in the case of amines and weakly alkaline media for phenols and enols. In order to eliminate the problem associated with the decomposition of hydrazones in strongly alkaline solutions, Hünig and Rauschenbach¹² have suggested the replacement of hydrazones with their N-sulphonyl derivatives (11).



(11)

R = aryl or alkyl

The mechanism¹³ of the reaction entails the oxidation of the amidrazone to a resonance-stabilized form (12),



(12)

which undergoes further oxidation after its reaction with the nucleophilic coupling component as in Chart 3.

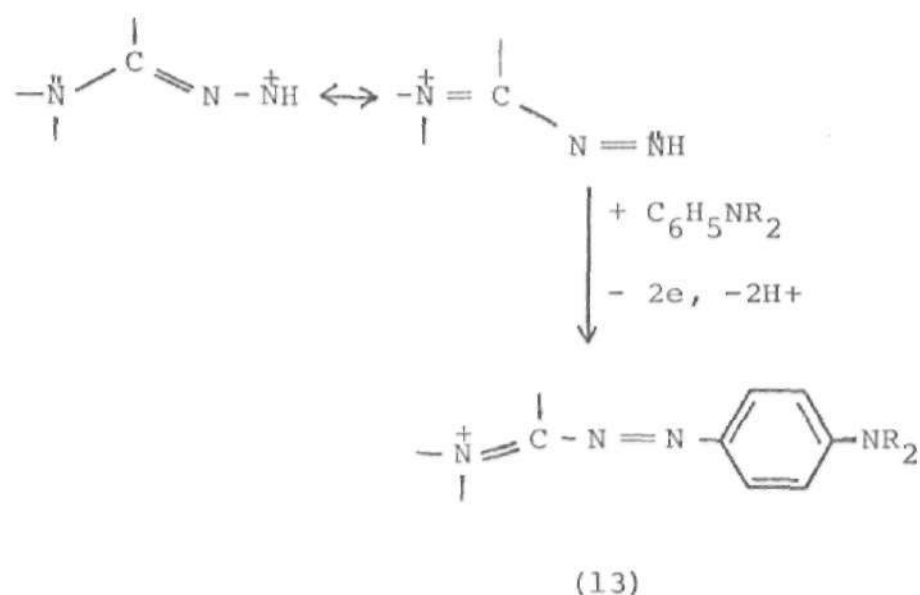


Chart 3. Proposed mechanism for oxidative coupling.

Another method of obtaining azo compounds is the condensation of nitroso compounds with amines.¹³ The condensation of nitrosobenzene with aniline affords azobenzene (Chart 4).

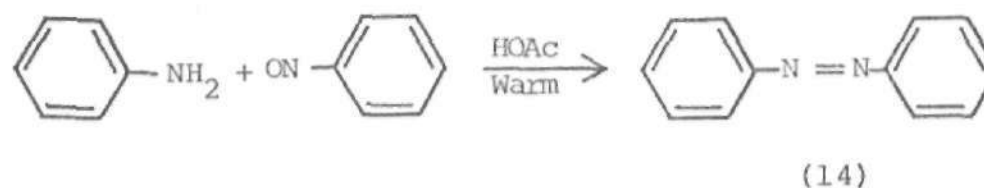
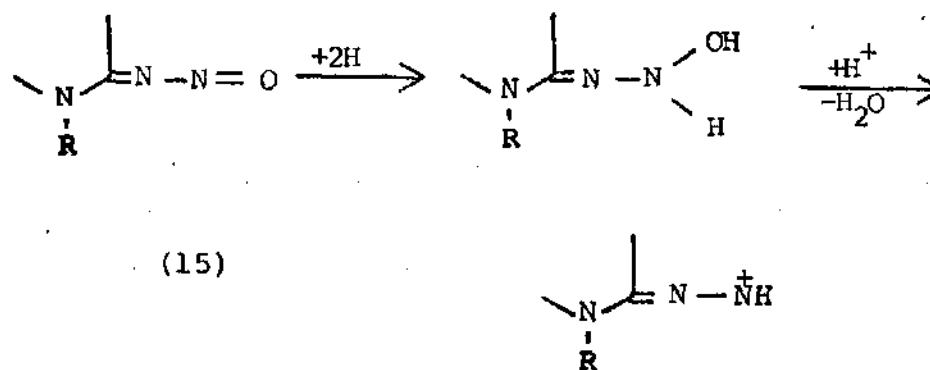


Chart 4. Condensation of nitrosobenzene with aniline.

A reductive coupling technique for preparing azo compounds has also been reported.¹⁴ It is supposed that the cation (12) is also produced by the reduction of nitrosoimino compounds of the type (15).



A typical reaction of this reductive approach is the treatment of N-methyl-2-nitrosoiminobenzothiazoline (16) with NN-dimethylaniline in the presence of zinc dust.¹⁴

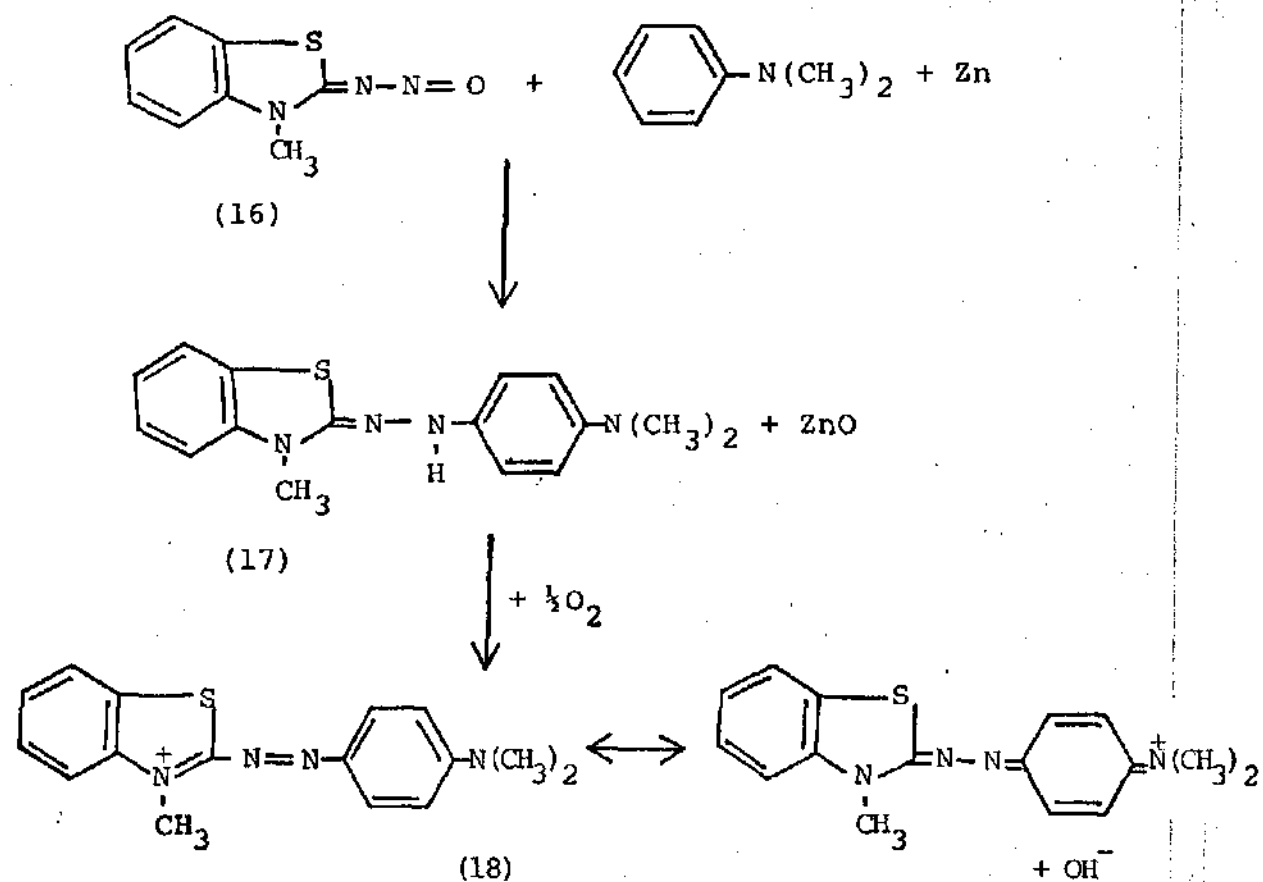


Chart 5. Preparation of azo compounds by reductive coupling.

The leucocompound (17) so formed is oxidized to the dye (18) by air.

(e) Diazotisation, Mechanism and Techniques

The actual mechanism of the process of diazotisation has long been a topic of controversy. Good summaries of the principles involved are contained in the treatises by Saunders³ and Zollinger.¹⁵ As pointed out by Ridd,¹⁶ the kinetics of the process of diazotisation are closely linked to the reacting media. The most probable route to the diazonium salt is the one given in Chart 6.

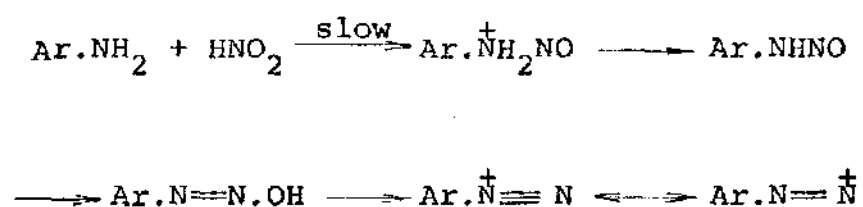


Chart 6. Mechanistic representation of the process of diazotisation.

For purely synthetic purposes, however, reaction techniques are of immense importance and are described below.

The readiness with which an amine can be diazotised is usually linked to its relative basicity. While aniline and related amines are usually diazotised by the so-called direct method, weak bases can only be diazotised by special techniques. Amines with nitro-groups have very low basicity and their diazotisation is usually effected by the use of

concentrated acids, as they no longer dissolve in aqueous acids. The procedure normally adopted is to dissolve the amine in either a weak acid, such as glacial acetic acid, or in concentrated sulphuric acid and then add this solution to one of nitrosylsulphuric acid at the diazotisation temperature.

The presence of carboxylic and sulphonic groups in an aromatic nucleus reduces drastically the solubility of the diazonium salt in water, thus hampering its diazotisation by the direct method. The inverse method is thus applied to overcome this solubility problem; sodium nitrite solution is added to an alkaline solution of the aminoarylsulphonic acid, this is then added to dilute acid.

The method due to Knoevenagel¹⁷ is sometimes used for water-soluble diazonium salts. In this method, amyl nitrite is the source of nitrous acid and the reaction medium is ethanol.

General methods as described in the literature are but a rough guide, since optimum conditions for diazotisation are so much the function of specific amines as the usage to which the diazonium compound is to be put. Thus, Hodgson¹⁸ discovered in his preparation of halogenonitro-compounds through the Sandmeyer reaction that dilution of the resultant diazonium solution prior to treatment with the copper salt was detrimental. If, for instance, the diazo solution of 2,4-dinitronaphthylamine is diluted, 4-nitronaphthalene-1-diazo-2-oxide is formed.

The use of organic solvents during the diazotisation of weakly basic amines has been recommended.¹⁹ Tertiary amines, viz, pyridine, quinoline and isoquinoline have been thoroughly investigated.^{19,20} The basic requirement for a successful diazotisation is that the amine should go into solution or be distributed in a very finely divided form in suspension. The main role of these solvents, is therefore, to hold the amine in solution and may additionally assist the release of nitrous acid from nitrosylsulphuric acid.¹⁹ The exothermic reaction which results from mixing pyridine with nitrosylsulphuric acid prolongs the diazotisation time. Quinoline and isoquinoline, although free from this heat generating effect, are known to hold the resultant azo compound in solution, unlike pyridine.

Investigations involving tetrahydrofuran as a possible solvent for diazotisation have been reported.²¹

Dickey in a series of patents²² has used nitrosylsulphuric acid in a mixture of glacial acetic acid and propionic acid to diazotise weak bases. The role of propionic acid as claimed is to depress the melting point of glacial acetic acid to zero or below.

A preparative difficulty can result if diazotisation is carried out with not enough acid. Thus, if aniline is diazotised in an acid deficient medium, the resultant diazonium salt reacts with yet undiazotised amine giving the unwanted diazoaminobenzene (19); this product would normally be converted into the azo compound on addition of

acid. Nevertheless, it is a problem which affects the overall yield of the diazonium salt produced.

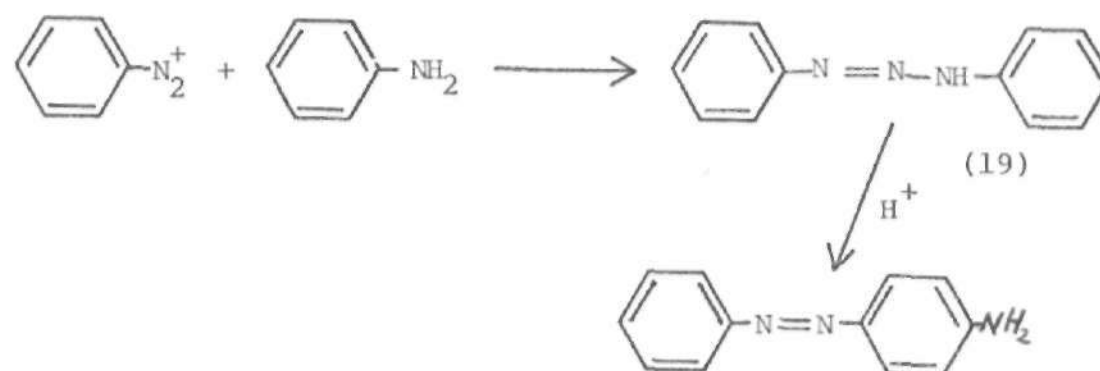


Chart 7. The formation of diazoamino compounds during the process of diazotisation.

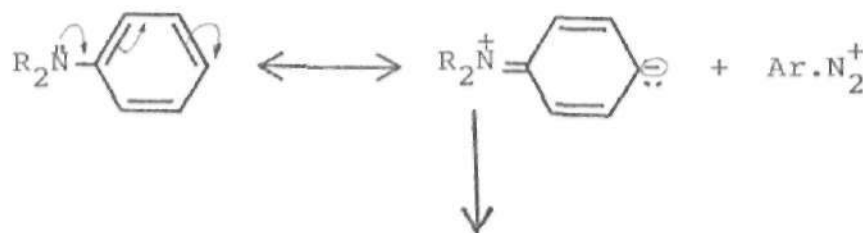
(f) Azo Coupling and the Significance of Couplers

Diazo coupling is regarded as an electrophilic substitution²³ by a diazonium cation which can be represented as a resonance hybrid.



(20)

The reaction with tertiary aromatic amines leading to the azo compound may be written mechanistically as in Chart 8.



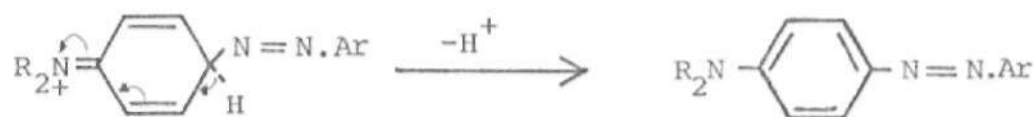


Chart 8. Mechanistic representation of a coupling reaction.

In practice, the diazo compound normally carries a strong electron-withdrawing group as the diazonium ion is a relatively weak electrophile. The fact that aromatic diazo compounds can undergo nucleophilic substitution reactions (Chart 9) creates a technical problem in azo dye preparation. The products of these decomposition reactions together with polymeric resins formed during the course of coupling account to a large extent for the poor yields usually associated with azo dye preparation.

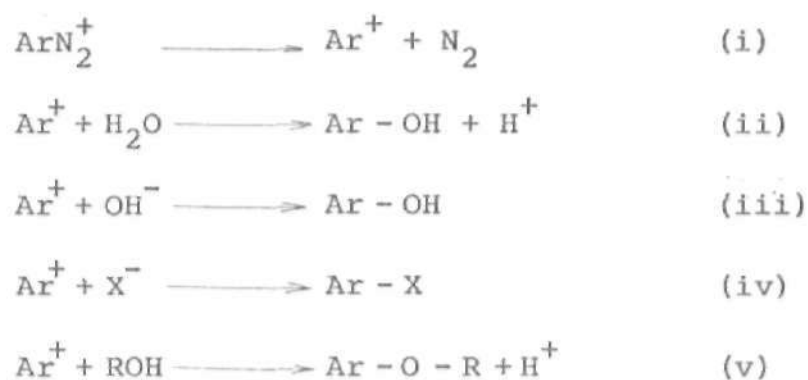
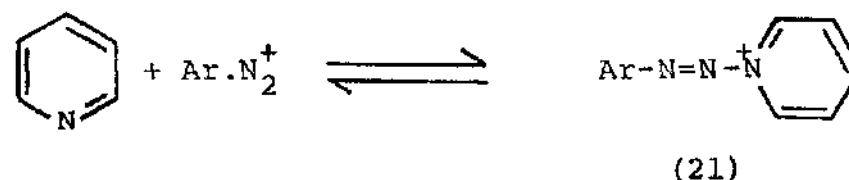


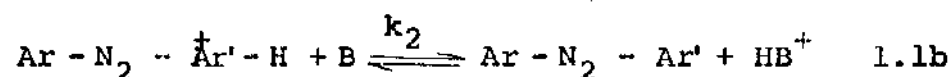
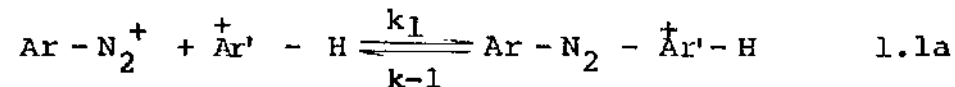
Chart 9. Diazo decomposition reactions.

The extent to which these side reactions occur depends on the reaction conditions.

The use of pyridine, especially in the manufacture of polyazo dyestuffs, has been studied²⁴ and different interpretations as to its role are contained in the literature. Hodgson and Marsden²⁵ came to the conclusion that in alkaline medium, pyridine stabilizes the diazo compound through the formation of a diazopyridinium ion (21).



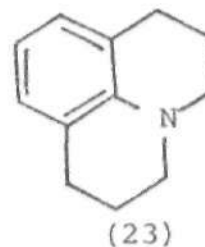
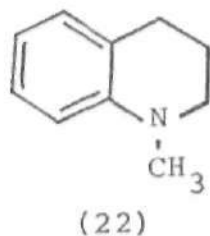
The postulate of Hodgson and Marsden has since been refuted by Pütter²⁶ and Zollinger.²⁷ According to these workers, the role of pyridine could best be understood from a base catalysis viewpoint. In fact, Zollinger has shown in his kinetic studies that pyridine acts as a proton acceptor in the second step of the kinetic system (1.1a - b).



The function of coupling components in azo dyes has reached a very high degree of complexity so that it can no longer be handled from a limited angle without serious omissions. In the early days of the dyestuff industry, the bulk of couplers were simple organic compounds, notably

phenols, naphthols, arylamines, pyrazolones and the like. Since the introduction of synthetic fibres, there has been a complete reappraisal of the dye structure to meet various demands. The use of a particular coupler may be influenced by synthetic as well as other considerations. For instance, primary amines can afford diazotizable groups for further azo links and naphthols and related hydroxy-compounds are useful couplers for metallisable dyes. Many naphthalenes bearing sulphonic acid groups are used extensively in the manufacture of water-soluble dyes. Aminonaphtholsulphonic acids are widely used as couplers for wool, cotton and leather dyes. Specific groups may be introduced into the coupling component for specific reasons. In the last ten years numerous patented references have appeared in the literature dealing with couplers for azo dyes, covering a wide range of properties, inter alia, bathochromic shifts, wash fastness, light fastness enhancement, and increased reactivity during the process of dyeing. Most of the patented couplers in use at the moment carry electron-donating groups which appear ortho to the azo linkage, a device which greatly enhances the polarity of the dye molecule thus leading to bathochromic shifts. In some cases heterocyclic systems have been used.²⁸ In the present work, terminally bridged systems such as (22) and (23), in which more effective conjugation is achieved through the interaction of the nitrogen lone pair with the benzene ring, have been studied. These systems have been used with di- and

triphenylmethane dyes²⁹ and also with some simple azo systems.³⁰



2. Classification of Azo Dyes

(a) According to Constitution

Azo dyes form approximately two-thirds of all dyes coded in the Colour Index.³¹ The large number of azo dyes notwithstanding, they all form one structural unit, characterised by the presence of at least one azo group $-N=N-$. A breakdown of azo dyes depending on the actual number of azo groups present in the dye structure is as follows:

- (i) monoazo dyes
- (ii) disazo dyes
- (iii) trisazo dyes
- (iv) tetrakisazo dyes
- (v) higher polyazo dyes

There is a standard practice of representing the various subdivisions of azo dyes which amounts to a chemical shorthand. This symbolised system of representation, coined from

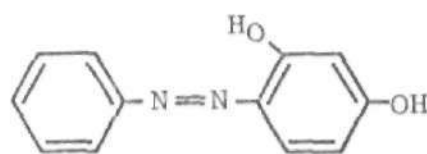
the six main intermediates used in azo dye manufacture, was adopted by Lapworth.³² The code letters used and their significance are as follows:

- A Diazotizable primary amine; if several such amines are used, they are differentiated as A¹, A², etc.
- D Tetrazotizable diamine
- E Coupling component; if more than one, they are similarly represented E¹, E², etc.
- Z Coupling components able to couple with two or more equivalents of a diazonium compound or different diazonium salts.
- M Represents a middle component, it is usually a primary amine which can be coupled to a diazonium compound to give an aminoazo compound which may be diazotised and coupled again.
- T is a second component which has three coupling positions and can be coupled with three moles of diazonium salts.

In order to distinguish the various types of azo dyes, these code letters are used along with arrows, which signify 'diazotised and coupled with'. In polyazo dyes the arrows are usually numbered to show the order of coupling and it is customary to indicate the medium of a particular coupling position. Typical examples may help to illustrate the various types of azo dyes described by these symbols.

(i) Monoazo Dyes

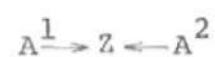
Typified by the dye C.I. Solvent Orange I



(24)

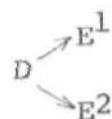
(ii) Disazo Dyes

These are further subdivided as illustrated.



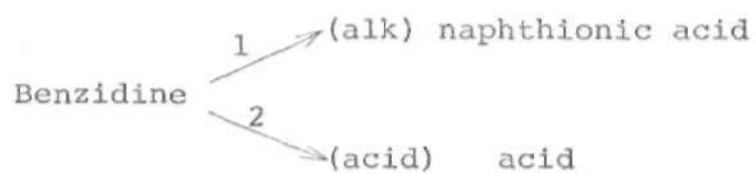
An example is Naphthalene Black 12B (ICI) p -Nitroaniline $\xrightarrow{1}$
(acid) H acid (alk) $\xleftarrow{2}$ aniline

or



Exemplified by

Chlorazol Bordeaux B (ICI)



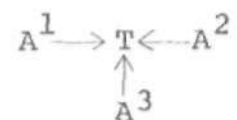
Another type is illustrated by the disperse dye,
Dispersol Fast Orange B (ICI)



Aniline $\xrightarrow{1}$ (acid) α -naphthylamine $\xrightarrow{2}$ (alk)phenol

(iii) Trisazo Dyes

These may fall into the following categories:

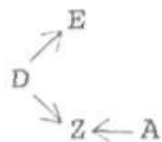
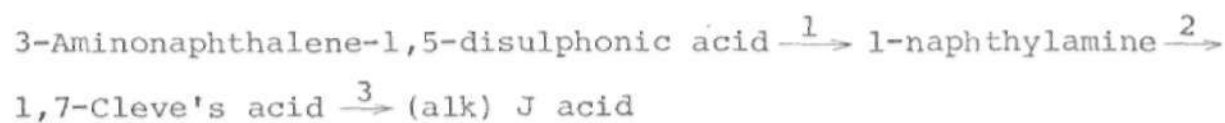


T is resorcinol or m-phenylenediamine or their derivatives;



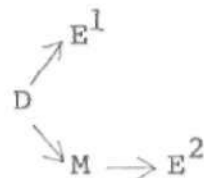
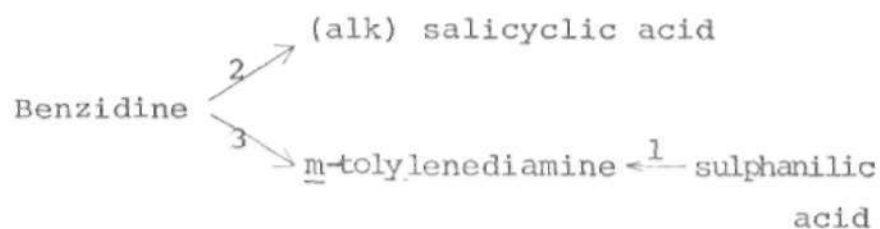
Example:

Durazol Blue 2R (ICI)

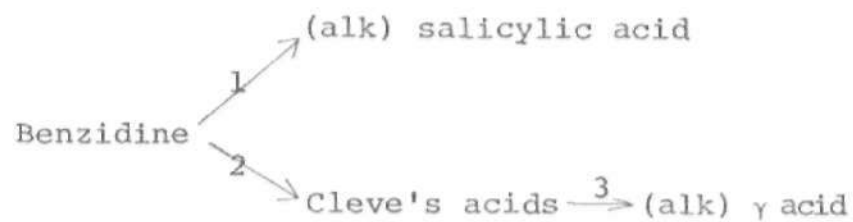


Example:

Chlorazol Orange Brown X (ICI)

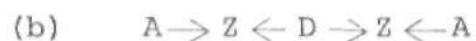


Example: Chlorazol Drab RH (ICI)



(iv) Tetrakisazo Dyes

These may fall into the subdivisions



There are very few examples of this group in technical practice; some commercial examples are made by further coupling of disazo or trisazo dyes on the fibre. Higher azo dyes are even less accessible technically, although there are a few examples quoted in the Colour Index of azo dyes with more than four azo groups.

(b) Classification According to Usage

The classification of dyes according to application is expanding as fast as more uses are found for synthetic dyes. As far as azo dyes are concerned, they are included in almost every known grouping, usually dominating the lighter colours. They form substantial parts of solvent dyes, azoic dyes, acid dyes, mordant dyes and many other non-textile application groupings. Other uses of azo dyes include the colouring of foodstuffs, cosmetics, anodised aluminium, drugs, biological stains and polymers. Azo dyes with special structures are used for colouring petroleum products and inks and as analytical indicators. The various uses to which azo dyes are put make their classification according to usage highly challenging.

3. Link Between Colour and Constitution of Azo Dyes

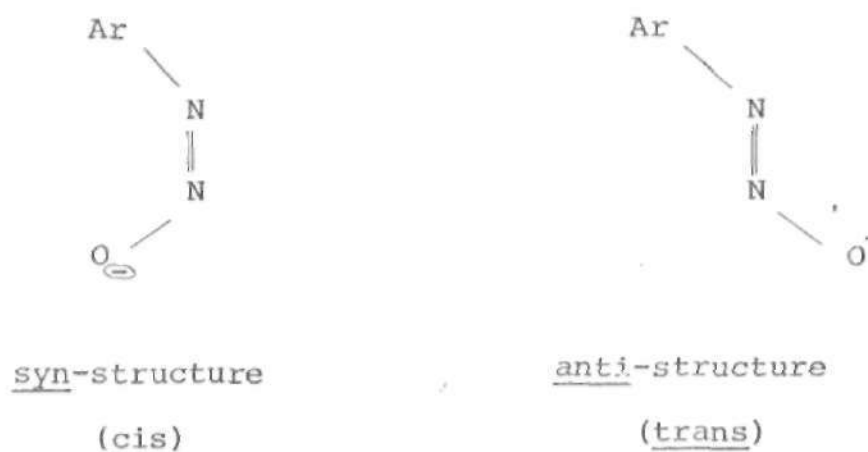
(a) Early Theories

The host of theories advanced in an attempt to explain the link between the colour of organic compounds on the one hand and their chemical constitution on the other is an indication of the complexity of this subject. The piecemeal approach is in agreement with developments in other branches of chemistry and related fields. It was Graebe and Liebermann³³ who initiated the correlation between colour and constitution. These workers ascribed the colour of all the then known organic compounds to unsaturation, following their observation that all coloured compounds were decolourized on reduction. Witt's³⁴ introduction of chromophores and auxochromes to describe organic dyes was no more than an elaboration of Graebe and Liebermann's original concept, as almost all chromogens contain highly unsaturated groups. Nietzki³⁵ held the view that the colour of a dye could be deepened by merely adding groups that would increase its molecular weight. Obviously, such thinking reflected the gloomy atmosphere that hung over colour structure-relation at the time. The quinonoid theory of Armstrong³⁶ in 1888 was a bold generalisation, as no satisfactory explanation could be found at the time to back up the colour-yielding property of quinone; furthermore, there were outstanding exceptions like the case of azobenzene. The contribution by Hewitt and Mitchell³⁷ made in respect of azo dyes, in

which the length of the 'conjugate chain' accounted for the depth of the colour was supported by many researches.³⁸ Stieglitz³⁹ considered dyes to be intermediate states of oxidation containing both oxidising (chromophoric) as well as reducing (auxochromic) groups. He argued that the presence of the two groups in the molecule resulted in an intramolecular electron transfer.

(b) Stereoisomerism and Tautomerism

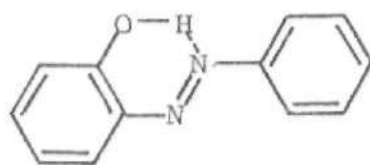
In 1937, Hartley⁴⁰ observed the existence of two forms of azobenzene, cis and trans isomers. An analogous observation for diazotates had been made by Hantzsch and Werner almost half a century earlier.⁴¹



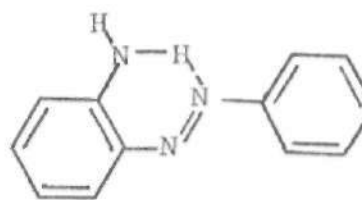
(25)

Until the discovery of Hartley, azobenzene was considered to exist almost exclusively in the stable trans-form.⁴² Hartley found that if azobenzene was exposed to strong light there occurred a partial conversion of the trans-form into the cis-isomer. This observation was supported by physical

properties. The change was, however, reversed on storage. This trans-cis isomerism has been detected also in substituted azobenzenes and azonaphthalenes.⁴³ The isomeric behaviour gives rise to the phenomenon of phototropy (the change in shade of simple azo dyes when applied to non-polar fibres such as cellulose acetate and exposed to strong light). It is believed⁴⁴ that phototropy is possible only on fibres in which dyes dissolve, hence the absence of the trans-cis conversion in dyed fibres of cellulose or protein in which the dye molecules are known to be firmly held by absorption. Fortunately, this undesirable behaviour of some simple disperse azo dyes is greatly minimised in o-hydroxyazo and o-aminoazo dyes, whose trans-forms are supposedly locked through hydrogen bonding between the hydroxyl or amino group and the azo nitrogen atom as shown in (26) and (27).



(26)



(27)

As mentioned earlier in this section, Zincke and Bindewald¹⁰ discovered that diazotised aniline coupled to 1-naphthol gave the same product as the condensation reaction between phenylhydrazine and 1,4-naphthoquinone.

Spectroscopic evidence has shown that, in fact, an equilibrium exists between the hydroxyl and carbonyl groups of the reaction products; in other words, tautomeric structures are responsible for the characteristic bands observed. The two tautomeric forms for *p*- and *o*-hydroxyazo-compounds are shown in Chart 10.

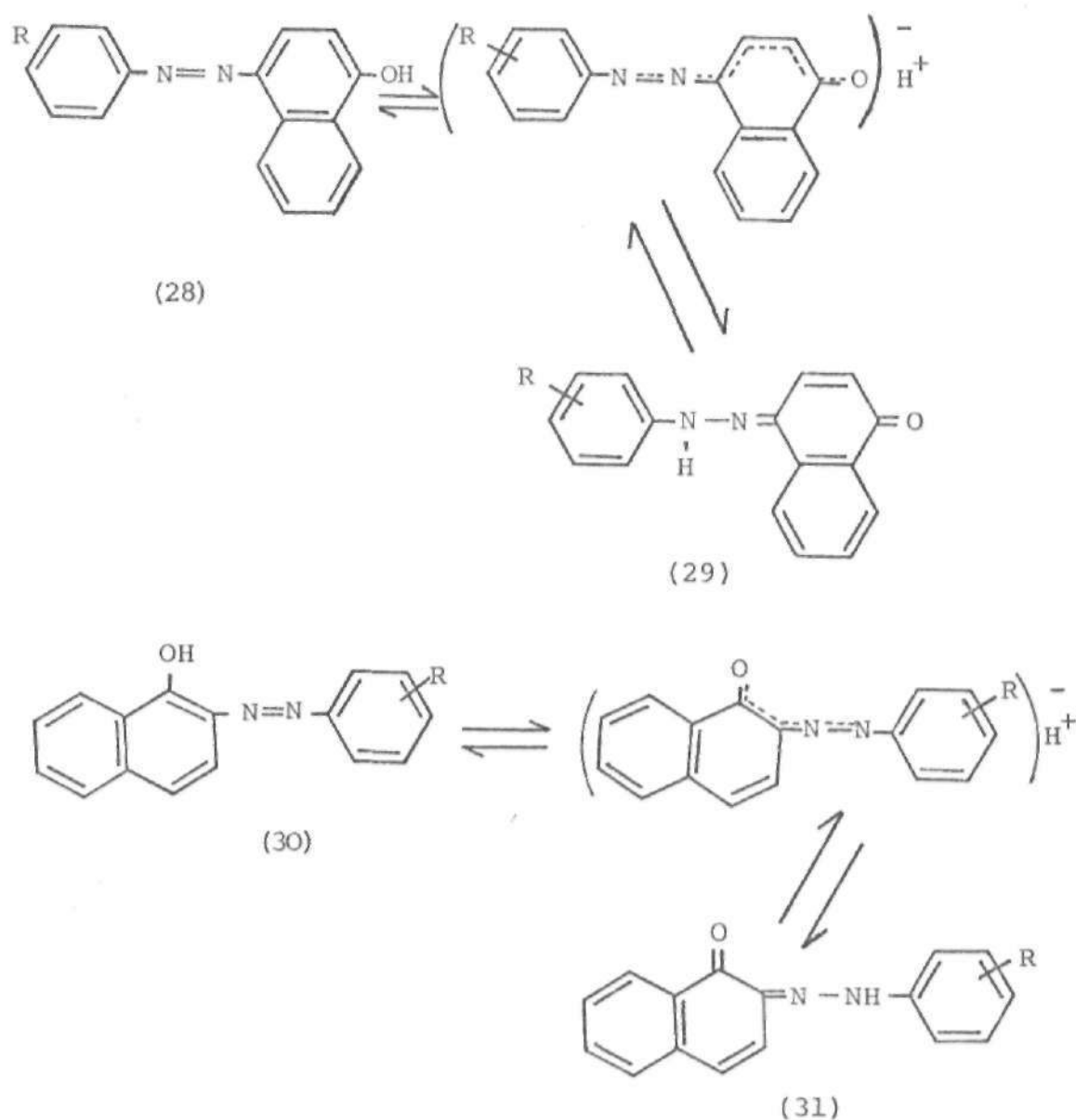


Chart 10. Tautomerism in *p*- and *o*-hydroxyazo-compounds.

This azo-hydrazone tautomerism is solvent dependent⁴⁵ and is also greatly influenced by substituents. Increase in the polarity of the solvent is believed to displace the equilibrium towards the more polar quinone hydrazone form. The formation of hydrogen bonding with the solvent on the other hand tends to shift the equilibrium in favour of the azo-tautomer. There is experimental evidence to support the view that the hydrazone tautomer absorbs at longer wavelength than the corresponding azo form. Experimental results from different sources are tabulated in Table 1.

Table 1. Visible absorption maxima and dominant tautomeric forms for some azo-hydrazone systems*

Compound	$\lambda_{\text{max, azo}}$ form [nm] ^a	$\lambda_{\text{max, hydrazone}}$ form [nm] ^a	Tautomer(s) present in EtOH	Ref.
1-Phenylazo- 2-naphthol	410	480	both	46
4-Phenylazo- 1-naphthol	400	470	both	47
2-Phenylazo- 1-naphthol	-	490	hydrazone	48
3-Phenylazo- 2-naphthol	440	-	azo	49

a Solvent ethanol

* adopted from reference 7.

A thorough review of the phenomenon is to be found in the work of Bershtein and Ginzburg.⁵⁰ The subject of azo-hydrazone tautomerism is of paramount importance in the investigation of colour-chemical structure relationships.

(c) Protonation

The behaviour of p-aminoazo-compounds in acidic solutions has been the subject of prolonged controversy amongst chemists since the pioneering work of Hantzsch and his collaborators.⁵¹ These workers had proposed the existence of a cationic species in acidic solutions of this class of compounds. The protonated form was in all respects different from the neutral azo compound and its formation was ascribed to the addition of hydrogen ions to the β -azo nitrogen atom as shown in 33(a).

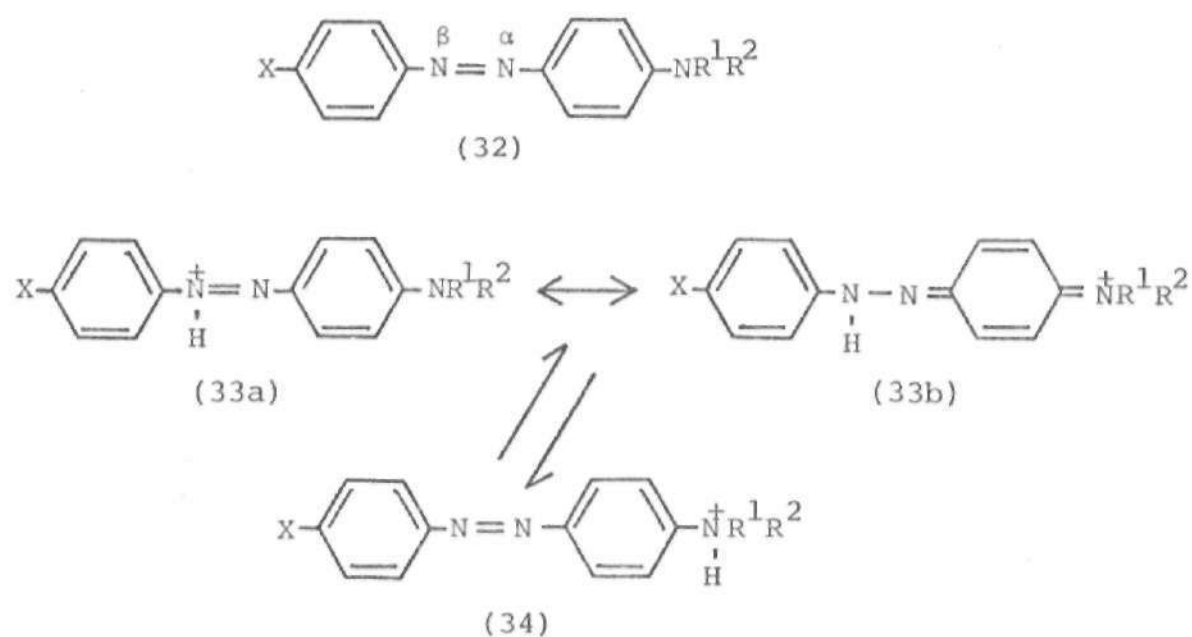


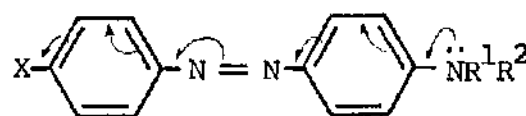
Chart 11. Protonation of p-aminoazo-compounds.

This view that protonation occurred solely at the azo-group was supported by many researches.⁵²⁻⁵⁴ The opponents of this azonium ion theory proposed instead an ammonium structure (34).⁵⁵⁻⁵⁸ The thorough investigations of Sawicki⁵⁹ and others have helped to establish once and for all the tautomeric equilibrium that exists between the azonium and the ammonium structures ($33 \rightleftharpoons 34$).

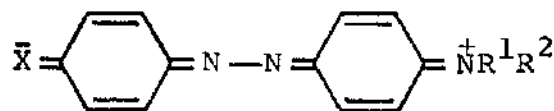
The absorption maxima for azobenzene, 4-aminoazobenzene and N-substituted analogues in aqueous ethanolic solutions lie at 320, 380 and 410-440 nm respectively.⁶⁰ This band has been attributed to the $\pi \rightarrow \pi^*$ transition and has been referred to as the K-band. The red shift shown by the N-substituted compounds is hardly surprising since there is an improved conjugation between the terminal nitrogen and the azo group; this situation is greatly enhanced in the terminally bridged systems.³⁰ The addition of acid to solutions of these azo dyes is usually accompanied by the deepening of their colour (halochromism) and the appearance of two new peaks, one in the 500-540 nm region and the other at approximately 320 nm. Badger et al. have designated these two new bands as Q and K' lying in the visible and ultraviolet regions of the spectrum, respectively. The band in the visible is believed to be due to the azonium species, while the ultraviolet band is caused by the ammonium cation.⁶¹

(i) Substitution Effects

The effect of substitution on the colour of dialkyl-amino azo dyes has been studied in great detail by Yagupolskii and Gandel'sman.⁶² These workers pointed out that λ_{max} underwent minimal changes when X in structure (32) was the fluoro, methyl, methoxy or amino groups. In other words, electron-donor substituents have very little effect on the position of the absorption maxima. On the other hand bathochromic shifts of up to 70 nm in some cases were observed with electron-withdrawing groups in the 4'-position. This difference in behaviour was explained on the basis of two extreme resonance canonicals (35) and (36).



(35)



(36)

$R^1, R^2 = \text{alkyl groups}$

The neutral structure (35) will undoubtedly predominate over the zwitterionic form, as the latter will expend energy in the separation of charges and the formation of quinoid rings. If X is the acceptor group (e.g. NO_2), electrons will be transmitted from the dialkylamino group to the other

end of the molecule, thus bringing the two structures (35) and (36) closer and leading to the halochromic effect observed in practice. An opposite effect is to be expected if X is a donor group. Castelino and Hallas have prepared a number of *p*-substituted julolidine dyes and these have shown clearly the effect of *p*-substitution on the value of the absorption maxima. As has been mentioned before, the julolidyl group confers maximum conjugation on the system as the amino nitrogen atom has been forced into coplanarity with the rest of the molecule by means of the methylene bridges. The absorption bands for 9-phenylazojulolidine in ethanol and acidified ethanol are shown in Table 2 together with the corresponding intensities.

Many attempts have been made to correlate substituent effects with spectral shifts. Perhaps the most useful of all is the qualitative approach of Yagupol'skii and Gandel'sman. In a purely empirical manner, these workers established a linear relationship between the first absorption band of dyes and their azonium salts with appropriate Hammett σ -constants. Hammett^{63a} had earlier suggested that a quantitative measure of the electronic effect would be given by the difference between the pK_a of the substituted benzoic acid and that of benzoic acid itself. Thus,

$$\sigma = \log K_x - \log K_o, \quad 1.2$$

Table 2 Absorption bands of *p*-substituted derivatives
of 9-phenylazojulolidine.

<i>p</i> -Substituent	Hammett constant	$\lambda_{\text{max}}[\text{nm}]$ EtOH	$10^{-4}\epsilon_{\text{max}}$	$\lambda_{\text{max}}[\text{nm}]$ EtOH+100 equiv. HCl	$10^{-4}\epsilon_{\text{max}}$	$\Delta\lambda$
OH	-0.52	449	2.74	574	5.81	125
OCH ₃	-0.27	452	2.76	564	5.60	112
CH ₃	-0.17	446	2.72	537	5.83	91
H	0.00	442	2.70	523	5.93	81
F	0.06	450	2.76	524	5.88	74
I	0.28	467	3.26	532	5.93	65
Cl	0.23	461	3.10	525	5.88	64
Br	0.23	464	3.18	526	5.75	62
CF ₃	0.55	471	3.10	507	5.60	36
NO ₂	0.78	518	3.58	518	6.63	0

in which K_x is the dissociation constant of a substituted benzoic acid and K_0 that of benzoic acid itself. In this manner Hammett values as quoted in Table 2 are obtained. It is to be remembered, however, that these parameters vary with the position of attachment in the benzene ring and also that the relationship (see eqn. 1.2) is best expressed in the form

$$\Delta\nu = \nu_X - \nu_H = \rho \cdot \sigma_X \quad 1.3$$

where ν_X and ν_H are the absorption frequencies of the substituted and unsubstituted chromogens respectively, and σ_X is the appropriate Hammett constant for substituent X. In the above equation, ρ is a measure of the sensitivity of the absorption band to constituent effects, such that if ρ is positive a bathochromic shift is experienced with increasing electron donating strength and vice versa. This relationship is well illustrated graphically using the values quoted in Table 2 for the 9-phenylazojulolidine dyes (see Fig. 1.1).

It is, however, difficult to establish categorically the practical significance of the halochromic effect, but it is reasonable to suggest that dyes with large shifts on either side of the scale will be useful acid-base indicators. Textile dyes on the other hand should show minimal changes in going from neutral to acidic media. Nevertheless, there are examples in technical practice whereby the same dye

has played the dual role of an indicator as well as a textile colorant, e.g. Congo Red.

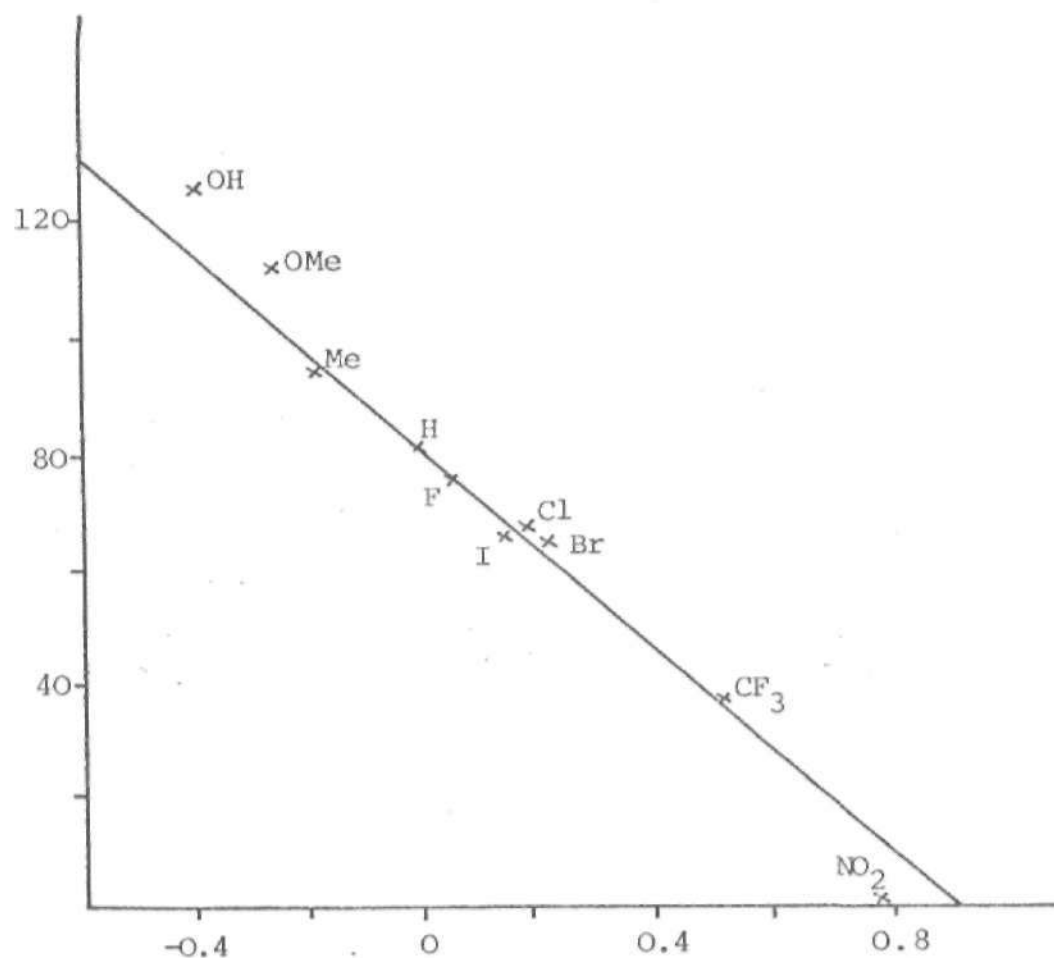


Fig. 1.1. Relation between σ -constants and $\Delta\lambda$.

So far discussion has been restricted to dyes with *p*-substituents in the acceptor ring of alkylaminoazo-benzene derivatives. It is usually accepted that interaction of π -electrons in a π -system is maximal when the skeleton of the system is planar. The introduction of bulky groups into the system will no doubt alter the geometry of the molecule and will have pronounced effects on the colour of the dye, monitored through its electronic absorption spectrum.

(ii) Steric Effects

If bulky groups are introduced into the dye molecule, steric strain may result. In order to relieve this strain, the dye molecule may undergo deformation, distortion or rotation.

Deformation is a high-energy process involving the stretching or compressing of bonds and must be considered most unlikely to occur. Of the two low-energy processes, rotation will take place in preference to distortion, which requires the decrease or increase of bond angles in the molecule. Furthermore, rotation about single bonds involves no energy changes at all, while that about double bonds is quite low.

Steric effects in dyes with substituents (mostly alkyl groups) in both the recipient⁶³ and donor⁶⁴ rings have been studied. While it is generally accepted that steric hindrance brings about a decrease in the intensity of the absorption band (hypochromic effect), no parallel generalisation can be made regarding the position of λ_{max} . In most cases hypsochromic effects are observed, but red shifts are by no means ruled out. The concept that a hypsochromic effect will result if steric hindrance increases the energy of the excited state more than it does that of the ground state and vice versa for red shifts has proved very satisfactory. A quantitative treatment of this view will be considered in a later chapter. A graphical representation of energy changes (bond orders) in the ground and

excited states during the process of bond rotation is shown in Fig. 1.2.

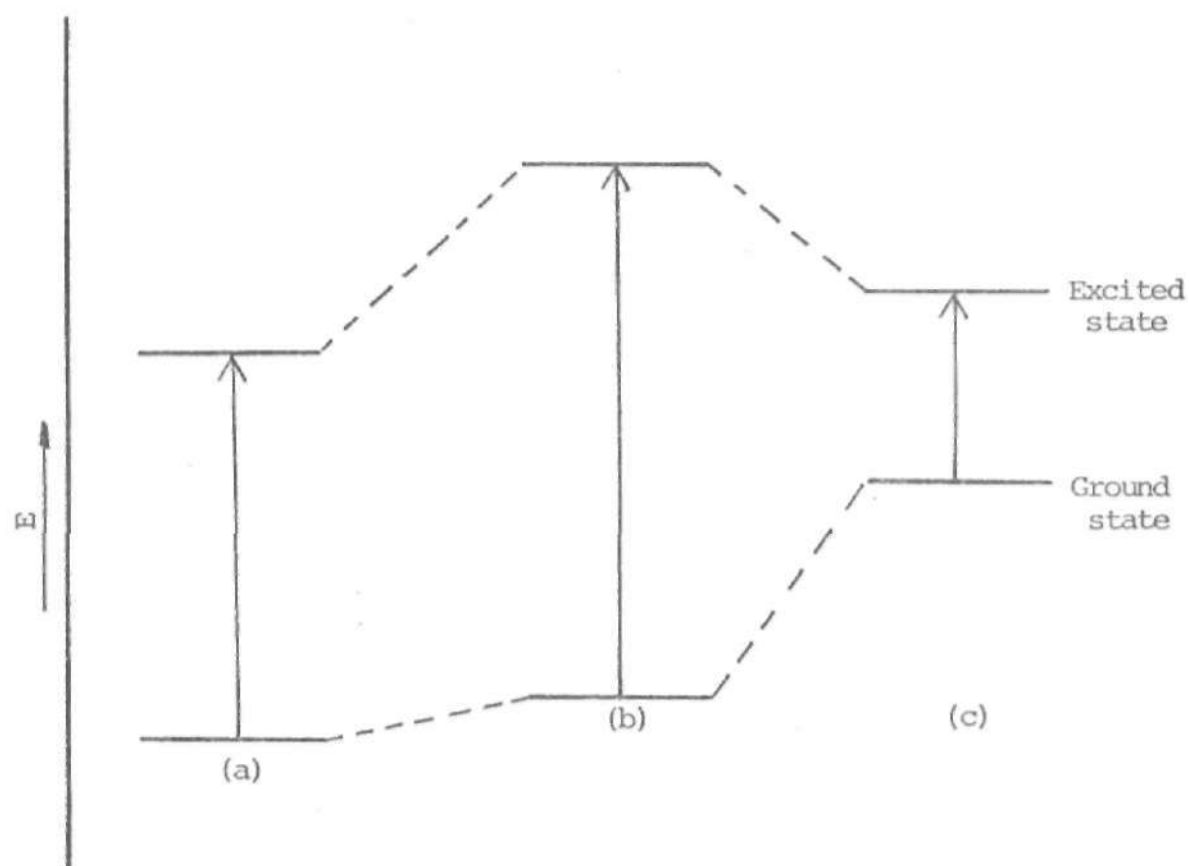
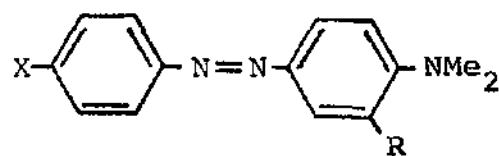


Fig. 1.2.* The effect of bond rotation on the ground and excited state of a molecule.

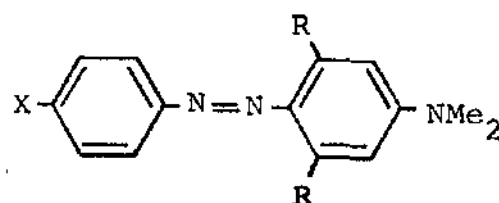
- (a) planar situation
- (b) rotation about a bond of increased bond order in the excited state (hypsochromic shift)
- (c) rotation about a bond of reduced bond order in the excited state (bathochromic shift).

* From ref. 7.

Roospiekar⁶⁴ examined dyes of the general structures (37) and (38) and in each case he observed hypsochromic shifts.



(37)



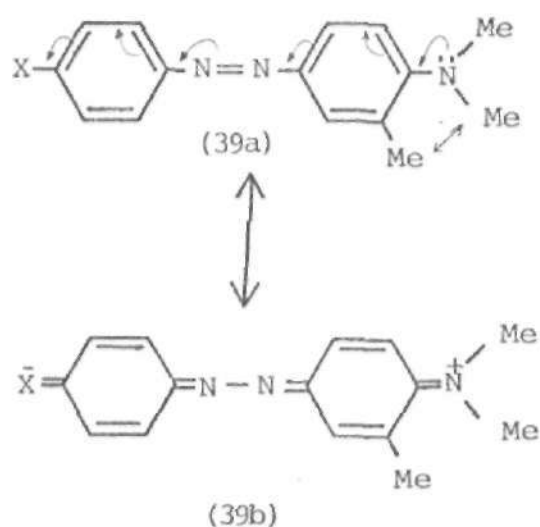
(38)

Experimental data of $\lambda_{\max}$ and $\epsilon_{\max}$ are shown in Table 3 for structure (37).

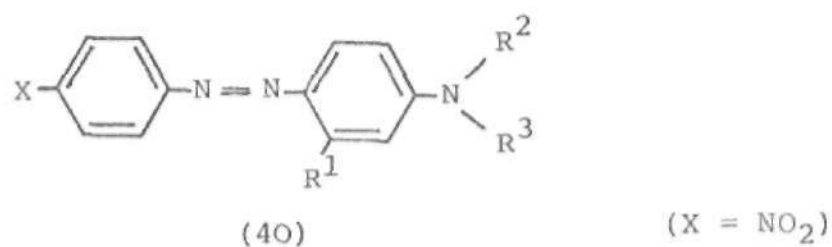
Table 3. Effects on $\lambda_{\max}$ in sterically hindered systems

X	R = H		R = CH ₃			
	$\lambda_{\max}$	$10^{-3} \epsilon_{\max}$	$\lambda_{\max}$	$10^{-3} \epsilon_{\max}$	$^H \lambda_{\max}$	$^{-CH_3} \lambda_{\max}$
H	409	24.5	395	16.4		14
Cl	418	27.2	388	13.0		30
CH ₃ CO	446	29.7	404	18.6		42
CN	450	32.2	402	19.0		48
NO ₂	480	30.4	422	18.6		58

The hypsochromic shifts experienced in all the cases were believed to have arisen from the interference of the methyl group with the p-orbital of the amino group, thus giving rise to a high-energy zwitterionic form (39.b).



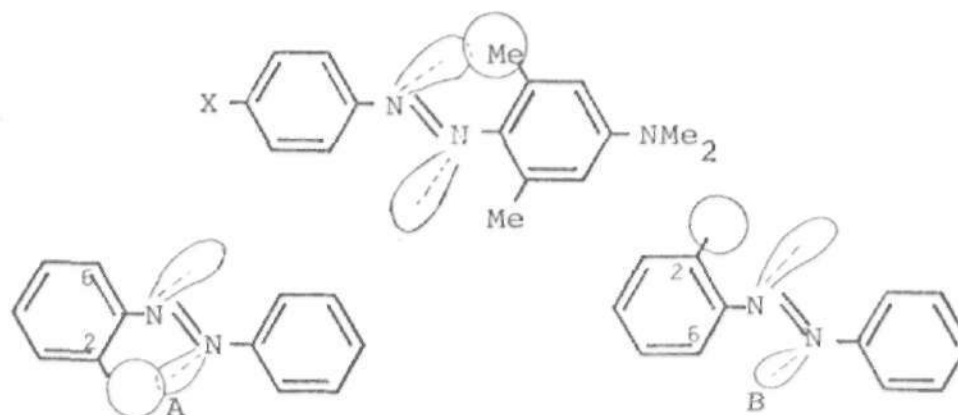
Bridgmann and Peters⁶⁵ prepared a large number of substituted azobenzenes and observed that in dyes of the general structure (40), a bulky substituent (R^1) does not bring about a hypsochromic effect due to steric hindrance. Thus, for ($R^1 = R^2 = H$ and $R^3 = C_2H_4CN$) and ($R^1 = Me$, $R^2 = H$ and



$R^3 = C_2H_4CN$) absorption maxima are 443 and 451 nm) respectively. This observation holds good only for monosubstituted dyes,

as shown by scale drawings for the disubstituted dye (38). There is an overlap of one of the bulky methyl groups with the lone pair of electrons of the β -nitrogen atom of the azo group.

A similar argument has been advanced by Hoyer *et al.*⁶³ for substituents in the acceptor ring. Generally, a planar trans-azobenzene with one substituent on C-2 can assume conformation A or B, that of B being sterically more favourable than that of A. Thus, stronger steric hindrance is to



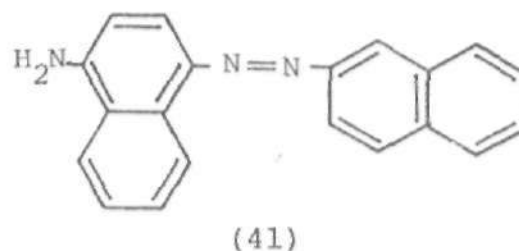
to be expected only when C-2 and C-6 of one benzene ring are both substituted so that one substituent overlaps the sp^2 electrons of the nitrogen atom as shown.

(d) Extension of Conjugation

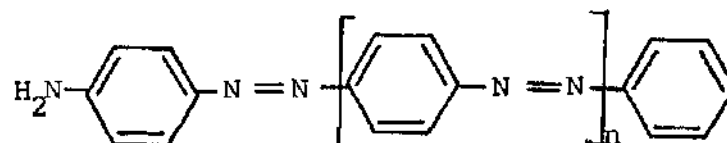
Sometimes the spectral characteristics of a dye molecule can be altered tremendously by extending the conjugation of the system. The main goal of a conjugation extension is to shift the position of $\lambda_{\max}$ towards longer wavelength; the influence on absorption intensity is usually a secondary consideration, although there are many examples

in which bathochromic shifts as well as hyperchromic shifts have been observed. In practice, there are various ways of extending the conjugation of a system. This may be accomplished through the inclusion of the naphthalene rather than the benzene rings in the system. Hallas⁶⁶ and his students have prepared many di- and triarylmethane dyes in which conjugation has been extended both transversely and longitudinally using the naphthalene ring. Mononaphthalene analogues of Crystal Violet, Malachite Green and Michler's Hydrol Blue all showed red shifts in 98% acetic acid.⁶⁶ It was observed, however, that conjugation through the 1- and 4-positions was more effective than that through the 2- and 6-positions. Similarly, phenanthrene and 9,9-dimethylfluorene were used in the preparation of these basic dyes and they all showed bathochromic shifts in comparison with the parent dyes.⁶⁷

The dye (41) absorbs at 465 nm in ethanol compared



with p-aminobenzene which absorbs at 385 nm in the same solvent.⁶⁸ Longitudinal extension can also be achieved by increasing the number of benzene rings and azo groups⁶⁹ as shown in (42). Heterocyclic ring systems are useful devices for extending the conjugation in monoazo dyes since



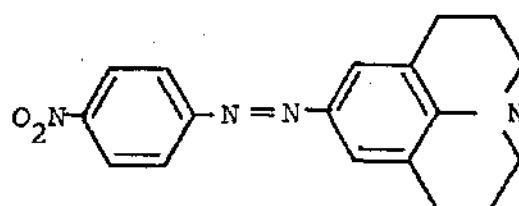
(42)

for $n = 1$, $\lambda_{\max}$ is 416 nm^b

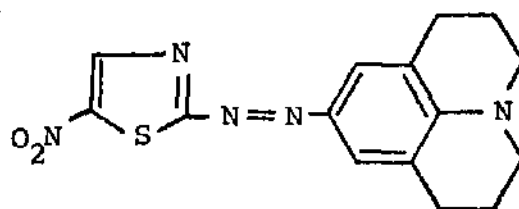
$n = 2$ " " 428 nm

b - solvent benzene

they produce deep colours from a relatively low mass molecular structure; an example is the 5-nitrothiazole derivative of julolidine (44), which absorbs at 625 nm (5.35×10^4) compared with the *p*-nitroaniline analogue (43) which has a $\lambda_{\max}$ of 518 nm (3.78×10^4), both measured in ethanol.³⁰



(43)



(44)

(e) Recent Developments

Modern understanding of the relationship between colour and chemical constitution owes its existence to developments in quantum mechanics. There is the general consensus amongst theoreticians that absorption in the ultraviolet, visible and infrared regions of the electromagnetic spectrum can no longer be treated in isolation, but as a single topic. In the early approaches there was overplaced emphasis on the position of the absorption maximum; this imbalance is being corrected. Thus, both λ_{max} and the corresponding absorption intensities are treated with the same degree of importance. This realisation has considerable meaning in practice, since the intensity of a dye molecule is of immense importance during application. Quantum mechanical methods developed to explain the link between colour and constitution are becoming increasingly popular, with the advent of computer programming, which can handle complex molecules, such as dyes. In the present work, most of the dyes prepared have been studied in some detail with the help of the Pariser-Parr-Pople approach. As the number of physical methods is ever increasing, careful choice is of paramount importance, as some methods are more suitable to certain classes of dyes than others. This fact if ignored would lead to poor correlations as is sometimes found in the literature.

DISCUSSION OF RESULTS

Part A Spectroscopic Investigations

(i) Preparation of solutions for spectroscopic measurements.

An accurately weighed sample of pure dye (ca.0.001 mole) was dissolved in ethanol and made up to 100 ml in a volumetric flask. In most cases it was first necessary to warm the dye in a small quantity of solvent to ensure efficient dissolution before adding the cooled solution to the volumetric flask. A measured volume of the stock solution (graduated pipette) was then diluted in a 25-ml volumetric flask to give an approximately 10^{-5} M solution.

(ii) Ethanollic hydrogen chloride

Dry hydrogen chloride gas was passed into ethanol and the concentration of the acid in solution was determined volumetrically by titration with a standard solution of sodium hydroxide.

Spectral measurements were first carried out in ethanol alone. Known quantities of ethanollic hydrogen chloride (equated in equivalents of acid) were then added so as to progressively vary the concentration of the acid. The addition of acid was continued until an equilibrium had been established.

1. N,N-Diethylaniline dyes

Various monoazo dyes of general form (45) have been derived from N,N-diethylaniline as the common coupling component; spectral data are listed in Table 2.1.

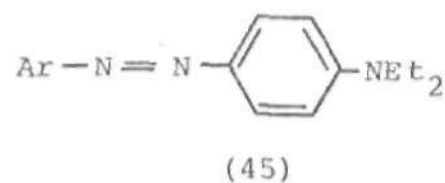


Table 2.1. Spectral data for solutions of N,N-diethylaniline dyes (45) in ethanol.

ArNH ₂		$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$
Aniline	(46)	415	2.70
2-Nitroaniline	(47)	450	2.24
4-Nitroaniline	(48)	488	3.53
2-Amino-1-nitro-naphthalene	(49)	474	4.17
1-Amino-4-nitro-naphthalene	(50)	502	3.16
1-Amino-5-nitro-naphthalene	(51)	460	2.45
2-Amino-6-nitro-naphthalene	(52)	480	3.55
2-Amino-8-nitro-naphthalene	(53)	466	3.13
2-Amino-9,10-dihydro-phenanthrene	(54)	433	2.04

2-Amino-3-nitro-			
9,10-dihydrophenanthrene	(55)	475	3.41
2-Amino-7-nitro-			
9,10-dihydrophenanthrene	(56)	470	3.49
2-Amino-7-nitro-			
phenanthrene	(57)	466	2.86
3-Amino-9-bromophenanthrene	(58)	452	3.58
3-Amino-9-cyanophenanthrene	(59)	476	3.90

In general, the replacement of a benzene ring by a polycyclic system does not greatly alter the absorption of the dyes.

(a) Overall comparison of phenylazo dyes with polycyclic-azo dyes

Longitudinal extension of the conjugation brings about a bathochromic shift of the first absorption band. Thus, the dihydrophenanthrene dye (54) and the parent dye (46) absorb at 433 and 415 nm, respectively, a red shift of 18 nm. Similarly, dye (55) having λ_{max} at 475 nm shows a bathochromic shift of 25 nm when compared with the corresponding benzenoid dye (47) which absorbs at 450 nm. This bathochromic pattern breaks down, however, if dyes (48) and (56) are compared; the latter compound has a λ_{max} value of 470 nm while the 4-nitroaniline parent (48) absorbs at 488 nm, a hypsochromic shift of 18 nm. Although it can be argued that in the 9,10-dihydrophenanthrene dye (56) the two benzene rings are twisted out of coplanarity, it is also relevant

that the acceptor nitro group in this system is somewhat remote from the electron donor substituent (NEt_2).

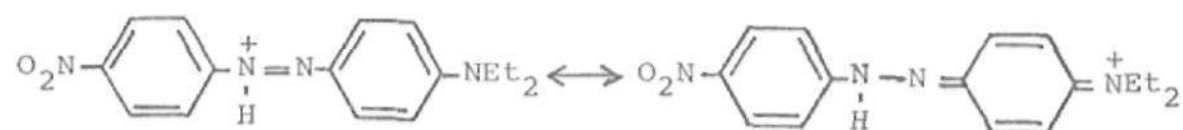
Perhaps the most closely related dyes for comparison purposes are dyes (48), having λ_{max} at 488 nm, and (50), with λ_{max} at 502 nm; the red shift of 14 nm is in accord with the additional benzene ring in the naphthalene system. Replacement of naphthalene by phenanthrene appears to have but little effect on the position of the absorption maxima as shown by the limited range of dyes examined (57, 58 and 59); this observation is in keeping with the poor colour-yielding ability of the phenanthrene chromogen referred to elsewhere.

(b) Behaviour of N,N-diethylaniline dyes in acid media

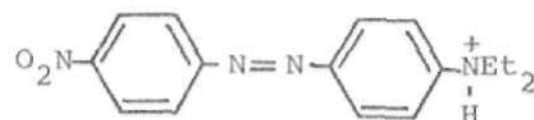
In ethanolic hydrogen chloride, dye (48) shows no change in the position of absorption maximum initially; there is, however, a slight increase in the absorption intensity ($10^{-4} \Delta \epsilon = 0.06$) after an addition of 5 equivalents of acid. As the concentration of the acid is increased, there is a gradual shift towards longer wavelengths and a corresponding increase in absorption intensity, until equilibrium is reached with the addition of 1000 equivalents of ethanolic hydrogen chloride. At the equilibrium position, the absorption maximum has shifted from 488 to 510 nm (positive halochromism) and a slight increase in absorption intensity ($10^{-4} \Delta \epsilon = 0.22$) is observed; a broad band also appears in the 320 -330 nm region. This behaviour is typical of mono-acid salts of

derivatives of 4-aminoazobenzene.⁵⁹ Under identical conditions, however, the intensity of dye (50) falls rapidly with no change in the position of the absorption maximum. By the time 10,000 equivalents of acid have been added, there is hardly any peak in the visible region; instead a weak band appears at 390 nm (Fig. 2.1).

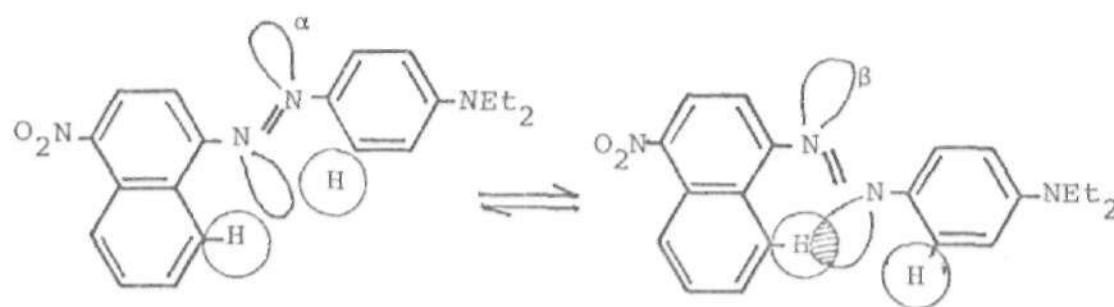
The spectral results (Fig. 2.1) indicate that in the case of the phenylazo dye (48) an equilibrium mixture of two tautomeric forms obtains in which the proton is attached to the azo-linkage and to the amino-group, respectively. The azonium form, which can be represented as a charge-resonance system (60a), absorbs at longest wavelength and predominates.



(60a)



(60b)



preferred

(61a)

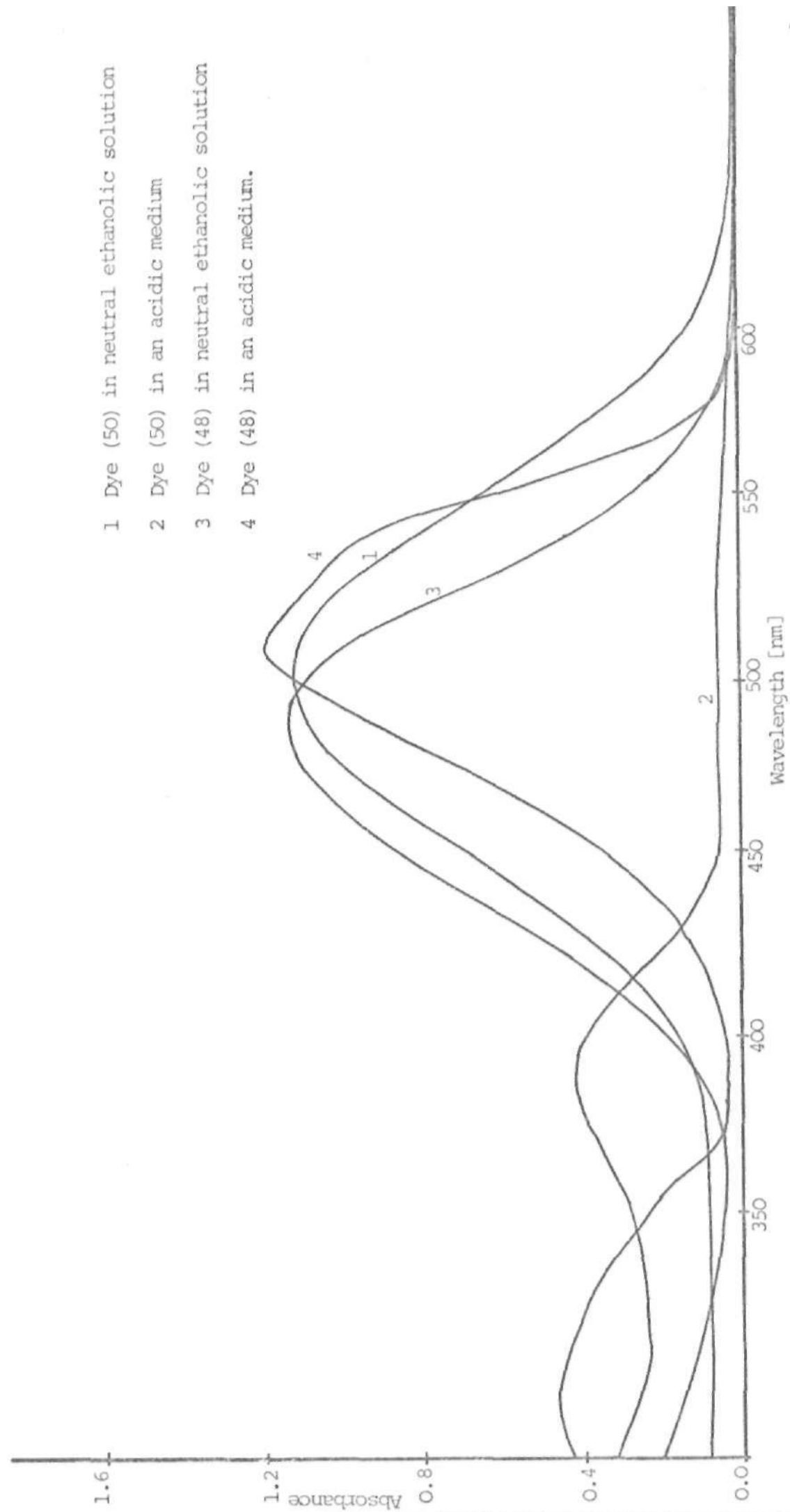
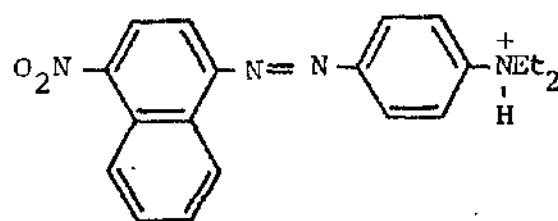


Fig.2.1. Absorption spectra of dyes (48) and (50) in ethanol and in acid media.



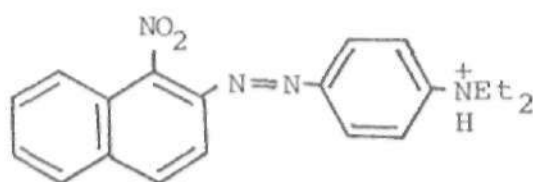
(61b)

Chart 2.1. Azonium and ammonium structures for dyes (48) and (50).

The naphthalene dye (50) appears to exist exclusively in the ammonium form (61b) as indicated by the absence of an absorption peak in the visible region of the spectrum in strong acid. It seems likely that protonation at the azo group is peri-hindered (61a) since it is probable that the preferred conformation of the dye is that in which attack at the β -nitrogen is most difficult. This suggestion is in accord with the results of Hoyer, Schickfluss and Steckelberg,⁶³ who have argued against the existence of an alternative conformation in which the α -nitrogen is sterically hindered, on the grounds of overcrowding. Similar behaviour is shown by the related isomer (51). The dye derived from 2-amino-1-nitronaphthalene (49) also shows the absence of an azonium form in ethanolic hydrogen chloride. The spectrum is similar to that of dye (50); spectral changes in acid are shown in Table 2.2.

Again, the absence of protonation can be associated with the presence of a substituent adjacent to the azo linkage;

the o-nitro group presumably hinders protonation both sterically and by a reduction in basicity so that the ammonium derivative (62) is the preferred species in acid solution.



(62)

A rather different pattern of results is observed in the spectra of dyes (52) and (53) in which the nitro group is situated in the second benzene ring of the naphthalene system. Like the 4-nitroaniline dye (48), the spectra of these compounds show absorption bands in both the visible and the ultraviolet regions; a gradual fall in intensity is observed as the acidity is increased. This situation is illustrated for dye (53) in Table 2.3. It is significant that the azo group is no longer sterically hindered in dyes (52) and (53).

(c) Naphthalene dyes

From the limited spectral data available, it is difficult to effectively compare the conjugative power of the 1- and 2-positions in the naphthalene chromogen as represented by (63) and (64), respectively.

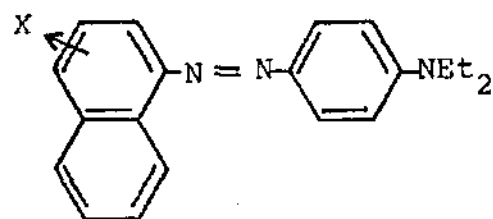
Table 2.2. Absorption bands of some N,N-diethylaniline dyes in ethanolic hydrogen chloride.

Dye	Equiv. of HCl	$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$	$\Delta\lambda$	$10^{-4}\Delta\epsilon$
48	1,000	510	3.75	22	0.22
49	10,000	335	2.87	-139	-1.30
50	10,000	380	1.36	-142	-1.80
51	10,000	370	1.80	- 80	-0.65
52	10,000	540	2.13	60	-1.42
53	1,000	530	2.00	64	-1.13
54	1,000	570	1.06	137	-0.98
55	1,000	370	1.63	-105	-1.78
56	1,000	560	2.59	90	-0.90
58	500	562	1.95	110	-1.63
59	1,000	550	2.74	74	-1.16

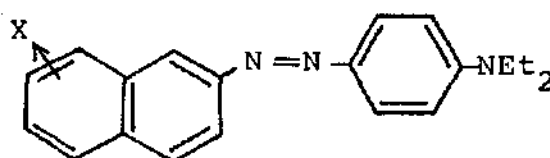
Table 2.3. Changes in λ_{max} and ϵ_{max} for dye (53) in
ethanolic hydrogen chloride.

Solvent	$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$	$\Delta\lambda$
Ethanol	466	3.13	-
Ethanol + 10 equiv. of HCl	470	2.83	4
Ethanol + 50 equiv. of HCl	476	2.45	10
Ethanol + 100 equiv. of HCl	486	2.18	20
Ethanol + 200 equiv. of HCl	526*	2.12	60
Ethanol + 300 equiv. of HCl	528*	2.09	62
Ethanol + 400 equiv. of HCl	528*	2.09	62
Ethanol + 500 equiv. of HCl	528*	2.09	62
Ethanol +1000 equiv. of HCl	530*	2.00	64

* with a shoulder



(63)



(64)

The inability to dissect the spectral properties of these dyes along the pattern shown in the above structures is perhaps due to the different influence the mesomeric substituent (NO_2) exerts on the naphthalene molecule from the various positions of attachment. This positional influence on the spectra of naphthalene dyes has been observed by Brode and Eberhart,⁷⁰ who examined a large number of naphthalene dyes with sulphonic acid groups in different positions.

The present dyes derived from naphthalene have their absorption maxima in the order (Table 2.1).

$$50 > 52 > 49 > 53 > 51$$

This order agrees closely with the mesomeric interactions between the amino and nitro groups in the corresponding intermediates⁷¹ as shown by the charge separation structures 65-69 in Chart 2.2.

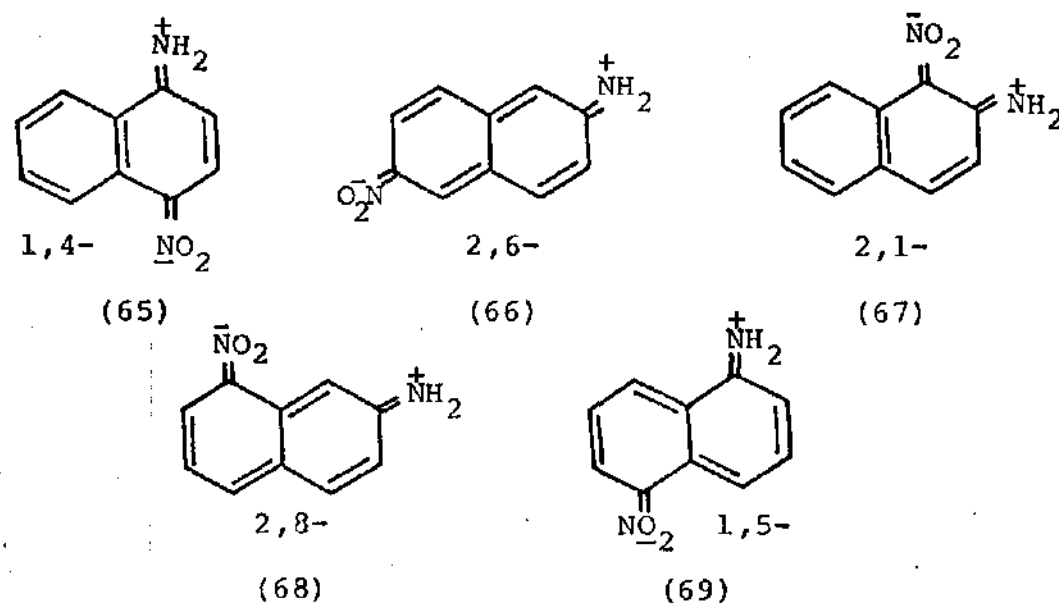


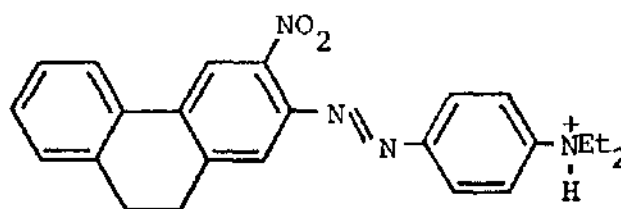
Chart 2.2. Mesomeric interactions in nitronaphthylamine intermediates.

Although useful correlations can be made between dyes and their appropriate intermediates, it does not necessarily follow that the conjugative abilities observed in the dyes will exactly parallel those found in the corresponding intermediates.

(d) 9,10-Dihydrophenanthrene and phenanthrene dyes

The parent 9,10-dihydrophenanthrene dye (54) absorbs at 433 nm while the λ_{max} values for dyes (55) and (56) with the nitro groups in the 3- and 7-positions lie at 475 and 470 nm, respectively.

In acidic media, both (54) and (56) exhibit two peaks, one in the visible region and the other in the ultra-violet. It can therefore be concluded that the azonium and the ammonium structures are in equilibrium; dye (54) shows a positive halochromism of 132 nm, while (56) has a positive halochromic shift of 90 nm. Dye (55), on the other hand, does not absorb in the visible region in a fairly strong ethanolic hydrogen chloride solution, but a band appears at 370 nm indicating the formation of the ammonium structure (70).



(70)

The characteristic changes for dyes (55) and (56) in ethanolic hydrogen chloride are shown in Table 2.4.

As shown in Table 2.4, the intensity of the band (dye 55) gradually falls as the concentration of the acid is increased, probably owing to protonation at the amino group. It may again be concluded that the presence of an *o*-nitro substituent hinders protonation at the azo group both sterically and by reducing the basicity.

Table 2.4. Spectral properties of dyes (55) and (56) in
ethanolic hydrogen chloride

Equiv. of HCl	Dye (55)		Dye (56)	
	$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$	$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$
1	475	3.44	470	3.66
5	"	-	"	3.53
10	"	3.35	472	3.19
50	"	3.18	478	2.59
100	"	2.71	no definite peak	
200	"	2.20	-	-
1000	370	1.63	370	3.02
			560	2.59
10,000	-	-	370	3.36
			560	2.16
20,000	-	-	370	3.62
			560	2.07

Three dyes incorporating the fully conjugated phenanthrene ring have been prepared, namely dyes (57), (58) and (59); their λ_{max} values in ethanol are 466, 452 and 476 nm, respectively (Table 2.1). Curiously, dye (57) shows a hypsochromic shift of 4 nm in comparison with the 9,10-dihydrophenanthrene analogue (56); a similar result predicted by the computer calculations is discussed later on in the present work. However, both dyes (56) and (57) show positive halochromism in acid.

The relative electron-withdrawing abilities of the bromo and the cyano groups have been demonstrated by the spectral data given in Table 2.1. In ethanolic hydrogen chloride, dyes (58) and (59) show a rapid decrease in intensity and a gradual build-up of peaks in the visible (around 570 nm) and the ultraviolet (about 360 nm) regions of the absorption spectrum. When 1000 equivalents of acid have been added, the band in the visible begins to fall in intensity and at the same time the intensity of the ultraviolet band begins to rise. This behaviour is again consistent with an equilibrium between azonium and ammonium species.

2. N-2-Cyanoethyl-1,2,3,4-tetrahydroquinoline dyes

The spectra of some monoazo dyes (71) derived from N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline as the coupler were recorded in ethanol and in ethanolic hydrogen chloride and the results are listed in Tables 2.5 and 2.6.

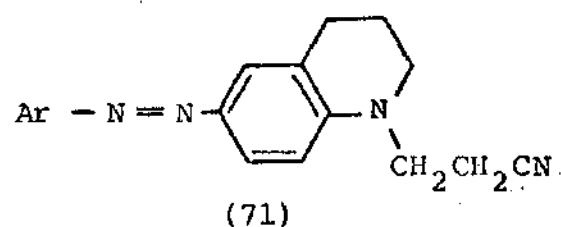
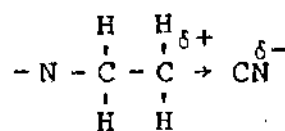


Table 2.5. Spectral data for solutions of N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline dyes (71) in ethanol

ArNH ₂		$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$
2-Nitroaniline	(72)	442	2.50
4-Nitroaniline	(73)	477	2.76
2-Amino-1-nitro-naphthalene	(74)	462	-
1-Amino-4-nitro-naphthalene	(75)	494	2.25
1-Amino-5-nitro-naphthalene	(76)	454	2.47
2-Amino-7-nitro-9,10-dihydrophenanthrene	(77)	460	2.36
3-Amino-9-cyano-phenanthrene	(78)	464	1.35

All the N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline dyes show hypsochromic shifts in comparison with the dialkylamino analogues (Table 2.1). This trend towards shorter wavelengths for the bridged system may appear contradictory at first sight but, as has been pointed out by Bridgeman and Peters,⁶⁵ the electron displacement resulting from the strong -I effect of the cyano group (79) reduces the conjugative power of the bridging nitrogen atom with the rest of the system, thereby leading to overall hypsochromic shifts.



(79)

Table 2.6. Absorption bands of some N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline dyes in ethanolic hydrogen chloride.

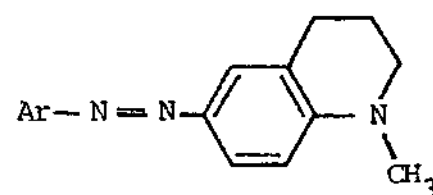
Dye	Equiv. of HCl	$\lambda_{\text{max}}/\text{nm}$	$10^{-4} \epsilon_{\text{max}}$	$\Delta\lambda$	$10^{-4} \Delta\epsilon$
(72)	30,000	520	4.67	78	2.17
(73)	22,000 ^a	540	2.84	63	0.08
(75)	10,000	514	2.53	20	0.28
(76)	20,000	495	2.22	41	-0.25
(78)	10,000	560	4.81	96	3.46

^a system optimally protonated

The diversity of the diazonium components in this series of dyes does not allow for a simple comparison, but it is noteworthy that the greatest halochromic shift (positive) is shown by the relatively weakly conjugated cyano dye (78); the 1-amino-4-nitronaphthalene derivative (75) has the smallest shift (20 nm). This finding is in agreement with the work of Hallas and Ng⁷² who have shown that strong electron withdrawal brought about by more than one electron attracting group in monoazo dyes can in fact lead to negative halochromism. As is often the case, the absorption intensities of the present dyes are devoid of any recognisable pattern.

3. Kairoline (N-methyl-1,2,3,4-tetrahydroquinoline)
dyes

For comparison purposes, several monoazo dyes (80) were prepared from kairoline and their spectral properties are listed in Table 2.7.



(80)

Table 2.7. Spectral data for solutions of some kairoline dyes in ethanol

ArNH_2		$\lambda_{\text{max}}/\text{nm}$	$10^{-4}\epsilon_{\text{max}}$
2-Nitroaniline	(81)	460	2.79
4-Nitroaniline	(82)	498	3.16
1-Amino-4-nitro-naphthalene	(83)	514	2.77
1-Amino-5-nitro-naphthalene	(84)	474	2.29
2-Amino-6-nitro-naphthalene	(85)	488	2.16
2-Amino-8-nitro-naphthalene	(86)	476	2.78
2-Amino-7-nitro-9,10-dihydrophenanthrene	(87)	478	1.38*

* low solubility in ethanol

All the azokairolines show bathochromic shifts with respect to the corresponding dialkylamino analogues (Table 2.1); the average shift observed is about 10 nm. Surprisingly, the absorption intensities of the kairolines are marginally lower than those of the corresponding dialkylamino dyes.

In ethanolic hydrogen chloride, each of the azokairolines shows a positive halochromism and exists almost exclusively in the azonium protonated form as illustrated in Figure 2.2 for dye (86). The spectral data for the protonated species of the dyes are listed in Tables 2.8, 2.9 and 2.10.

Table 2.8. Spectral changes of dyes (81) and (84) in ethanolic hydrogen chloride

Dye (81)			Dye (84)		
Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4} \epsilon_{\max}$	Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4} \epsilon_{\max}$
10	465	2.77	5	474	2.28
100	473	2.79	10	474	2.22
500	502	3.94	50	474	2.20
1000	506	4.41	100	474	2.12
3000	508	4.83	500	485	2.16
5000	510	4.97	1000	494	2.07
10,000	510	4.97	3000	508	2.22
20,000	510	5.14	5000	515	2.41
22,000	510	5.19	10,000	520	2.59
			20,000	522	2.75
			22,000	522	2.75

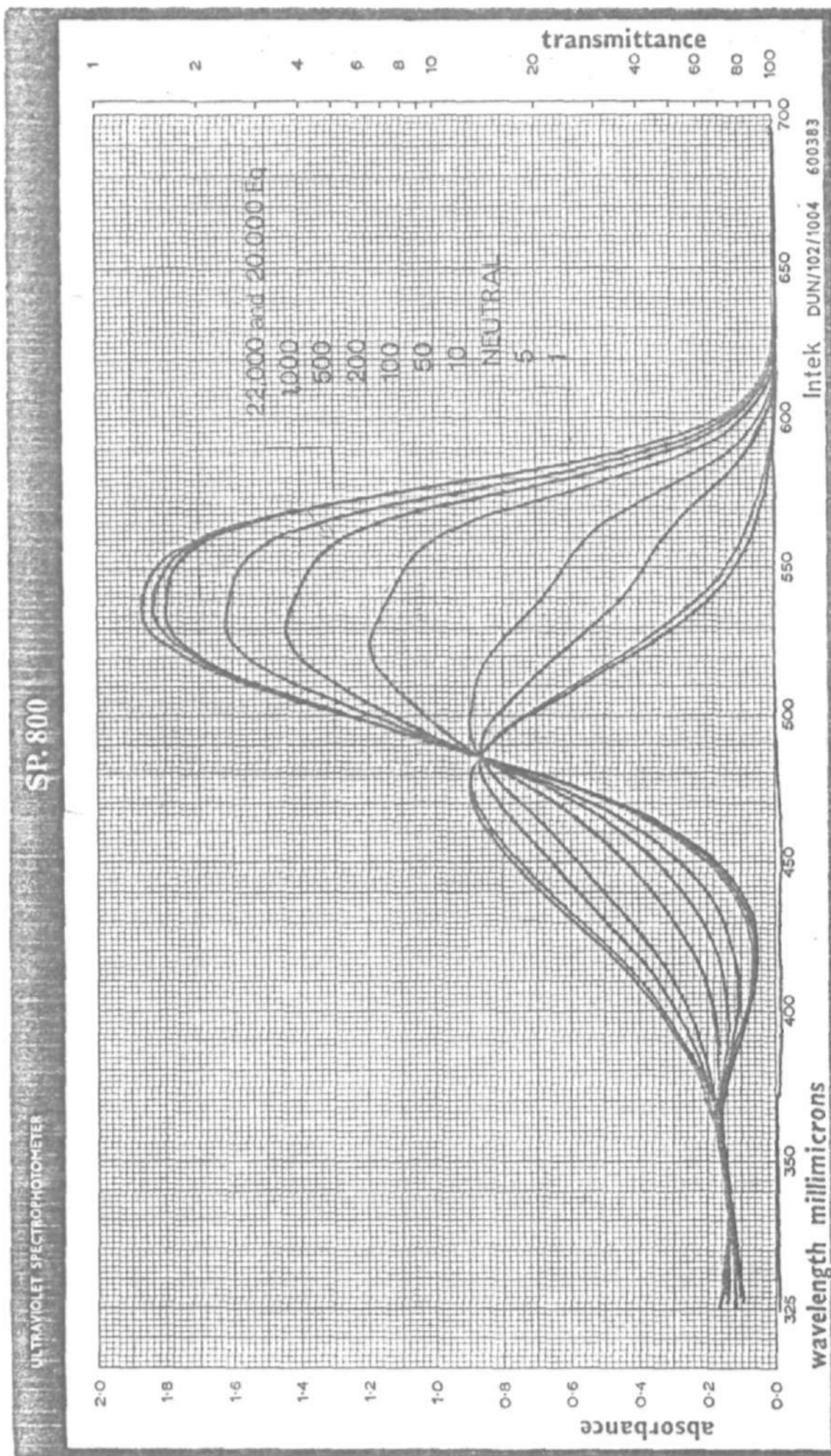


Fig. 2.2. Absorption spectra of 6-(8-nitro-2-naphthylazo)kairolone (86) in ethanol containing various concentrations of hydrogen chloride.

Table 2.9. Spectral data for dyes (85) and (86) in ethanolic hydrogen chloride

Dye (85)			Dye (86)		
Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4} \epsilon_{\max}$	Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4} \epsilon_{\max}$
1	488	1.84	1	476	2.75
50	520*	2.70	5	485	2.69
100	525*	3.50	10	499	2.78
200	533*	4.58	50	524*	3.68
500	540	5.91	100	528*	4.45
1000	540	5.98	200	532*	5.00
10,000	540	6.04	500	538	5.53
20,000	540	6.10	1000	538	5.65
22,000	540	6.10	20,000	538	5.75
			22,000	538	5.75

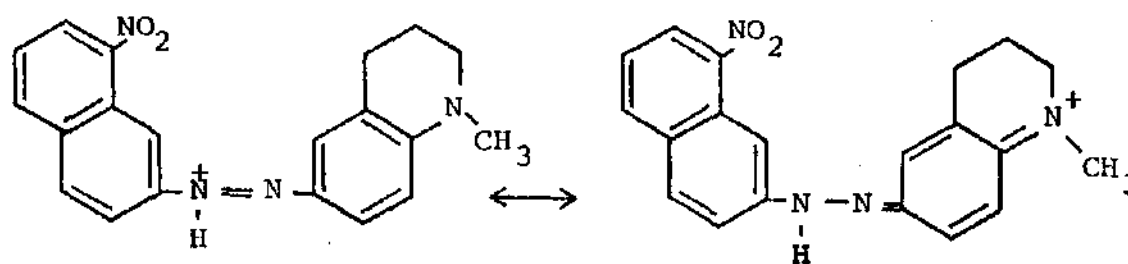
* with a shoulder

Table 2.10. Spectral changes for dye (87) in ethanolic hydrogen chloride

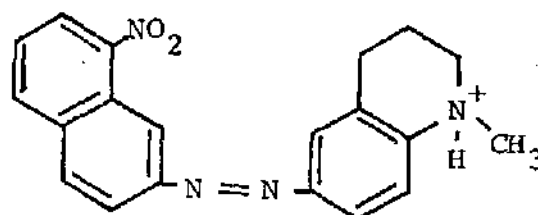
Equiv. of HCl	$\lambda_{\max}/\text{nm}^*$	$10^{-4} \epsilon_{\max}$
1	478	1.11
100	554	2.24
200	554	3.13
500	554	4.83
1000	554	4.95
5000	554(360)	5.60(0.06)
10,000	554(360)	5.82(0.08)

* system not optimally protonated

In this system, the azonium charge-resonance species (88a) is predominant with little evidence of the ammonium tautomer (88b). It is likely that the position of the equilibrium can be related to the electron-donating strength of the terminal nitrogen atom since powerful donation of the lone pair will favour the azonium cation; the bridged kairolone end group is a better electron donor than diethylamino.



(88a)



(88b)

Depending on the nature of the accepting system, however, even with the kairoline system in operation it is still possible to detect the ammonium tautomer. Thus, as acid is added to a solution of the dihydrophenanthrene dye (87) there is a gradual build up of a band around 360 nm as well as the visible azonium peak at 554 nm.

4. Julolidine (2,3,6,7-tetrahydro-1H,5H-benzo[ij]quinolizine) dyes

It has previously been pointed out^{29,30} that julolidine is a very powerful electron donor because of the strain-free overlap of the sp^2 electrons of the nitrogen atom with the rest of the chromogen. In the present work, a selected number of julolidine dyes (89) have been prepared and their spectroscopic behaviour studied in ethanol and in ethanolic hydrogen chloride; spectral data are given in Tables 2.11, 2.12 and 2.13.

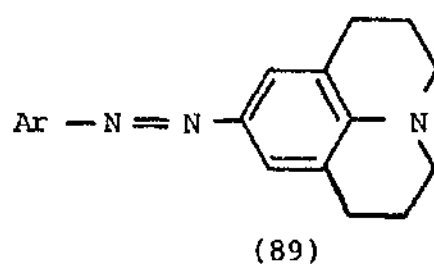


Table 2.11. Spectral properties of some julolidine dyes in ethanol

ArNH ₂		$\lambda_{\text{max}}/\text{nm}$	$10^{-4} \epsilon_{\text{max}}$
2-Nitroaniline	(90)	480	2.74
4-Nitroaniline	(91)	518	3.58
2-Amino-1-nitro-naphthalene	(92)	500	4.03
1-Amino-4-nitro-naphthalene	(93)	538	3.16
2-Amino-6-nitro-naphthalene	(94)	510	3.36
2-Amino-8-nitro-naphthalene	(95)	496	3.15

The julolidine dyes show red shifts of between 25 and 40 nm in comparison with the analogous dialkylamino derivatives; bathochromic shifts within this range have been observed by Castelino and Hallas.³⁰ The absorption intensities in the two series are comparable.

Table 2.12. Spectral data for dyes (90) and (91) in ethanolic hydrogen chloride

Dye (91)			Dye (90)		
Equiv. of HCl	$\lambda_{\text{max}}/\text{nm}$	$10^{-4} \epsilon_{\text{max}}$	Equiv. of HCl	$\lambda_{\text{max}}/\text{nm}$	$10^{-4} \epsilon_{\text{max}}$
1	518	3.77	1	483	2.84
2	518	4.16	5	492	3.09
3	518	4.89	10	498	3.44
4	518	5.18	50	505	4.04
5	518	5.37	100	509	4.42
10	518	5.90	200	510	4.67
25	518	6.19	1000	510	4.95
50	518	6.48	5000	510	5.00
100	518	6.68	10,000	510	5.04
200	518	6.87			
500	518	6.97			
1000	518	7.01			
10,000	518	7.01			

In ethanolic hydrogen chloride, the behaviour of the julolidine dyes depends on the position of the nitro group. Thus, while dyes (90) and (91) both show increases in intensity, the former exhibits a positive halochromic shift unlike the latter whose wavelength remains constant at 518 nm (Table 2.12). This difference in behaviour can be associated with the relative electron accepting capacities of the *o*- and *p*-nitro groups. It has already been pointed

out that the overall halochromism depends on (a) the electron donating power of the terminal nitrogen atom and (b) the electron accepting capability at the other side of the azo linkage. These factors operate in such a way that the greater the disparity between the two parts of the dye the more likely it is that the halochromism will be negative. Thus, dye (90) has a positive halochromism of 30 nm whereas the halochromism in dye (91) is zero (Table 2.12).

Table 2.13. Spectral properties of dyes (92), (94) and (95) in ethanolic hydrogen chloride.

Equiv. of HCl	Dye (92)		Dye (94)		Dye (95)	
	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$
1	500	4.03	512	3.42	500	3.15
3	500	4.03	535	5.74	524	3.90
5	500	4.03	538	5.86	530	4.78
10	502	4.09	540	6.10	535	5.36
50	503	4.12	542	6.40	-	-
100	504	4.12	542	6.67	540	6.30
500	510	4.39	545	6.82	-	-
1000	514	4.58	545	6.82	540	6.42
10,000	520	5.04			540	6.42
25,000	520	5.03				

These differences permit a distinction to be made between the various substituted naphthalene derivatives in terms of their conjugative abilities. Thus, dye (93) shows

a negative halochromism of 8 nm (Table 2.14) whereas the positive halochromism of the remaining naphthalene dyes increases in the order (92), (94) and (95) (Table 2.13). This sequence can therefore be taken to represent the decreasing ability of the nitro group to conjugate at the various positions in the naphthalene ring.

Differences in halochromism are observed when the electron-donating power of the terminal nitrogen atom is altered. For example, the kairoline dye (83) shows a positive halochromism (Table 2.14) whereas that of the julolidine analogue (93) is negative. Illustrative spectra of dyes (83), (91) and (93) are shown in Figures 2.3, 2.4 and 2.5 respectively.

Table 2.14. Spectral changes for dyes (83) and (93) in ethanolic hydrogen chloride

Dye (83)			Dye (93)		
Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$	Equiv. of HCl	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$
1	514	2.77	10	538	3.39
10	514	2.84	50	538	3.52
100	520	3.04	100	536	3.58
500	523	3.28	200	535	4.00
1000	525	3.45	500	532	4.61
2000	526	3.61	1000	530	4.85
3000	528	3.78	10,000	530	5.21
5000	530	4.12	20,000	530	5.46
10,000	530	4.16	22,000	530	5.45
20,000	530	4.16			

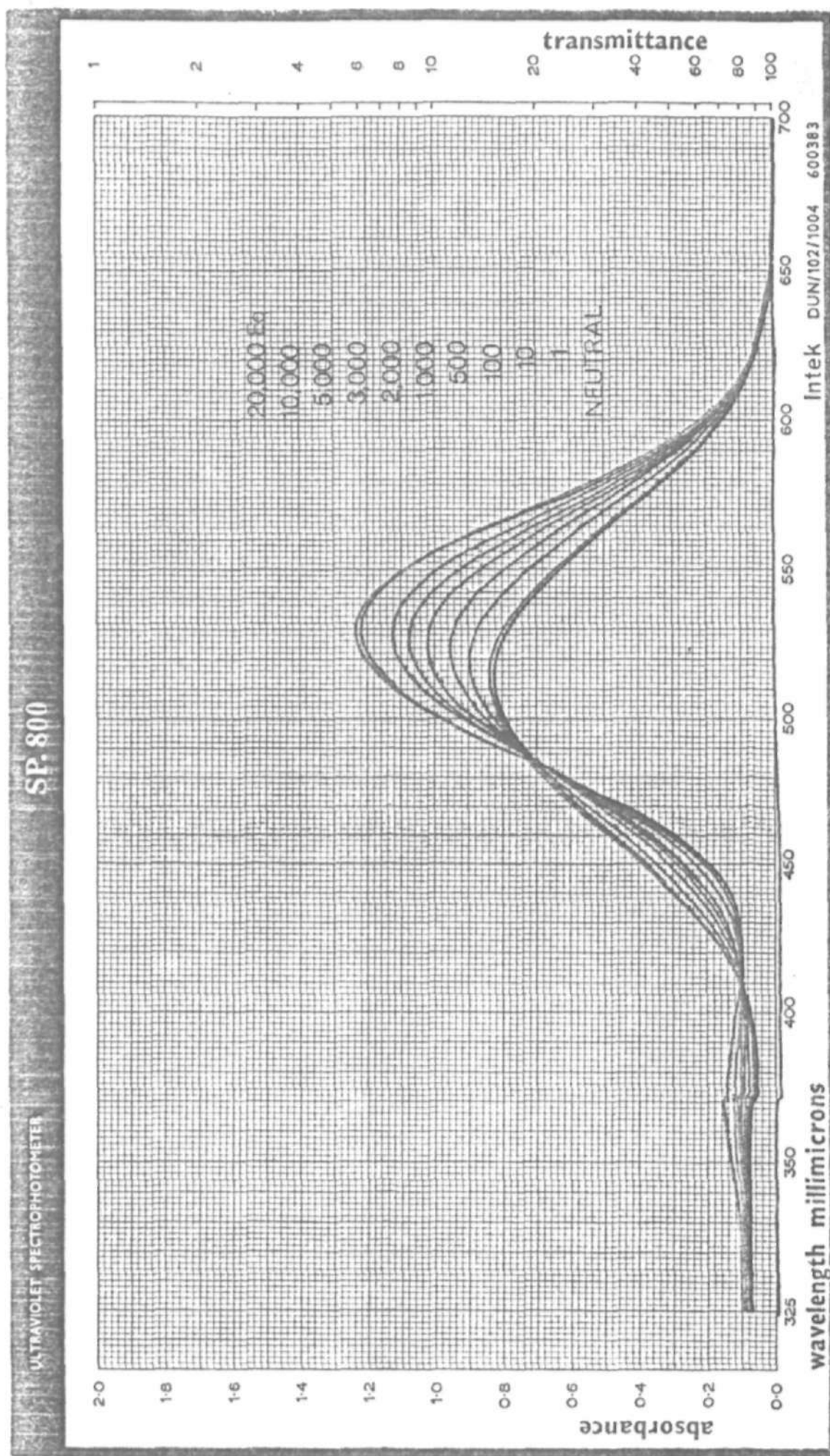


Fig. 2.3. Absorption spectra of 6-(4-nitro-1-naphthylazo)kairolin (83) in ethanol containing various concentrations of hydrogen chloride.

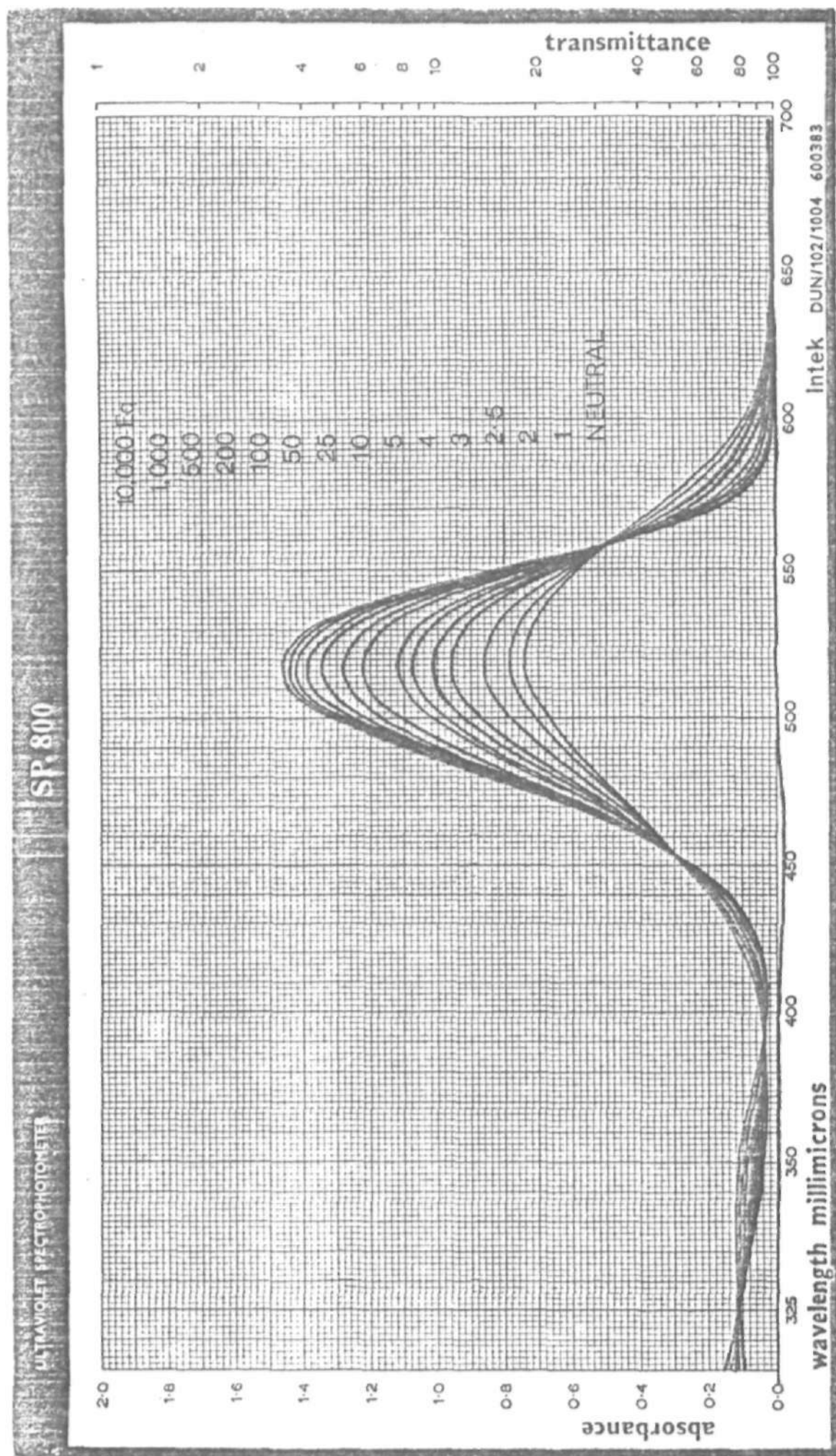


Fig. 2.4. Absorption spectra of 9-(4-nitrophenylazo)julolidine (91) in ethanol containing various concentrations of hydrogen chloride.

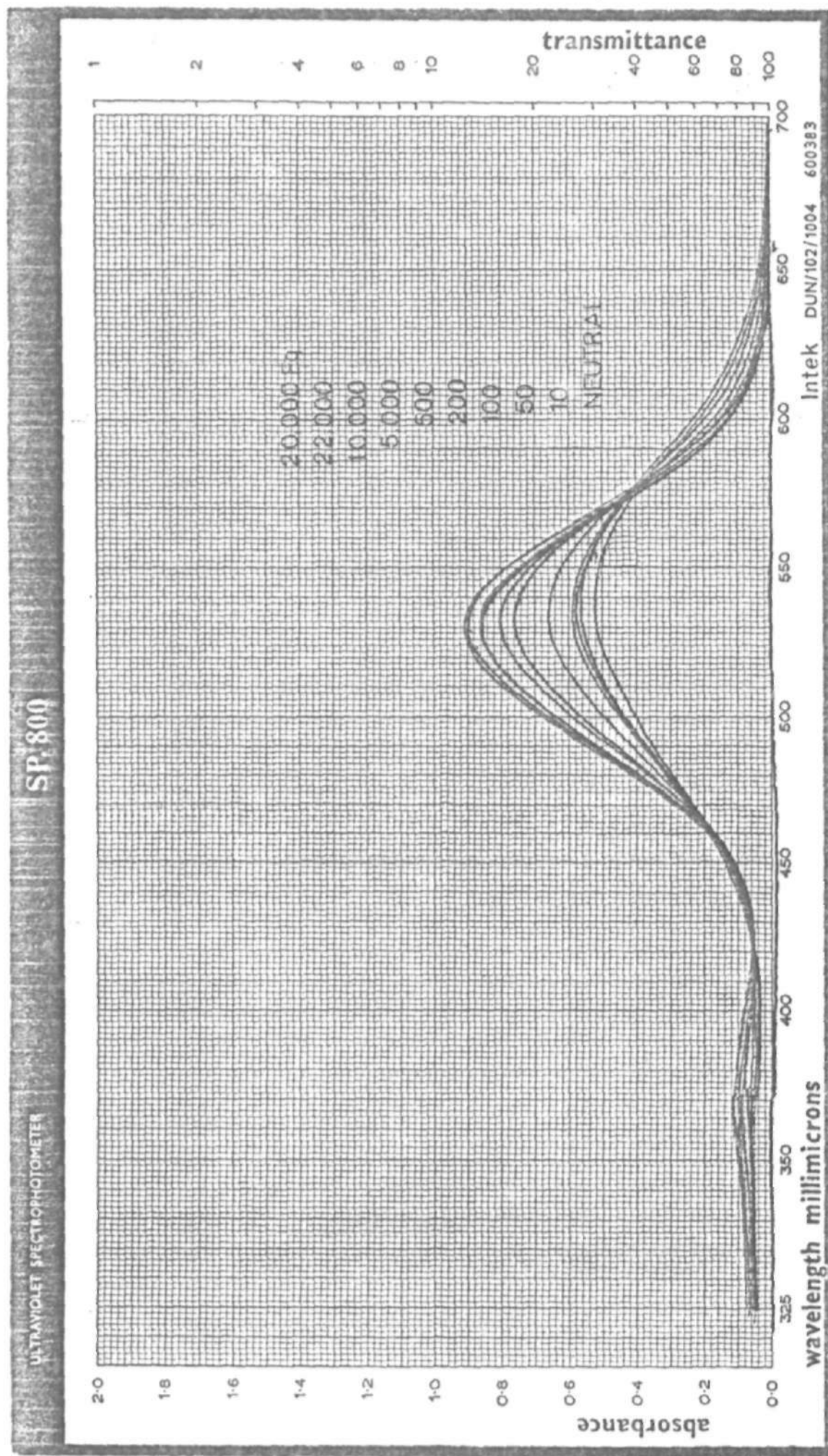


Fig. 2.5. Absorption spectra of 9-(4-nitro-1-naphthylazo)julolidine (93) in ethanol containing various concentrations of hydrogen chloride.

5. Comparison between the different couplers

A comparison between the four couplers is shown in Table 2.15 by reference to the absorption maxima of the derived dyes.

Table 2.15. Absorption maxima of dyes obtained from the same diazonium component and different couplers*

Diazonium component	λ_{max} (DEA)	λ_{max} (CEQ)	λ_{max} (K)	λ_{max} (J)
2-Nitroaniline	450	442	460	480
4-Nitroaniline	488	477	498	518
1-Amino-4-nitro-naphthalene	502	494	514	538
1-Amino-5-nitro-naphthalene	460	454	474	-
2-Amino-6-nitro-naphthalene	480	-	488	510
2-Amino-8-nitro-naphthalene	466	-	476	496
2-Amino-7-nitro-9,10-dihydrophenanthrene	470	460	478	-

- * N,N-Diethylaniline (DEA)
N-2-Cyanoethyl-1,2,3,4-tetrahydroquinoline (CEQ)
 Kairolin (K)
 Julolidine (J)

From the data given in Table 2.15 it follows that the relative strength of the coupler decreases in the order



The relative strengths of the CEQ and DEA groups have already been discussed. It is clear that the singly bridged kairoline system is less effective than the doubly bridged julolidine chromogen and it is believed that conjugation of the nitrogen atom is optimal in the julolidine system.²⁹

6. Solvatochromism

It is generally observed that the absorption spectrum of a substance when measured in the vapour phase exhibits fine structure which is usually absent in solution.⁷³ Ideally, spectra should be determined in the vapour phase, but this is frequently prevented by the low volatility of most organic compounds.

When the absorption spectrum of a given compound is measured in different solvents, various changes are observed. Some of these variations are associated with physical solvent effects, while others are due to chemical interactions. Overall, these changes give rise to the phenomenon known as solvatochromism (the change in position and intensity of an absorption band accompanying a change in solvent). The physical solvent effects may depend on

- (a) the nature of the solvent
- (b) the type of absorption transitions (e.g. $\pi \rightarrow \pi^*$ or $n \rightarrow \pi^*$)

(c) the nature of the solute.

In the present investigation, factors (b) and (c) are essentially constant as the two dyes examined, (83) and (93), have similar structures and the absorption bands in both cases are associated with a $\pi \rightarrow \pi^*$ electronic transition. As can be seen from Tables 2.16 and 2.17, the results are complex and it is not possible to correlate λ_{max} with just one physical parameter, namely, the dielectric constant of the solvent.

It has been suggested⁷⁴ that solvent shifts can best be handled by considering solvent-solute interactions in the ground state and in the excited state separately. Thus, dyes (83) and (93) are both less polar in the ground state than in the excited state due to charge migration (in the latter state) from the electron donor to the nitro group and should therefore behave bathochromically in polar solvents in accordance with theoretical considerations.⁷⁵ This general trend has in fact been observed in moving from the non-polar solvent cyclohexane to the more polar solvent methylene chloride. In polar protic solvents such as ethanol and acetic acid it is clear that hydrogen bonding will affect the absorption spectra in a complex manner.

Table 2.16. Changes in the spectroscopic properties of dye (83) in various solvents.

Solvent	Dielectric constant	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$
Cyclohexane	2.02	479	3.99
Toluene	2.38	503	2.95
Benzene	2.28	505	2.97
Acetic acid	6.15	510	2.16
Ethanol	24.3	514	2.77
Acetone	20.7	518	2.62
Methylene chloride	9.08	522	2.20

Table 2.17. Changes in the spectroscopic properties of dye (93) in various solvents

Solvent	Dielectric constant	$\lambda_{\max}/\text{nm}$	$10^{-4}\epsilon_{\max}$
Cyclohexane	2.02	504	-
Toluene	2.38	526	4.19
Benzene	2.28	528	3.03
Acetic acid	6.15	532	4.36
Ethanol	24.3	536	3.15
Acetone	20.7	540	3.20
Methylene chloride	9.08	549	3.05

Part B Dyeing and fastness properties

The dyeing and fastness properties of the current dyes were examined on polyester and the results obtained are briefly discussed in this section.

1. Dyeing procedure

The dye (20 mg) was dissolved in the minimum amount of acetone (ca. 5 ml) and added to an aqueous suspension of a dispersing agent [Dispersol (10 ml) in water (500 ml)]. The resulting mixture was heated to about 80°C and a weighed piece of Terylene (2 g), previously wetted, was added to the hot mixture. The temperature of the dye-bath was gradually raised to the boil during 30 min and kept at this temperature for 2 h. In most cases a carrier [Dicane 70 (0.5 ml)] was also introduced to the hot suspension.

The dyed fabric was then washed with warm water and heated for 3-4 min. with a 2% solution of sodium hydroxide (50 ml) to which a pinch of sodium dithionite had been added. Finally, the fabric was washed with warm water and dried at 40 - 50°C.

In a few cases the dye-bath was prepared as described but the dyeing was carried out under steam conditions; the resulting dyeings were marginally deeper in colour.

2. Light fastness properties

The light fastness ratings of the dyeings were determined in a Microscale Fadometer and the results were

assessed visually against the B.S.I. blue standards which were exposed simultaneously. Results of the light fastness tests and the corresponding hue of the dyes on polyester are listed in Tables 2.18, 2.19, 2.20 and 2.21.

Table 2.18. Light fastness properties of the N,N-diethyl-aniline dyes

<u>Dye</u>	<u>Colour on polyester</u>	<u>light fastness</u>
(46)	yellow	3-4
(48)	brick red	4-5
(49)	tangerine	1-2
(50)	pink	3-4
(53)	salmon pink	2-3
(55)	pink	3
(56)	straw-yellow	3
(58)	buttercup	3
(59)	marigold	3-4

Table 2.19. Light fastness properties of some N-2-cyano-ethyl-1,2,3,4-tetrahydroquinoline dyes.

<u>Dye</u>	<u>Colour on polyester</u>	<u>light fastness</u>
(73)	pink	3-4
(75)	pink	1-2

Table 2.20. Light fastness properties of some kairoline dyes

<u>Dye</u>	<u>Colour on polyester</u>	<u>Light fastness</u>
(84)	orange-red	2
(85)	pink	2
(86)	orange-red	2

Table 2.21. Light fastness properties of some julolidine dyes

<u>Dye</u>	<u>Colour on polyester</u>	<u>Light fastness</u>
(90)	orange	2
(92)	red	1-2
(93)	violet	1-2
(94)	pink	1-2
(95)	pink	1-2

The poor light fastness of dyes derived from julolidine has previously been noted.⁷⁶ No attempt was made to apply these dyes on other fabrics because it is generally agreed that disperse azo dyes give better light fastness on polyester than other fabrics.⁷⁷

It is well-known that the photochemical processes whereby a dyed fabric fades with the action of light are complex and cannot be explained in simple terms. Various factors are thought to be responsible for the rate at which a dyed fabric fades and these include:

- (i) the method of application,
- (ii) the chemical structure of the dye,
- (iii) the nature of the substrate,
- (iv) the presence of oxygen,
- (v) the effect of temperature and humidity,
- (vi) the effect of dye concentration on the fibre,
- (vii) the nature of dye-fibre interactions and
- (viii) the nature of any after treatments used on the coloured fabric.

The various effects have been treated in a semi-quantitative manner in certain cases.⁷⁸ In the present work, however, detailed investigation into the above factors was not carried out. It is clear, however, that the introduction of a polycyclic ring system leads to a decrease in light fastness as does the presence of a powerful electron releasing terminal nitrogen atom.

Part CConclusions

1. Replacement of a benzene ring by the naphthalene system in appropriate azo dyes generally brings about a bathochromic shift of the first absorption band irrespective of the position of substituents in the naphthalene ring. In particular, a comparison between two closely related dyes, (48) and (50), shows a red shift of 14 nm owing to the additional benzene ring present in the naphthalene system.
2. The poor colour-yielding ability of the phenanthrene chromogen has been confirmed as indicated by the $\lambda_{\max}$ values of dyes (57), (58) and (59).
3. The 9,10-dihydrophenanthrene dye (56) shows a bathochromic shift of 4 nm with respect to the fully conjugated phenanthrene analogue (57); this result is supported by PPP calculations which predict $\lambda_{\max}$ values of 447 and 435 nm, respectively.
4. As has been pointed out by Hallas, Waring and Paskins in studies on triarylmethane dyes, extension of conjugation in the naphthalene system is more effective through the 1,4-positions than through the 2,6-positions. The various dyes derived from the different couplers (Table 2.15) confirm this finding. Thus $\lambda_{\max}(\text{DEA})$, $\lambda_{\max}(\text{K})$ and $\lambda_{\max}(\text{J})$ differ by 22, 26 and 28 nm, respectively, in favour of the 1,4-linked dyes.

5. All the dyes derived from N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline show hypsochromic shifts with respect to their dialkylamino analogues. The blue shift is associated with the strong electron-withdrawing ability of the cyano group which weakens the overall conjugative power of the bridging system.
6. The strongly conjugated julolidine dyes show red shifts of between 25 and 40 nm when compared with the corresponding dialkylamino compounds.
7. The absorption intensities of dyes derived from the different couplers are of the same order ($\epsilon_{\text{max}} 2 - 4 \times 10^4$), with the julolidine dyes marginally higher than the others.
8. In ethanolic hydrogen chloride, all the dyes with a nitro group ortho to the azo-linkage protonate almost exclusively at the amino-group while the remaining isomers form both the azonium and the ammonium tautomers. The absence of the azonium form in the former cases is associated with a steric effect as well as with a reduction in basicity of the azo group arising from the presence of a strong electron withdrawing substituent in the vicinity of the azo-linkage.
9. In an acidic medium, dye (90) exhibits a positive halochromism of 30 nm whereas dye (93) shows a small negative halochromic shift of 8 nm; dye (91) is not halochromic. The electron-withdrawing abilities of the component groups in the above julolidine dyes decrease in the order 1-amino-4-nitronaphthalene > 4-nitroaniline > 2-nitroaniline.

It follows therefore, that the tendency towards negative halochromism is greatest the greater the difference between the donor and the acceptor groups. This general hypothesis is substantiated by the smaller positive halochromism (16 nm) shown by dye (83) in which the julolidyl group has been replaced by the kairoline system.

10. The close agreement between calculated and experimental λ_{max} values for the 9,10-dihydrophenanthrene dyes suggests that conjugation through the polycyclic system is not diminished by the small amount of twist induced into the biphenyl system by the bridging group.
11. All the monoazo dyes examined are more polar in the first excited state (increase in bond orders) than in the ground state. This increase in polarity is demonstrated by the bathochromic shifts observed in polar solvents.
12. The presence of a polycyclic system and a strong electron donor in an azo dye molecule leads to a poor light fastness rating.
13. The synthetic difficulties accompanying the preparation of appropriate polycyclic intermediates make their usage in commercial practice most unlikely.

PREDICTIVE METHODS IN ORGANIC CHEMISTRY

Predictive Methods in Organic Chemistry

1. Introduction

The prediction of Murrell and Harget⁷⁹ that the time will come when the computer will replace the laboratory bench as a cheaper and more reliable source of information regarding some organic problems may sound wishful thinking to the experimental chemist. Recent developments in physical organic chemistry have, in fact, demonstrated beyond any doubt that in cases where experimental data are hard to come by, or in related problems in which only limited practical data are available, theoretical alternatives are no mean substitutes. However, the sheer number of physical methods available coupled with their mathematical complexity has unhappily slammed the door against many would-be users. The newcomer to this branch of chemistry is first confronted by the problem of choice. This first hurdle is further heightened by the mere fact that many physical methods bear close resemblance to one another, thus making an isolated approach almost meaningless. It is against this background that this section of the present work is written.

While it is not intended to cover comprehensively all the available methods found in the literature, a brief treatment of an appropriate selection will greatly aid the comprehension of the subsequent discussion. Broadly speaking, one could group the various physical methods into simple and advanced methods. There is, however, no clear line of demarca-

tion in this rather crude classification. The so-called advanced methods in the Molecular Orbital context are those in which electronic interaction is considered explicitly as will be explained later. The failure of chemists and physicists to find 'exact' solutions to the general Schrödinger equation

$$H\psi_n = E_n \psi_n \quad 3.1$$

for many-particle molecules led to approximate methods, some of which are briefly discussed here under the following headings:

- (a) The Valence Bond (VB) method;
- (b) The Free Electron Molecular Orbital (FEMO) method;
- (c) The Hückel Molecular Orbital (HMO) method;
- (d) The Antisymmetrized Molecular Orbital (ASMO) method and ASMO CI (Configuration Interaction);
- (e) The Self-Consistent-Field (SCF) method;
- (f) The Pariser-Parr-Pople (PPP) method*.

* The molecular properties of all the dyes mentioned in this section of the thesis have been examined by the Pariser-Parr-Pople Self-Consistent-Field Molecular Orbital method with limited Configuration Interaction (PPP-SCF CI).

(a) The Valence Bond Method

The valence bond approach originated from the work of Heitler and London⁸⁰ and was developed extensively by Pauling. The theory is based entirely on empirical considerations, using the concept of electron pairs, and was first applied to the hydrogen molecule in 1922 by Heitler and London. Although the original formalism is unexplorable mathematically when dealing with complex molecules, owing to the large number of ionic structures that has to be considered, simplifying assumptions have brought some success in the qualitative application of the method to large molecules such as the symmetrical cyanine dyes.⁸¹

(b) The Free Electron Molecular Orbital Method

Like many other early Molecular Orbital methods, the Free Electron Molecular Orbital (FEMO) approach was framed on the σ - π separation principle. Thus, the method is limited in its scope being restricted to unsaturated molecules. This technique was first applied to open chain conjugated systems which were considered stripped of their π -electrons, thus giving rise to a set of points of unit positive charge arranged as a zig-zag line within a plane as shown in Figure 3.1.

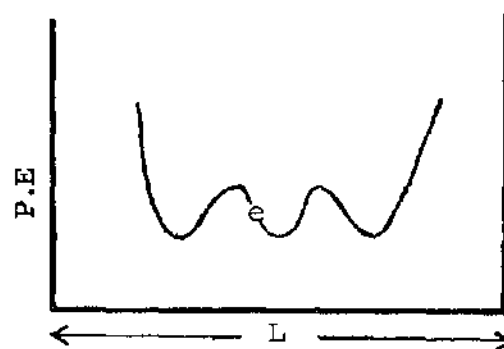


Fig. 3.1. The potential well situation for an electron confined in a π system.

Now, if one π -electron is fed into the molecular framework, the problem is identical with that of an electron in a one-dimensional box, for which the potential energy is assumed to be zero everywhere within the box. From quantum mechanical calculations, the energy of the various molecular orbitals is given by

$$E_n = \frac{n^2 h^2}{8mL^2} \quad 3.2$$

where

n is an integer (1, 2, ...),

h is Planck's constant (6.625×10^{-34} Js),

m is the electron mass,

and L is the length of the potential box.

Apart from the length of the box, the FEMO has no empirical parameters. This approach can also be extended to cyclic

conjugated systems in which the movement of the electrons is restricted to the periphery of a circle of diameter roughly equal to that of the molecule. The successful handling of the spectra of some polyenes, benzenoid systems and a few simple dyes⁸² notwithstanding, the FEMO method suffers from gross oversimplifications, vis a vis the $\sigma - \pi$ separation principle and the neglect of electronic interactions. The method is therefore unsuitable, particularly as a predictive tool for polyelectronic systems.

(c) The Hückel Molecular Orbital Method

In the early 1930s Hückel⁸³ introduced a number of approximations into the simple molecular orbital theory and applied them with qualified success to a number of organic compounds. When these approximations are included in the linear combination of atomic orbitals (LCAO) approach, the result is the well-known Hückel Molecular Orbital (HMO) method. Before going on to describe the various aspects of the HMO method, it is necessary to examine more closely the Schrödinger equation mentioned earlier; Schrödinger brought innovation to classical mechanics in an effort to demonstrate the wave character of interacting particles.

In classical mechanics, the energy (E) of a system of interacting particles is related to the kinetic (T) and potential (V) energies as in equation

$$T + V = E \quad 3.3$$

By introducing the idea of a linear operator, Schrödinger set up a wave equation

$$(T + V)\psi = E\psi \quad 3.4$$

For a simple one-electron system, the potential energy component is given by

$$V = -\frac{ze^2}{r} \quad 3.5$$

where r is the distance of the electron from the nucleus,

e is the electronic unit charge

and z is the charge on the nucleus.

The kinetic energy contribution is given by

$$T = -\frac{h^2}{8\pi^2 m} \nabla^2 \quad 3.6$$

where h and m have the usual meanings and the square of the Laplacian operator (∇) is given by

$$\nabla^2 = \frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial y^2} + \frac{\partial^2}{\partial z^2} \quad 3.7$$

By substituting for T and V in equation we obtain

$$\left(-\frac{h^2}{8\pi^2 m} \nabla^2 - \frac{ze^2}{r}\right)\psi = E\psi \quad 3.8$$

or simply

$$H\psi = E\psi \quad 3.9$$

In the above equation, H is the Hamiltonian operator for the system, ψ is the eigenfunction and E is the eigenvalue. For polyatomic systems, the Schrödinger equation is highly

complex and the total Hamiltonian embraces both nuclei and electrons. In practice, however, one is usually concerned only with the electronic Hamiltonian operator where the movement of the much heavier nuclei is regarded as constant. The full Schrödinger equation for any molecular system has an infinite number of solutions, only certain of which are acceptable. In other words, for each wavefunction ψ_n there will be a corresponding discrete energy E_n . It sometimes happens that two or more wavefunctions have identical energies and such solutions are said to be degenerate. The physical significance of the eigenfunction can be deduced from the well-known normalization condition

$$\int_{-\infty}^{+\infty} \psi^2 dv = 1 \quad 3.10$$

which equates the probability of finding an electron in the volume element dv to unity.

Absorption of light by dyestuffs in the visible region of the electromagnetic spectrum is usually associated (although not exclusively) with an electronic transition between the ground state and the first singlet excited state. This condition is given by the Planck-Einstein equation

$$E_{\text{excited}} - E_{\text{ground}} = h\nu \quad 3.11$$

It would appear, therefore, that knowing the exact eigenvalues for a molecule one could calculate all the electronic transitions that are taking place during excitation. Unfortunately,

the 'exact' solution of the Schrödinger equation is possible only for very simple systems such as H_2 , LiH and H_3 .

In the Hückel theory, the molecular orbitals ψ are written as a linear combination of atomic orbitals ϕ , so that

$$\psi_i = \sum c_{n,i} \phi_n \quad 3.12$$

In the above equation, c_n , the mixing coefficients (eigenvectors), have the significance that c_n^2 represents the fraction of the charge density of an electron in the molecular orbital ψ_i located upon the atom n . The one-electron π -orbitals of equation 3.12 are in effect solutions of the Schrödinger equation

$$H\psi = E\psi \quad 3.9$$

where H is the one-electron Hamiltonian. By mathematical manipulations, Huckel⁸⁴ derived the integrals

$$\alpha_n = \int \phi_n H \phi_n d\tau \quad 3.13$$

$$\beta_{mn} = \int \phi_m H \phi_n d\tau \quad 3.14$$

$$S_{nn} = \int \phi_n^2 d\tau \quad 3.15$$

$$S_{mn} = \int \phi_m \phi_n d\tau \quad 3.16$$

α_n is the Coulomb integral which is the measure of the

effective electronegativity of atom n , β_{mn} is the so-called resonance or bond integral and represents the π -bonding energy between atoms m and n . S_{nn} and S_{mn} are the overlap integrals, assumed to be unity and zero, respectively, in the Hückel approximations. Relative to the energy of an electron at infinity, both α and β are negative energy quantities.

(i) Shortcomings of the HMO Method

In the HMO procedure, the two parameters α and β are determined empirically, a fact which has led to endless controversy amongst chemists. Another serious assumption of the HMO method is the neglect of electron repulsion. As a result, it is usually found that the method is unreliable when applied to heteroatomic molecules owing to the non-uniformity in the π -electron charge distribution. In an attempt to compensate for this variation in the Coulomb integrals, the ω -technique was introduced by Wheland and Mann.⁸⁵

(ii) The ω -Technique

Wheland and Mann proposed a linear relationship between the value of α and the total π -electron density Q_n . Thus

$$\alpha_n = \alpha + (1 - Q_n) \omega \beta \quad 3.17$$

where α_n is the modified Coulomb integral for atom n , α is the standard Coulomb integral and ω is a dimensionless para-

meter estimated to suit experimental data.⁸⁶ In this procedure, a preliminary HMO calculation is carried out using constant α values to determine the coefficients in equation 3.12 and the electron densities. An improved α_n is then obtained by means of equation 3.17. This process is repeated several times until the system is self-consistent, that is, until a new set of coefficients and electron densities does not differ greatly from the precursor.

(d) The Antisymmetrized Molecular Orbital (ASMO) Method and ASMO CI

The first of the so-called advanced methods to be developed was the ASMO.⁸⁷ As the name suggests, the product wavefunctions for electron configurations are made antisymmetric with respect to each interchange of electron labels in fulfillment of the Pauli principle, as shown below for the ground state.

$$\psi = |\psi_1 \bar{\psi}_1 \dots \psi_j \bar{\psi}_j \dots \psi_m \bar{\psi}_m| \quad 3.18$$

In 1950, Craig⁸⁸ incorporated configuration interaction (see later) into the above method thus giving rise to the ASMO CI method.

(e) The Self-Consistent-Field (SCF) Method

Another of the nonempirical methods is the SCF method which was developed largely by Roothaan.⁸⁹ The main characteristic of the method is the iterative approach similar

to that described for the ω -technique of the HMO method. Many of the principles involved in this method have been incorporated into the Pariser-Parr-Pople (PPP) method due to be discussed.

(f) The Pariser-Parr-Pople (PPP) Method

Pariser and Parr⁹⁰ introduced empirical parameters into the purely non-empirical ASMO CI method and this variation is usually known as the Pariser-Parr method. Similarly, Pople⁹¹ introduced simplifying approximations into the SCF method. The combination of these approximations with the above-mentioned Pariser-Parr method is what is commonly referred to as the PPP-method. This procedure despite its strong emphasis on coplanarity is considered to be the most convenient method for the routine calculation of the electronic spectra of very large molecules.⁹² The choice of this method in the present work was greatly influenced by the extensive researches carried out on azo dyes by Griffiths and his students.^{93,94}

2. Application of the PPP Method

(a) Choice of Parameters in the PPP Method

The one stumbling block in the PPP method (and with advanced methods in general) is the need for careful parameterization which must take into account the effects of chemical environments. Two classes of parameters are used in the PPP method:

- (i) structural parameters (bond lengths and bond angles) and
- (ii) energy parameters, such as the valence state ionization potential (VSIP) and the electron affinity (A) for each atom within the π -system, and bond resonance (β) values for each pair of adjacent atoms.

Also required are π -electron densities and π -bond orders which are obtained via a preliminary Hückel calculation as explained later.

The values used for the physical parameters are those found in the literature and do not require further treatment. The energy integrals, however, deserve a closer examination since they differ significantly from the related HMO integrals. In general, the Coulomb and the resonance integrals are expressed⁹² in the form

$$\alpha_n = \alpha_n^{\text{core}} + (\text{RE})_n \quad 3.19$$

and

$$\beta_{mn} = \beta_{mn}^{\text{core}} + (\text{RE})_{mn} \quad 3.20$$

where α_n^{core} and β_{mn}^{core} refer to the attraction energy of the electron localised on atom n or between atoms m and n , respectively (the attractive force results from the positively charged core and the π -electrons). The $(\text{RE})_n$ and $(\text{RE})_{mn}$ energy terms associated with electronic interaction effects are rather complex and include physical quantities yet to be explained. One such quantity is the electron density which can be derived from the relation

$$\int \psi^2 dv = \int \sum (C_n \phi_n)^2 dv \quad 3.21$$

$$= \int \sum_n C_n^2 \phi_n^2 dv$$

$$+ \int \sum_{n \neq m} \sum C_n C_m \phi_n \phi_m dv \quad 3.22$$

now $\psi = \sum C_n \phi_n$ (LCAO procedure) and if it is further
assumed that for $m \neq n$ 3.12

$$\int \phi_n \phi_m dv = 0 \quad 3.23$$

then

$$\int \psi^2 dv = \sum_n C_n^2 \int \phi_n^2 dv \quad 3.24$$

where the quantity C_n^2 , as explained earlier, has the physical significance of partial π -electron density at atom n in the molecular orbital. The total electron density at atom n is given by

$$Q_n = \sum_i C_{n,i}^2 N_i \quad 3.25$$

where N_i is the number of electrons in each molecular orbital ψ_n and the sum is taken over all the molecular π -orbitals. This type of summation is ideal for the computer, particularly when it is realised that some of the present dyes have well over 20 π -centres.

(b) Bond Order

In 1939, Coulson⁹⁵ introduced the idea of partial bond order and since then this quantity has found wide application in bond classification. If atoms m and n are directly bonded to each other, then one can write down the total bond order for the m-n bond in the molecular orbital as

$$P_{mn} = \sum_i C_{m,i} C_{n,i} N_i \quad 3.26$$

where C_m , C_n and N_i have their usual meanings. In a strictly mathematical context (the physical significance of bond order is difficult to visualize), a large positive value for P_{mn} is an indication of a strong bond, a zero value corresponds to a non-bonding situation, while a negative bond order calls for an antibonding state of affairs.

It is now possible to define the one-centre electron repulsion energy term of equation 3.19 which is given by

$$(RE)_n = \frac{1}{2} Q_n \gamma_{nn} + \sum_{m \neq n} Q_m \gamma_{mn} \quad 3.27$$

where γ_{nn} is the repulsion energy between two p-electrons on atom n and γ_{mn} is similarly defined but for two electrons each on different atoms m and n.

Now

$$\gamma_{nn} = VSIP - A_n \quad 3.28$$

where A_n is the electron affinity for atom n.

while⁹⁶

$$\gamma_{mn} = \frac{14.39(\gamma_{mn} + \gamma_{nn})}{[(\gamma_{mn} + \gamma_{nn})d_{mn} + 28.78]} \quad 3.29$$

where d_{mn} is the distance between m and n . In a very similar manner, the two-centre repulsion energy $(RE)_{mn}$ is given by

$$(RE)_{mn} = -\frac{1}{2} P_{mn} \gamma_{mn} \quad 3.30$$

The inclusion of bond orders and π -electron densities in the PPP method parameterization necessarily calls for the knowledge of these parameters prior to molecular orbital calculation. A way out of this trap is to solve the secular equations iteratively which involves obtaining a rough estimate of the coefficients from a Hückel calculation. These values, in turn, afford rough π -electron densities and bond orders. By then making use of the estimated electron densities and bond orders to set up the PPP secular determinant, an improved set of coefficients is obtained and the process is repeated until consistency is established.

(c) Configuration Interaction (CI)

Configuration interaction is, by definition, the mixing up of energy levels over specified orbitals. This extension is considered essential if improved molecular properties in the excited state are required, since the

results of a PPP calculation strictly refer to the ground state molecule. In practice, there is usually a provision in the computer programme which allows for the transfer of electrons within a specified range of orbitals. In order to cut down the time element involved in this process, mixing-up was carried out within a five orbital range, 3 above and 2 below the highest filled orbital. As has been pointed out by Lockwood,⁹³ the inclusion of limited configuration interaction has very little effect on the first transition and this fact has been confirmed by many of the dyes currently investigated.

(d) Oscillator Strength (OS or f)

It is a common practice to characterize an absorption spectrum by the maximum wavelength and the corresponding absorptivity ($\epsilon_{\max}$). The integrated intensity (A), however, affords a better measure of the band intensity and is given by

$$A = \int_{\nu_1}^{\nu_2} \epsilon_{\nu} d\nu \quad 3.31$$

where ν_1 and ν_2 are the wave numbers at lower and higher limits of the absorption band. For relatively symmetrical absorption bands, the absorbance approximates to

$$A \approx \epsilon_{\max} (\Delta\nu)_{\frac{1}{2}} \quad 3.32$$

where $(\Delta\nu)_{\frac{1}{2}}$ is the half-band width in cm^{-1} . In the computer output the oscillator strength, a related quantity, is given.

According to the classical vibration theory, oscillator strength is the number of oscillators (electrons), each of mass m and charge e , giving rise to the absorption band, and is given by

$$f = 10^3 mc^2 \ln 10 / \pi e^2 N \int \epsilon_v dv \quad 3.33$$

where m and e are the mass and charge of the electron, respectively, c is the velocity of light in vacuum, and N is the Avogadro number. In the case of a smooth symmetrical absorption peak

$$f = 4.31 \times 10^{-9} \epsilon_{\max} (\Delta\nu)_{\frac{1}{2}} \quad 3.34$$

For intense absorption bands, the oscillator strength is of the order of 1, and calculated values are usually in excess of the experimental ones.

The computer used in the present work was the ICL 1906A at the Computer Centre, University of Leeds, and the programme was EBREK.BIN. The values of the various parameters employed are listed in Table 3.1.

Table 3.1. Parameters used in the PPP-SCF-CI MO calculations

Bond Type	Atom		β_{XY}	α_Y	A_Y	Z_Y	r_{XY}
	X	Y					
Aromatic	C	C	-2.39	11.16	0.03	1	1.395
Azo	N	N	-2.90	15.0	2.50	1	1.23
Nitro	C	N	-2.00	24.8	12.53	2	1.486
	$\begin{array}{c} 2+ \\ \text{N} \end{array}$	$\begin{array}{c} \text{O}^- \\ \text{O}^- \end{array}$	-3.05	16.3	1.80	1	1.208
Cyano	C	C $\equiv$	-2.39	11.19	0.01	1	1.395
	C	$\equiv$ N	-2.675	14.18	3.50	1	1.15
Amino	C	NH_2	-2.75	21.0	9.26	2	1.38
Dimethyl -amino	C	NMe_2	-2.75	12.0	9.26	2	1.38
Diethyl -amino	C	NEt_2	-2.75	10.0	9.26	2	1.38
Julolidine equivalent	C	NEt_2	-2.75	8.0	9.26	2	1.38
Aromatic	C	N	-2.48	11.16	0.03	1	1.395

Explanation of symbols

β_{XY} = Resonance integral between atoms X and Y

α_Y = Valence state ionisation potential of atom Y
(VSIP)

A_Y = Electron affinity of atom Y

Z_Y = number of π -electrons contributed by atom Y

r_{xy} = Bond distance between atoms X and Y.

3. Further Application of the PPP Method

(a) Naphthalene Intermediates

As most of the dyes that have been examined by the PPP method were prepared by coupling nitronaphthylamine with an appropriate coupler, a trial of the method on this group of intermediates was considered worthwhile. The primary aim of the exercise was to test the credibility of the reported parameters on a relatively simple structure and at the same to possibly identify any striking features of the compounds which might influence their reactivity. Initially it appeared that the programme might be used to determine the magnitudes of the dipole moments of the fourteen isomers involved. This task was subsequently abandoned for the following reasons. Firstly, since the PPP method afforded only the π -component (μ_{π}) of the dipole moment and in order to obtain an absolute value of this quantity for the molecule in question, it would be necessary to compute the σ -component (μ_{σ}) by devising another programme or, otherwise, a vectorial addition of the two components would then give the required dipole moment. An obvious simplification would be to neglect the σ -component, a step which in this particular case would lead to only a very small error, since the σ -electrons and the atomic nuclei are regarded as forming a nonpolarizable core. The over-riding argument against the determination of the dipole moments, however, stemmed from the fact that reliable values for dipole moments of many organic compounds

lie in the 1-5 Debye range.⁹⁷ As a result, most methods used in the determination of this quantity agree more among themselves than disagree; this fact makes the dipole moment an unattractive property from a diagnostic point of view. Details of the calculated $\lambda_{\max}$ values and the corresponding experimental results⁹⁸ for all the fourteen isomers are given in Table 3.2.

Table 3.2. Calculated and experimental $\lambda_{\max}$ values for the mononitronaphthylamines

(i) The X-nitro-2-naphthylamines

X	$\lambda_{\max}$ (calc)/nm	$\lambda_{\max}$ (obs)*/nm	$\lambda_{\text{calc}} - \lambda_{\text{obs}}$
1	390	396	-6
3	410	437	-26
4	379	383	-4
5	371	372	-1
6	339	365	-26
7	364	380	-16
8	395	392	3

(ii) The Y-nitro-1-naphthylamines

Y	$\lambda_{\max}$ (calc)/nm	$\lambda_{\max}$ (obs)/nm	$\lambda_{\text{calc}} - \lambda_{\text{obs}}$
2	387	404	-17
3	385	382	3
4	357	377	-20

5	399	385	14
6	369	385	-16
7	382	401	-19
8	379	384-396	-17

* the values of $\lambda_{\max}$ are measured in cyclohexane and were taken from ref. 98.

The calculated values of $\lambda_{\max}$ for all the fourteen nitronaphthylamine isomers were within acceptable range, as shown in Table 3.2, although in one or two cases a pronounced discrepancy exists. As previously mentioned, it is not possible to get a perfect fit for the various isomers with only one set of parameters. It must be borne in mind that the PPP method does not cater for all the physico-chemical changes that take place when a solution is exposed to a beam of light. The solvent in which the absorption maxima are measured is one obvious area of discrepancy; it is a well-known fact that in a polar solvent organic molecules will generally absorb at longer wavelengths (bathochromic shift) than in a non-polar solvent (solvatochromism). This fact is well illustrated qualitatively by structures (96a), (96b) and (96c) in Figure 3.2.

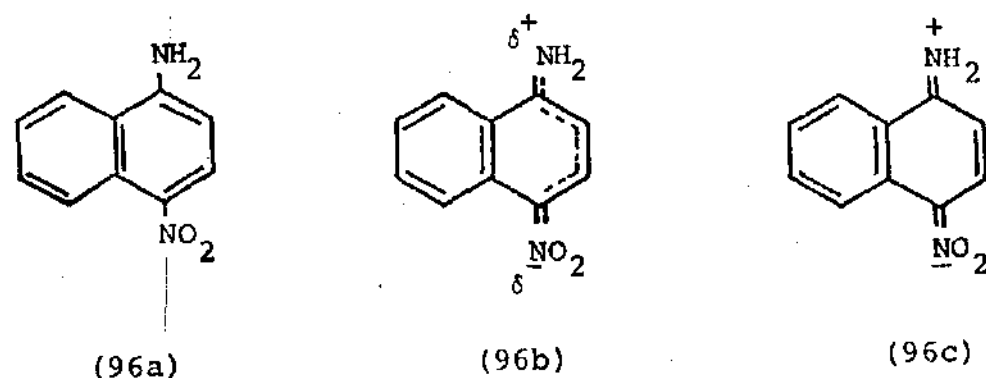


Fig. 3.2. Mesomeric interaction between the nitro and the amino groups in 1-amino-4-nitronaphthalene.

In the ground state, the nitronaphthylamine molecule can be represented by structure (96a) in a non-polar solvent, but on changing to a polar solvent, the same molecule effectively assumes the higher-energy structure (96b), as a result of mesomeric interaction. When the molecule absorbs light it is raised to the first excited state, depicted by structure (96c). The energy difference between structures (96b) and (96c) is less than that between structures (96a) and (96c) so that less energy is required to excite a nitronaphthylamine molecule in a polar than in a non-polar solvent (leading to the observed bathochromic shift). In almost all the cases quoted in this section, experimental λ_{max} values have been measured in the non-polar solvent cyclohexane so as to minimise solvatochromic effects. However, the structural

factors affecting experimental results are less likely to be solved by a mere change of solvent. Thus, in cases where the nitro and the amino groups are near each other, intramolecular hydrogen bonding is bound to occur, a fact which is not reflected in the parameterization of the PPP method. Furthermore, sterically hindered molecules will be forced out of coplanarity in direct contrast to one of the most fundamental assumptions on which this method is formulated.

The large difference between the calculated and experimental λ_{max} values for 2-amino-3-nitronaphthalene in part (i) of Table 3.2 is hardly surprising, since less energy is required to excite adjacent groups in the same nucleus. This situation obtains for the isomeric nitroanilines in cyclohexane where 4-nitroaniline absorbs at 320 nm, 3-nitroaniline at 344 nm and the ortho-isomer at 376 nm. The slight error made by the PPP method in predicting λ_{max} values for these isomers is as nothing compared with the complete failure of resonance theory to account for even the correct order of absorption.⁹⁹ Analogously, one could attribute the low λ_{max} value predicted for the 6-nitro-isomer to the great conjugating power of this isomer.⁶⁶ The overall picture is much more complex and could not be illuminated effectively without the complete reassessment of parameters. For practical purposes, however, the PPP method offers reliable spectral predictions for unsaturated planar molecules.

By way of illustration, ground state π -electron densities, bond orders and electron density changes as well

as transition moment directions are given for 2-amino-5-nitronaphthalene and 1-amino-3-nitronaphthalene in Figures 3.3 and 3.4, respectively.

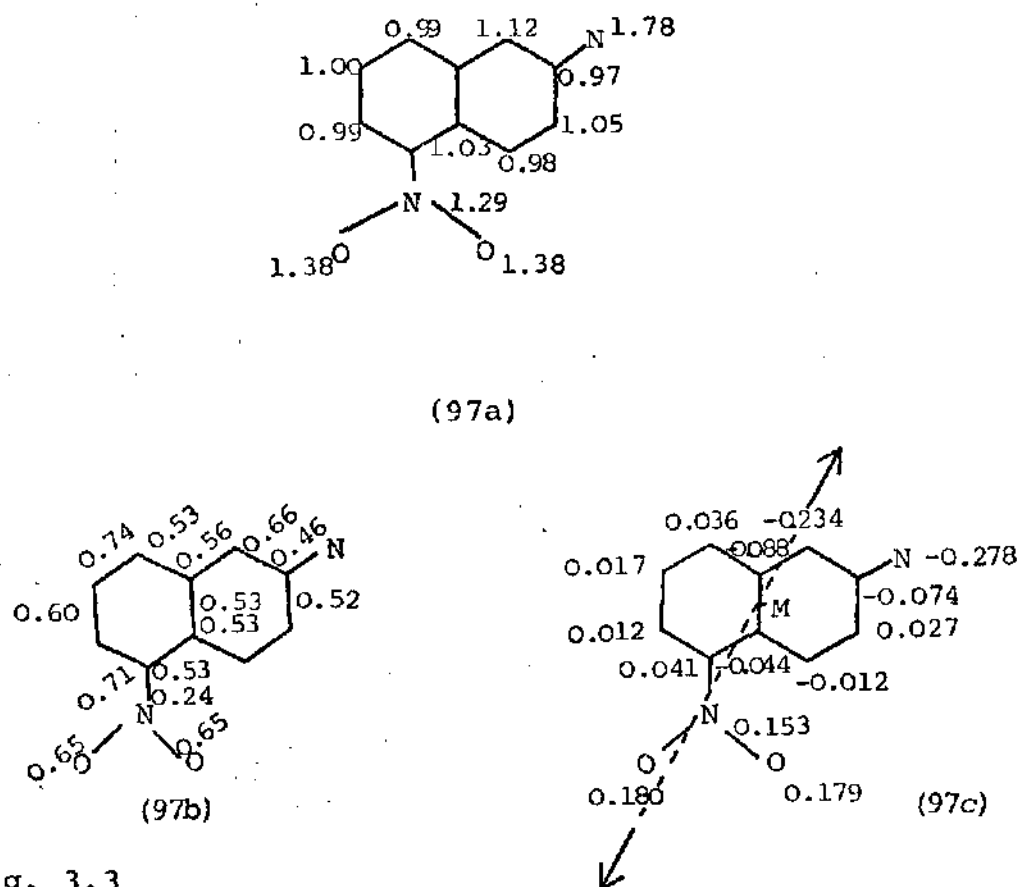


Fig. 3.3

- (97a) Ground state π -electron density distribution;
- (97b) Ground state bond orders;
- (97c) π -Electron density changes and transition moment (M) direction for the highest filled orbital (8) and the lowest unoccupied orbital (9) i.e. 8 $\rightarrow$ 9 transition of 2-amino-5-nitronaphthalene.

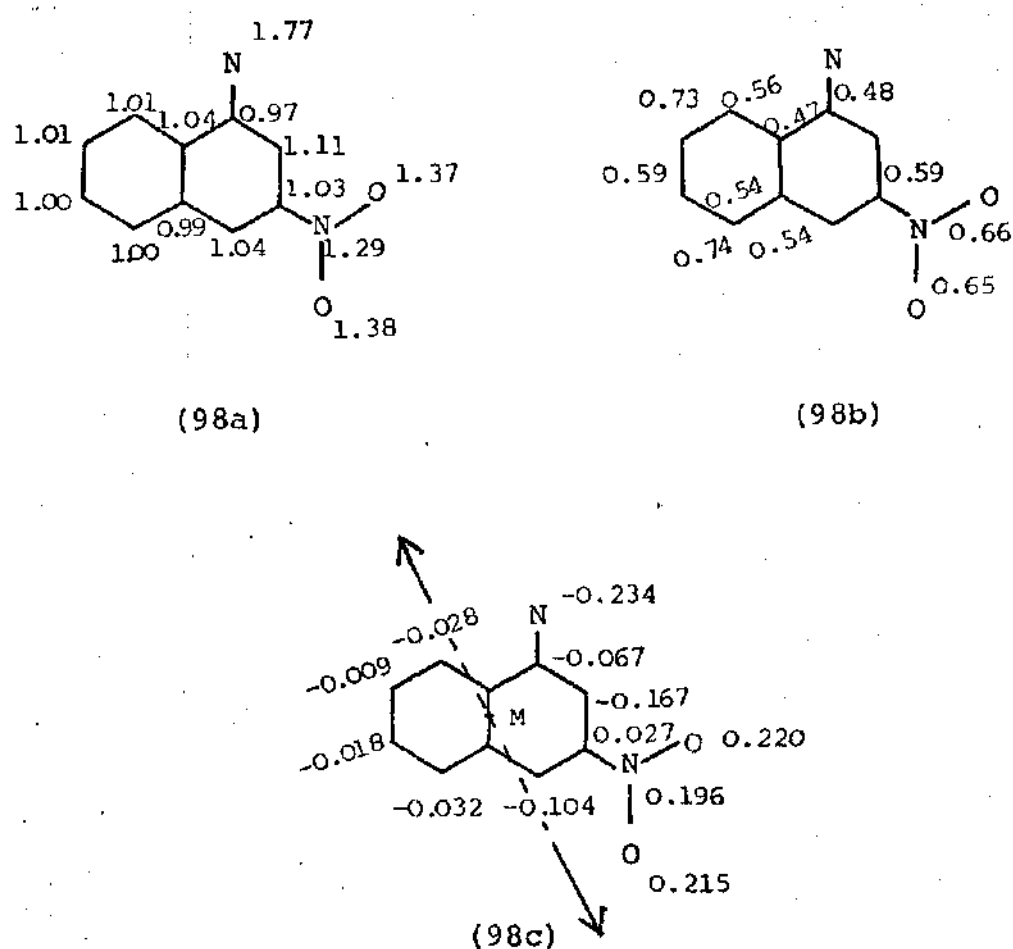


Fig. 3.4

- (98a) Ground state π -electron density distribution;
 (98b) Ground state bond orders;
 (98c) π -Electron density changes and transition moment
 (M) direction for the 8 $\rightarrow$ 9 transition of 1-amino-3-nitronaphthalene.

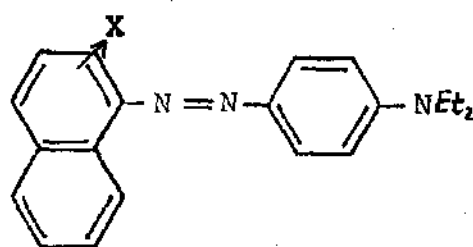
As expected, the π -electron densities for the substituted hydrocarbons are uniformly distributed in the ground state, with the terminal nitrogen of the amino group showing

the greatest electron build-up. There is almost complete bond alternation (ignoring the rather low value for the interannular bond) as indicated by the predicted bond orders. The very weak single bond between the nitro group and the rest of the molecule is particularly informative and indicates that this group could easily be twisted out of the plane thereby leading to hypsochromic shifts. There is small but significant depletion of electron density at positions ortho to the amino group in both cases. It would appear, therefore, that a mesomeric electron-donating substituent at this position would lead to a bathochromic shift, if steric hindrance is ignored. In all the cases investigated, the direction of polarisation was along the nitro-amino group axis, as would be expected.

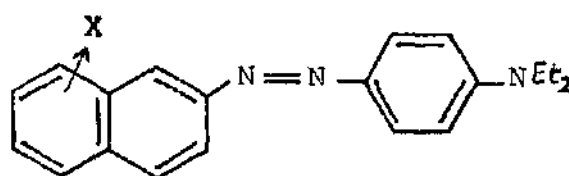
(b) Azo Dyes Derived from Naphthalene

Some of the intermediates listed in Table 3.2 were diazotised and coupled to N,N-diethylaniline. The experimental and predicted data for all these dyes are given in Table 3.3.

The close agreement between experimental and predicted visible absorption maxima for this series of dyes confirms the usefulness of the PPP method. It is usual in predictive work to evaluate parameters, to suit a parent like (63) or (64) ($X = X' = H$), and then to use the same parameters for the substituted dyes. In this particular case, however, the calculated $\lambda_{\max}$ values for the parent



(63)



(64)

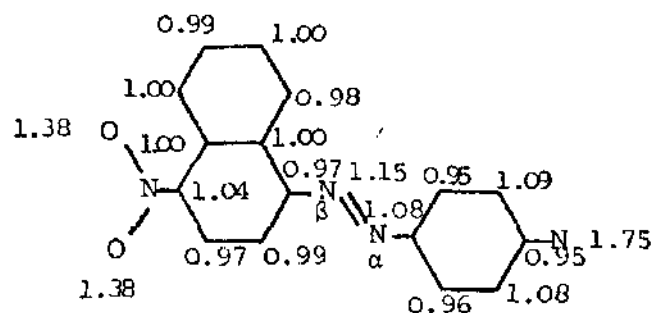
Fig. 3.5. General structures for the naphthalene dyes.

Table 3.3. Calculated and experimental spectral data for naphthalene derivatives coupled to N,N-diethyl-aniline.

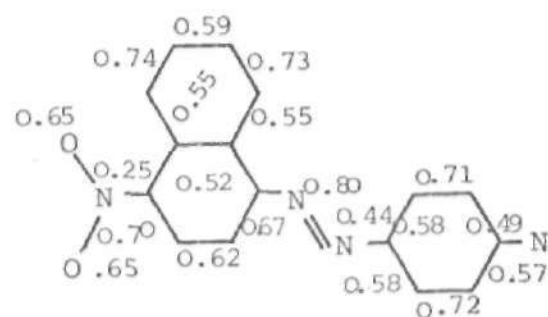
Compound		$\lambda_{\max}(\text{calc})$	$\lambda_{\max}(\text{obs})$	$\Delta\lambda$	f_{calc}
(63)					
X = H	(99)	454	-	-	1.40
X = 2-NO ₂	(100)	480	-	-	1.23
X = 4-NO ₂	(50)	486	477	9	1.46
X = 5-NO ₂	(51)	465	443	22	1.45
(64)					
X = H	(101)	432	-	-	1.49
X = 1-NO ₂	(49)	466	446	20	1.28
X = 6-NO ₂	(52)	444	455	-11	1.54
X = 8-NO ₂	(53)	444	442	2	1.39

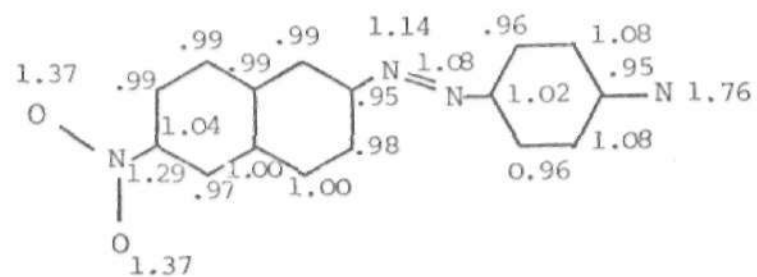
dyes were based on reliable results obtained from the substituted dyes. The resulting wavelengths are in fact quite reasonable since they illustrate clearly the greater conjugative power of the 1-position compared with the 2-position in the naphthalene molecule. The poor agreement in the dye (49), is yet a further confirmation of the steric hindrance operating when substituents are in adjacent positions. It has, in fact, been pointed out¹⁰⁰ that the large nitro group, when in the 1-position, is sterically hindered even by a hydrogen atom in the 8-position.

Ground state data and π -electron changes for the first electronic transition as well as the transition moment direction for dyes (50) and (52) are shown in Figures 3.6 and 3.7, respectively.

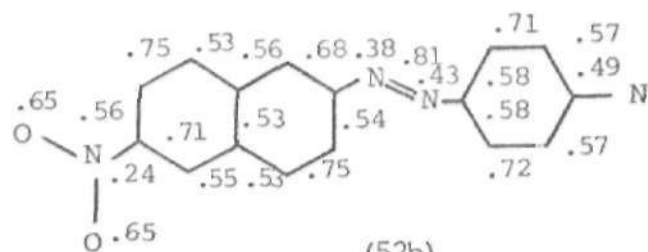


(50a)

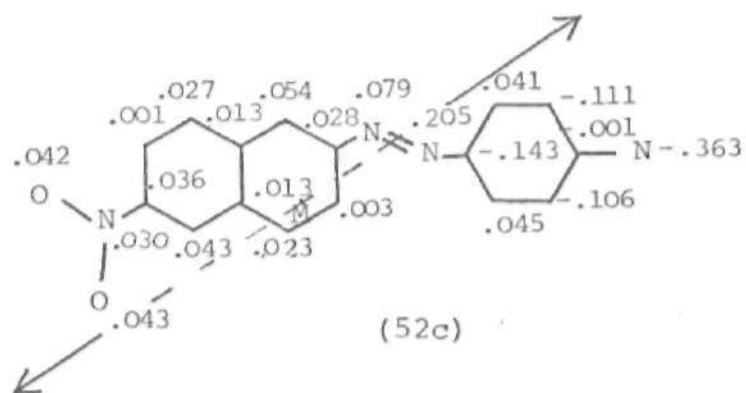




(52a)



(52b)



(52c)

Fig. 3.7

- (52a) Ground state π -electron density changes;
- (52b) Ground state bond orders;
- (52c) π -Electron density changes and transition moment (M) direction for the 12 + 13 transition of 4-(6-nitro-2-naphthylazo)-N,N-diethylaniline.

Comparison of the ground state data for the nitronaphthylamines in Figures 3.3 and 3.4 with those of the azo dyes in Figures 3.6 and 3.7 reveals that the coupling of these intermediates to N,N-diethylaniline has not greatly perturbed the spectral picture. There is the usual migration of electrons from the alkylamino group and the adjacent benzene ring towards the nitro group. In the case of the azo dyes, however, there is a build-up of electron density at the β -azo nitrogen and this indicates that the two nitrogen atoms of the azo group will behave differently during protonation as previously observed.

The generalisation that wide changes between ground and excited states data will lead to broad bands was tested for the C-NO₂ bond in (52b). The ground and first excited state values for this bond were 0.24 and 0.27, respectively, the small change in bond order being in keeping with the narrow peak obtained for this dye. Calculations in the excited state were carried out manually bearing in mind that the highest filled orbital and the lowest empty orbital will accommodate one electron each in the excited state; for the particular molecule in question, the orbitals involved were 12 and 13. The distribution of electron density indicates that these dyes are highly polarised in the excited state. Organic compounds whose excited state is more readily stabilised than the ground state are known to exhibit positive solvatochromism. Thus dye (52) absorbs at 455 nm in cyclohexane and at 480 nm in ethanol.

An investigation was also carried out into dyes containing the julolidyl group, since it has been shown that this is a better electron-donating group than -NEt_2 ; the parameters at the terminal nitrogen atom were adjusted to take this fact into account. By trial and error, it was found that lowering the value of the valence state ionisation potential (VSIP) for the terminal nitrogen atom from 10 to 8 eV gave good agreement with experimental values. The results obtained are listed in Table 3.4.

Table 3.4. Calculated and experimental spectral data of some azo dyes derived from julolidine[†]

Compound*		$\lambda_{\text{max}}^{\text{(calc)}}$ / nm	$\lambda_{\text{max}}^{\text{(obs)}}$ / nm	$\Delta\lambda$	$f_{\text{calc.}}$
9-(Phenylazo) julolidine	(102)	421	422	-1	1.26
9-(4-Methylphenylazo) julolidine	(103)	421	421	0	1.26
	(91)	476	485	-9	1.43
9-(4-Cyanophenylazo) julolidine	(104)	453	464	-11	1.48
	(93)	496	503	-7	1.42
	(94)	453	480	-27	1.50
	(95)	453	466	-13	1.36

* cf. Table 2.11

† measurements were taken in cyclohexane.

It is interesting to compare the predictions for dyes (91) and (93). The oscillator strength is the same in both cases, but the effective conjugation of the second benzene ring in naphthalene leads to a predicted bathochromic shift as found experimentally. It is difficult to account for the inability of the PPP method to differentiate between (94) and (95). From resonance theory considerations, one would expect dye (94) to absorb at a longer wavelength since the relevant intermediate possesses a doubly para quinonoid structure (65) in contrast to the ortho-para situation obtaining in (67). The relevant data for dye (94) are shown in Figure 3.9.

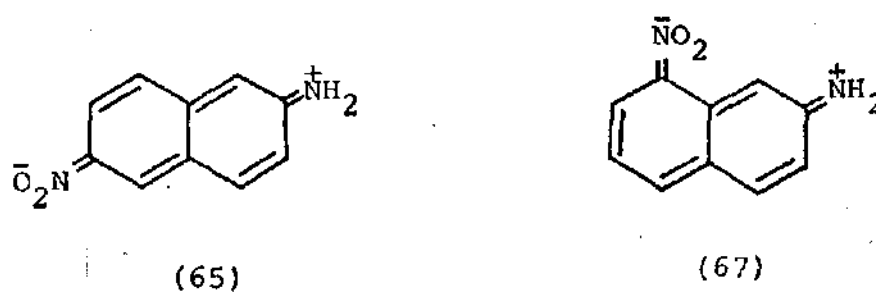
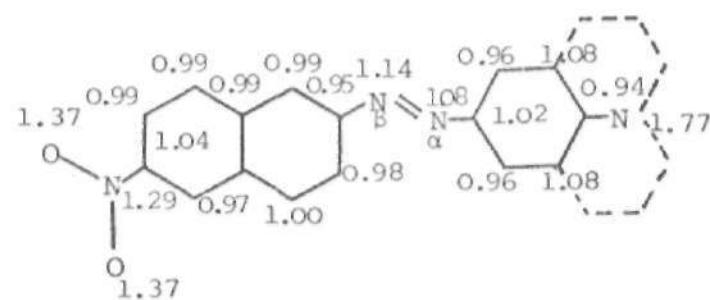
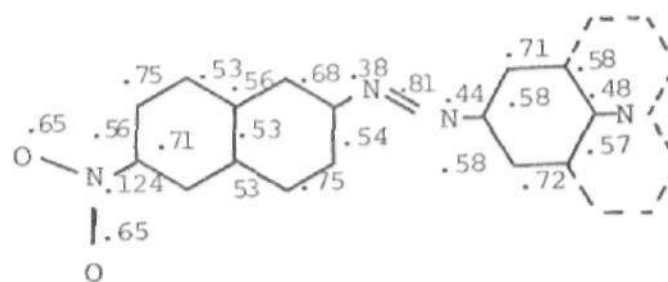


Fig. 3.8. Ionic resonance structures for two nitronaphthylamines

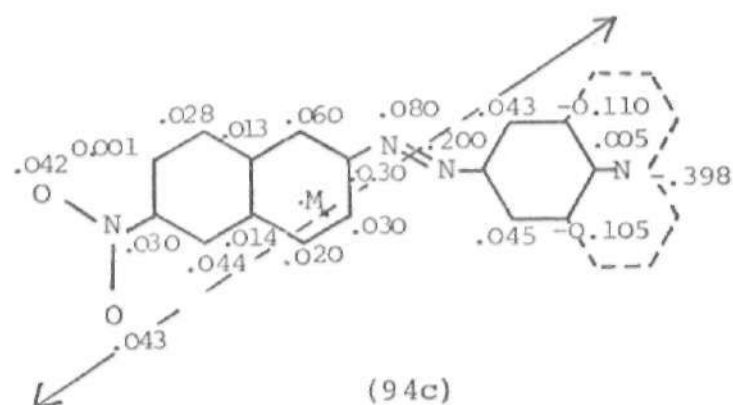
As can be seen from Figures 3.7 and 3.9, replacement of the -NEt_2 group by julolidyl has not altered the general pattern of electron distribution. The only significant change observed is the anticipated bathochromic shift.



(94a)



(94b)



(94c)

Fig. 3.9

(94a) Ground state π -electron density distribution;

(94b) Ground state bond orders;

(94c) π -Electron density changes and transition moment

(M) direction for the 12 $\rightarrow$ 13 transition of

9-(6-nitro-2-naphthylazo)julolidine

(c) Azo Dyes derived from 9,10-Dihydrophenanthrene and from Phenanthrene

It has been observed¹⁰¹ that the absorption band of ortho-bridged biphenyls (Fig. 3.10) suffers a monotonic hypsochromic shift and decrease in intensity (hypochromic effect) as the size of the bridging chain increases.

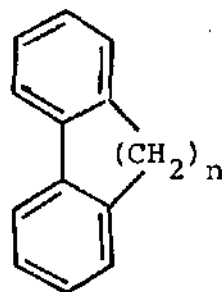


Fig. 3.10 2,2'-Bridged biphenyls.

Since fluorene ($n=1$), the first member of this series, absorbs at a longer wavelength than biphenyl (260 nm in ethanol compared with 247.5 nm in heptane), the obvious cause of the shift is the attainment of coplanarity. The interplanar angle between the two benzene rings in fluorene is reported¹⁰² to be near to zero owing to the enforced planar geometry. As a result of strain in the fluorene molecule, many workers¹⁰² have preferred to use the next member of the series 9,10-dihydrophenanthrene ($n=2$) for investigation purposes. The A band of 9,10-dihydrophenanthrene in ethanol is observed at 264 nm (ϵ_{max} 17,000)¹⁰² and the interplanar angle is estimated at 20° , based on a model in which the saturated carbon atoms maintain their tetrahedral valence

angle.¹⁰² The relatively low angle between the two benzene rings should permit reasonable results with the PPP method for derivatives of 9,10-dihydrophenanthrene, and this proved to be the case (Table 3.5).

Table 3.5. Calculated and experimental spectral data for 9,10-dihydrophenanthrene and phenanthrene derivatives coupled to N,N-diethylaniline.[†]

Compound*	$\lambda_{\max}(\text{calc})/\text{nm}$	$\lambda_{\max}(\text{obs})/\text{nm}$	$\Delta\lambda$	f_{calc}
(54)	438	426	12	1.57
(55)	462	450	12	1.45
(56)	447	448	-1	1.63
(57)	435	441	-6	1.58
(59)	459	458	1	1.73
3-Dimethylamino-2-(4-nitrophenylazo)phenanthrene	516	513	3	0.45

* As in Table 2.1 † in cyclohexane

A glance at the polarisation direction [Fig. 3.11(56c)] leads one to expect the dye to have a deeper colour than predicted, since the transfer of electrons involves the entire length of the molecule. The experimental result, however, confirms the fact that these polycyclic azo dyes are not deeply coloured compounds. The analogous dye (57), prepared from the phenanthrene molecule absorbs at even shorter wavelength, 441 nm, with a predicted $\lambda_{\max}$ value of 435 nm. Dye (55), with a nitro group ortho to the azo linkage absorbs at 450 nm, a bathochromic shift of 24 nm when compared with the parent

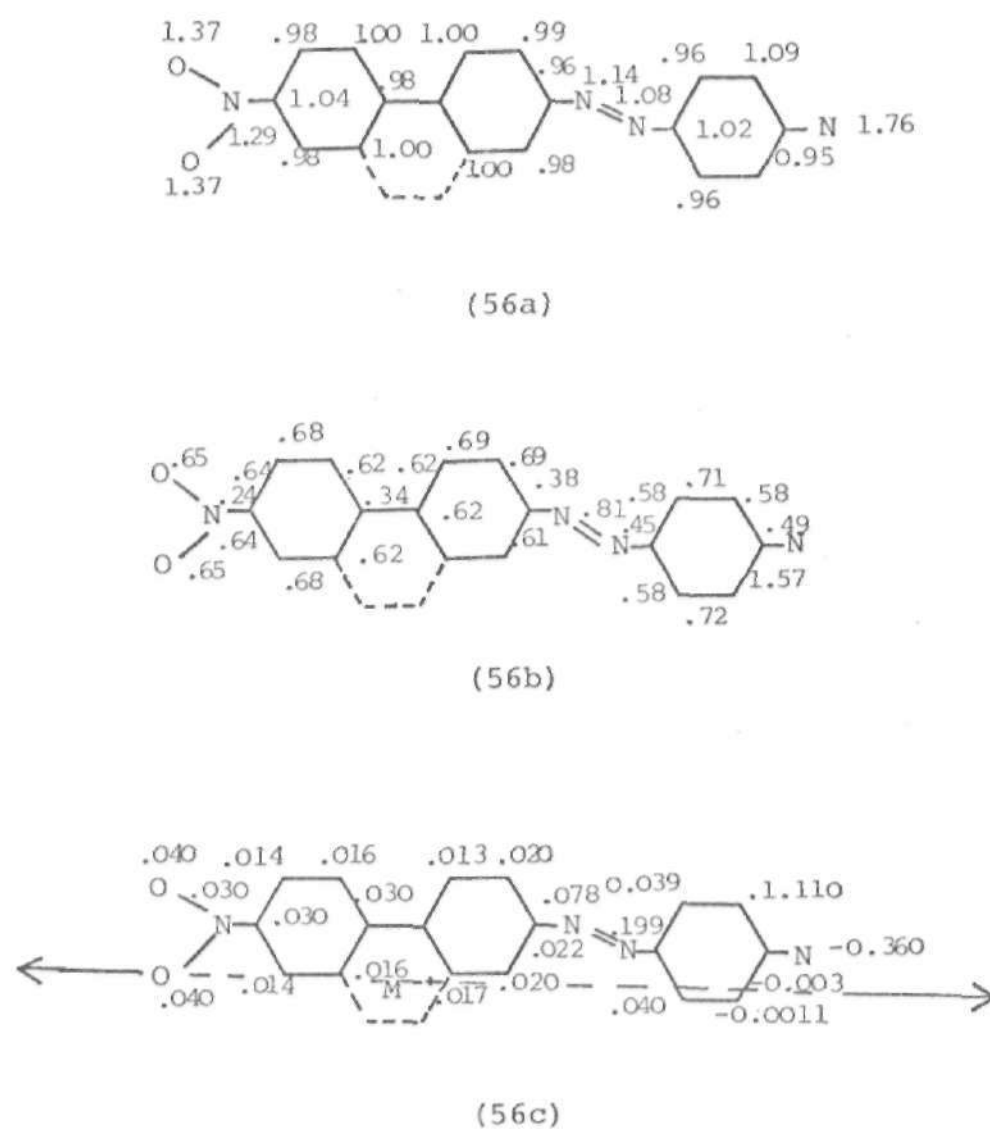


Fig. 3.11

- (56a) Ground state π -electron density distribution;
 (56b) Ground state bond orders;
 (56c) π -Electron density changes and transition moment (M)
 direction for the 13 $\rightarrow$ 14 transition of 4-(7-nitro-
 9,10-dihydro-2-phenanthrylazo)-N,N-diethylaniline.

dye (54). In general, the predictions for the 9,10-dihydro-phenanthrene dyes were rather better than one might have thought. It can therefore be suggested that the preferred conformations of these dyes in solution do not depart greatly from planarity.

The successful handling of the 9,10-dihydrophenanthrene dyes led to the application of this method to dyes containing other phenanthrene derivatives. The predicted data for 4-(9-cyano-3-phenanthrylazo)-N,N-diethylaniline (59) are given in Figure 3.12; the triple bond in the cyano group was correctly predicted. Efforts to prepare a similar dye with a nitro group in place of the cyano were not successful. Comparison of these two dyes would have revealed useful information relating to the two electron-withdrawing groups; the nitro group is the more powerful of the two, but the rod-like structure of the cyano group makes it more suitable in positions where steric hindrance is likely to occur.

An attempt was made to prepare a dye using an alkylated aminophenanthrene as a coupler. 4-Nitroaniline was diazotised and coupled to 3-dimethylaminophenanthrene but the resulting product appeared to be a mixture and very unstable. A purified sample was obtained from an alumina column and gave λ_{max} 513 nm; this value compares very favourably with a predicted λ_{max} of 516 nm for the 2-coupled product (Table 3.5). The oscillator strength of this dye was predicted to be 0.45. The computed λ_{max} value for the isomeric dye derived by coupling at position 9 in the phenanthrene ring was 472 nm. Owing to the instability of the dye, it was

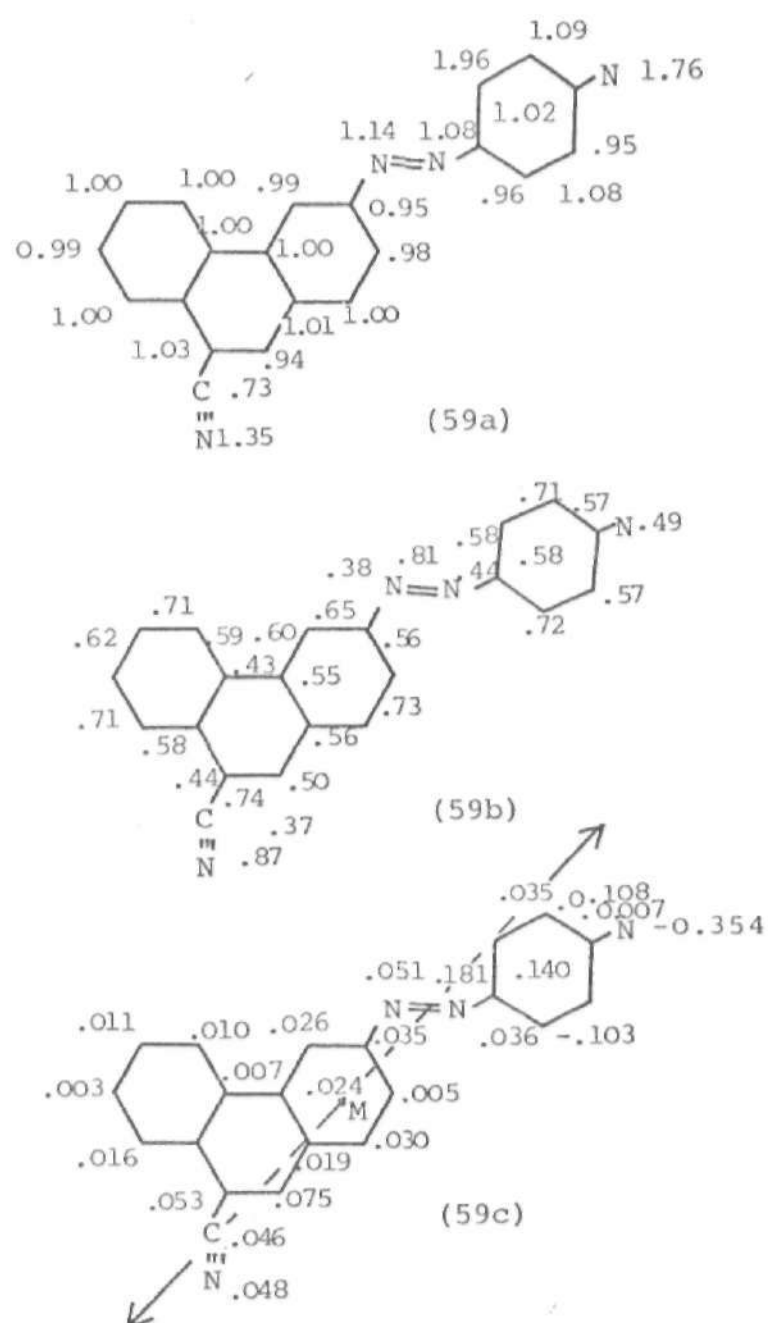
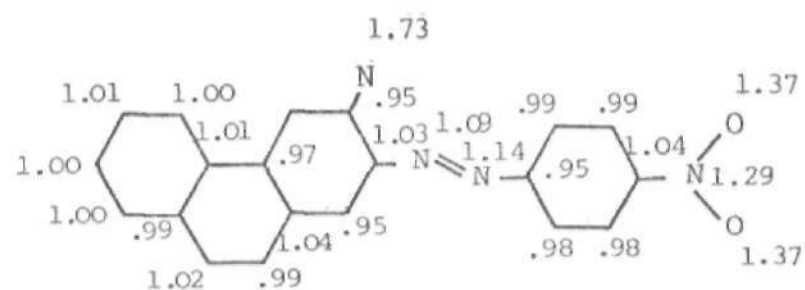
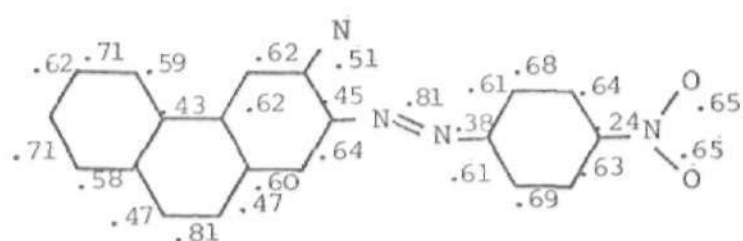


Fig. 3.12.

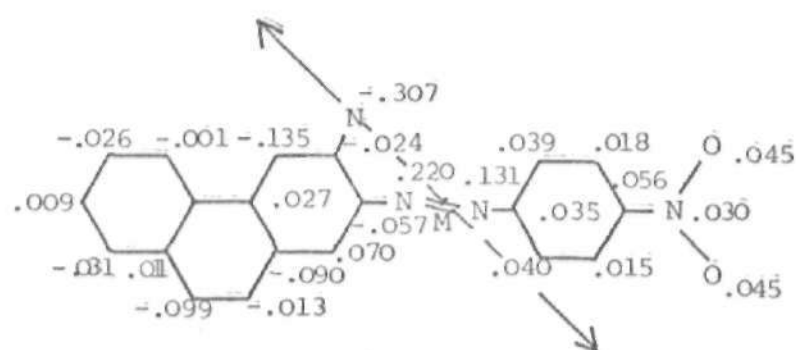
- (59a) Ground state π -electron density distributions;
- (59b) Ground state bond orders;
- (59c) π -Electron density changes and transition moment (M) direction for the 13 $\rightarrow$ 14 transition of 4-(9-cyano-3-phenanthrylazo)-N,N-diethylaniline.



(105a)



(105b)



(105c)

Fig. 3.13

(105a) Ground state π -electron density distribution;

(105b) Ground state bond orders;

(105c) π -Electron density changes and transition moment (M)

direction for the 14 $\rightarrow$ 15 transition of 3-dimethylamino-2-(4-nitrophenylazo)phenanthrene.

not possible to purify sufficient material for an NMR spectrum to confirm the coupling position. However, it seems likely that coupling takes place mainly at the 2-position but also at the 9-position in accordance with the data in Figure 3.13.

4. Conclusions

The obvious advantage of the PPP method over similar techniques in colour prediction is its versatility. Unlike the HMO method, the PPP approach handles heteroatomic systems satisfactorily, although the paucity of literature data concerning such systems requires urgent attention. The ease of computational manipulation coupled with a good correlation between the geometry of the system and the in-fed parameters makes this method particularly suitable for dyes where colour is strongly dependent on the geometry of the molecule.

The results reported for the nitronaphthylamines do not reveal any features of particular interest for reactivity purposes, but provide, nevertheless, confirmation that the characteristics of such compounds in the ground state are uniformly distributed. The electronic changes predicted after the transfer of an electron from the highest occupied orbital to the lowest unoccupied orbital are particularly helpful, as they give the movement of electrons in the entire molecule in a pictorial form which is easy to follow.

The choice of parameters could not be treated with the same degree of confidence as the results therefrom. The various parameters can be divided into (a) 'key' parameters and (b) 'ordinary' parameters. The so-called 'key' parameters are those which on alteration appreciably affect the predicted $\lambda_{\max}$, whereas those in the second category have little effect on the value of $\lambda_{\max}$. The valence state ionisation potential

(VSIP), whose value had to be reassessed in some cases on a trial and error approach is one such 'key' parameter. It was found that by lowering the VSIP for the terminal nitrogen atom (with constant electron affinity) the predicted $\lambda_{\max}$ value increased linearly (Figure 3.14). Thus, by using five different values of VSIP in a programme designed for 9-(8-nitro-2-naphthylazo)julolidine the simple relationship shown in Figure 3.14 was obtained. An increase in VSIP, which is equivalent to lowering the electronegativity of the terminal nitrogen atom results in a hypsochromic shift. For instance, when the VSIP is changed from 8eV to 12 eV, the corresponding $\lambda_{\max}$ moves from 453 nm to 434 nm, which is reasonable if the julolidyl group is replaced by a dimethyl-amino group.

Since certain dyes containing the phenanthrene molecule were successfully handled by this method (e.g. dye 57), other derivatives with novel substitution patterns were also investigated. Thus, the dye derived from 3-amino-6-nitrophenanthrene and *N,N*-diethylaniline should absorb at 442 nm with f 1.52. This result suggests that conjugation is not very effectively extended through the phenanthrene system. It may tentatively be concluded that azo dyes derived from ring systems more complex than naphthalene are not likely to find commercial application.

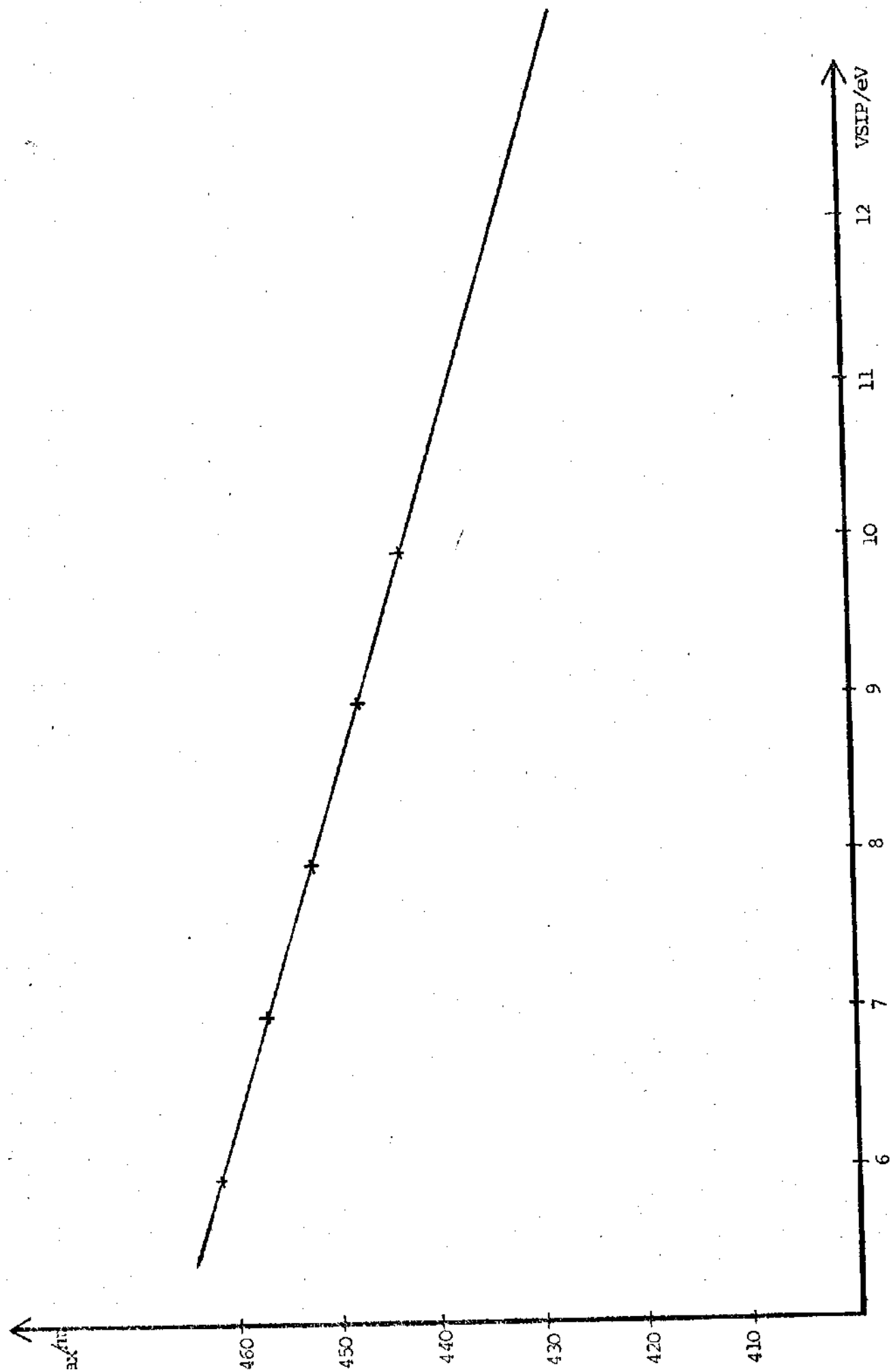


Fig.14. Relationship between predicted $\lambda_{\max}$ against VSIP for 9-(8-nitro-2-naphthylazo)julolidine.

DISCUSSION OF EXPERIMENTAL

I. Intermediates

In order to prepare representative monoazo dyes from polycyclic systems, various unsymmetrically substituted dihydrophenanthrene, phenanthrene and naphthalene derivatives were required. Since very few azo dyes incorporating the phenanthrene chromogen have been reported, probably largely owing to synthetic difficulties and the inherent poor colour yielding property of the parent system, it was considered desirable to include at least one powerful electron acceptor substituent at an appropriate position within the dye molecule.

A thorough survey of the phenanthrene literature afforded no useful combinations which could be deployed for the preparation of azo dyes. Furthermore, only the 2,7-, 3,6-, and 3,9-linked compounds would, theoretically, permit the necessary conjugation (Fig. 4.1).

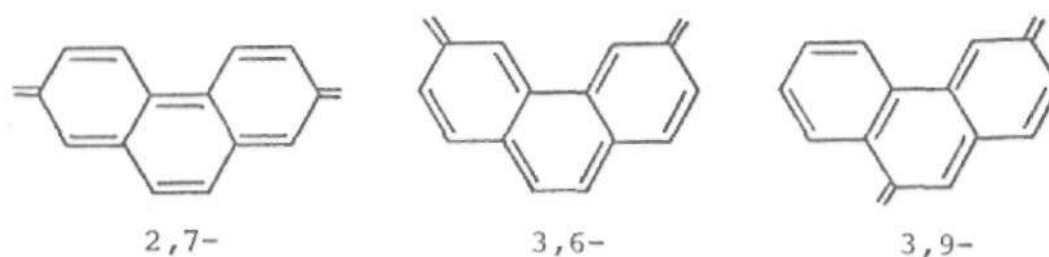


Fig. 4.1. Conjugation through the phenanthrene molecule.

In phenanthrene, the 9,10-bond shows strong double bond character¹⁰³ and is susceptible to addition reactions. The generalisation that the 9,10-bond is different from the

other bonds in the molecule is evidenced by the relative ease with which it is reduced or oxidised to 9,10-dihydrophenanthrene and to 9,10-phenanthraquinone, respectively.

The choice of appropriate substituents for inclusion in the diazonium components in these polycyclic rings was made on the basis of arrangements such as that shown in Table 4.1.

Table 4.1. Classification of substituents

<u>Group</u>	<u>Dipole moment (μ)^a</u>	
NH ₂	1.5	Electron-donating groups
OMe	1.2	
Me	0.3	
H	0.0	
Cl	1.6	
CHO	2.8	Electron-withdrawing groups
CN	3.7	
SO ₃ H	3.8	
NO ₂	3.9	

a taken from P. Sykes, "A Guidebook to Mechanism in Organic Chemistry", p.138

According to this classification, based on the dipole moments of monosubstituted benzenes, the top and bottom substituents represent the most powerful electron-donating and electron

withdrawing groups, respectively. Thus, the diazotizable primary amino group and the strongly electron withdrawing nitro group were chosen as the most suitable pair. The same conclusion is reached on the basis of Hammett substituent constants.¹⁰⁴ The solubilising nature of the sulphonic acid group makes it unsuitable for spectral investigations and the easily convertible aldehyde group is unacceptable from a preparative point of view. Whereas all the fourteen nitro-amines of the naphthalene system have been prepared, the synthesis of the various phenanthrene analogues is laborious and cumbersome. Consequently, there has been an overconcentration of efforts towards the more accessible methyl, methoxy and carboxy substituents. In theory, there are three basic approaches to the preparation of substituted phenanthrenes:

- (i) substitution via the 9,10-dihydro derivative followed by aromatisation,
- (ii) cyclisation of appropriate benzene or naphthalene derivatives,
- (iii) direct substitution of the phenanthrene molecule.

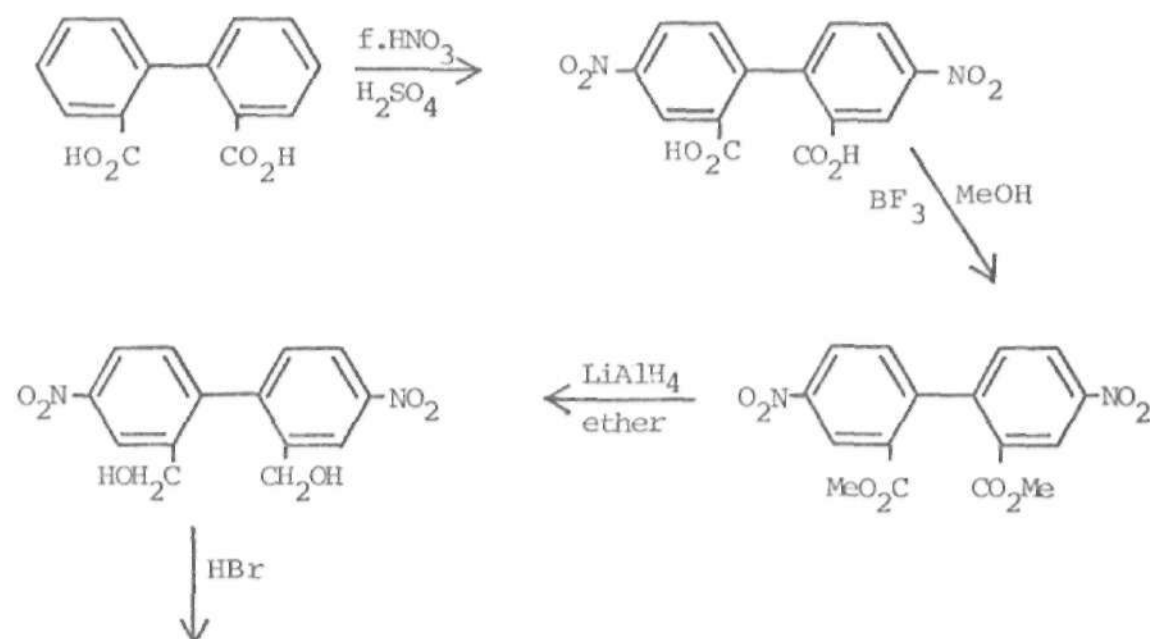
Of the three methods, the third is the most unreliable and is rarely used for mono and disubstituted phenanthrene derivatives; both the first and the second techniques have been used extensively in the present work.

1. 2,7-Disubstituted Phenanthrenes(a) 2,7-Dinitrophenanthrene

The preparation of 2,7-dinitrophenanthrene has been reported.¹⁰⁵ In the present work, this intermediate was obtained in a number of ways.

First Method

The first route involved the esterification of 4,4'-dinitrobiphenyl-2,2'-dicarboxylic acid, followed by reduction of the ester to the dialcohol which was subsequently brominated. The dibromo compound was treated with triphenylphosphine to give 4,4'-dinitro-2'-bromomethyl-2-biphenylmethylphosphonium bromide from which the 2,7-dinitro compound was obtained in reasonable yield using sodium methoxide. Details of this route are shown in Chart 4.1.



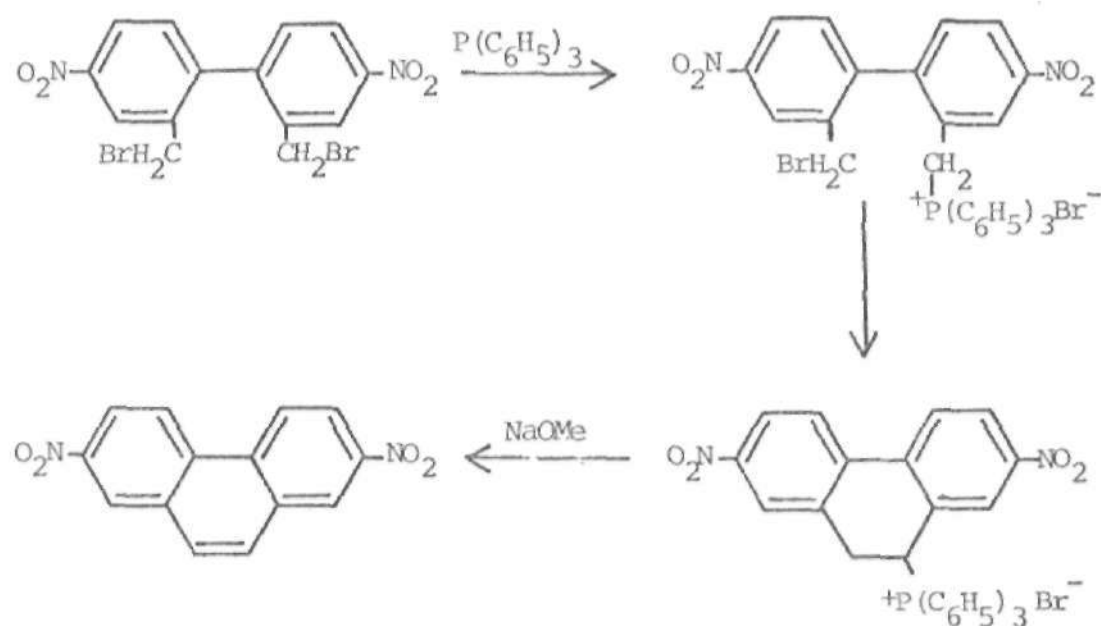


Chart 4.1. Preparation of 2,7-dinitrophenanthrene from biphenyl-2,2'-dicarboxylic acid.

4,4'-Dinitrobiphenyl-2,2'-dicarboxylic acid used in the first stage of the preparation was obtained through a modified procedure of Kuhn and Albrecht.¹⁰⁶ Biphenyl-2,2'-dicarboxylic acid was dissolved in concentrated sulphuric acid and cooled externally in an ice-water bath. An equal volume of fuming nitric acid was slowly added, keeping the temperature of the reaction below 20°C . After the addition of the acid, the reaction vessel was gradually warmed to $40\text{--}50^\circ\text{C}$ and maintained at that temperature with constant stirring. In this manner the dinitro compound was obtained after work-up in yields exceeding 80%. A recent reference¹⁰⁷ has reported the preparation of the same compound through an obscure procedure which afforded the desired dinitro

compound on a very small scale. The identity of 4,4'-dinitrobiphenyl-2,2'-dicarboxylic acid prepared as described above was confirmed by its NRM spectrum. The main setback in the first route was the low yield at the esterification stage. Several modifications were tried but there was no substantial increase in the overall yield.

Second Method

Direct nitration of 9,10-dihydrophenanthrene followed by aromatization afforded the desired compound in a relatively pure state. Nitration of 9,10-dihydrophenanthrene occurs mainly in the 2,7-positions in the presence of an excess of acid, in agreement with reported characteristics of this hydrocarbon and related compounds; it has been shown on several occasions that 9,10-dihydrophenanthrene behaves more like biphenyl than phenanthrene.¹⁰⁸ The nitration of biphenyl in the 4,4'-positions has been carried out;¹⁰⁹ similar treatment of fluorene in acetic acid with an excess of fuming nitric acid gave a mixture of predominantly 2,7-dinitrofluorene together with some of the 2,5-isomer.

The dinitration of 9,10-dihydrophenanthrene (Chart 4.2) proved to be a very useful step in the preparation of 2,7-disubstituted phenanthrene derivatives as discussed in the next section.

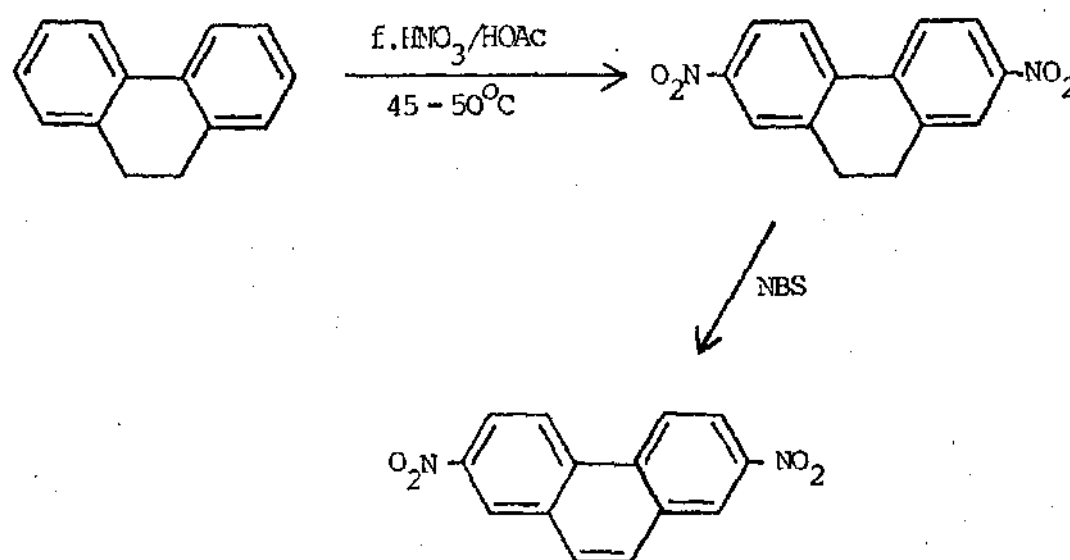


Chart 4.2. Preparation of 2,7-dinitrophenanthrene from 9,10-dihydrophenanthrene.

Callow and Gulland¹¹⁰ attempted the dinitration of phenanthrene by following the procedure of Schmidt and Heinle¹¹¹ using fuming nitric acid but obtained unidentified dinitrophenanthrene described as pale buff needles melting between 255 and 260°C after repeated crystallisations from acetic acid; 2,7-dinitrophenanthrene has a melting point of 333-336°C.¹¹²

Third Method

It has been claimed^{107,113} that phenanthrene and its derivatives can be prepared from 2,2'-diacylbiphenyls via cyclic azines under the influence of hydrazine (Chart 4.3).

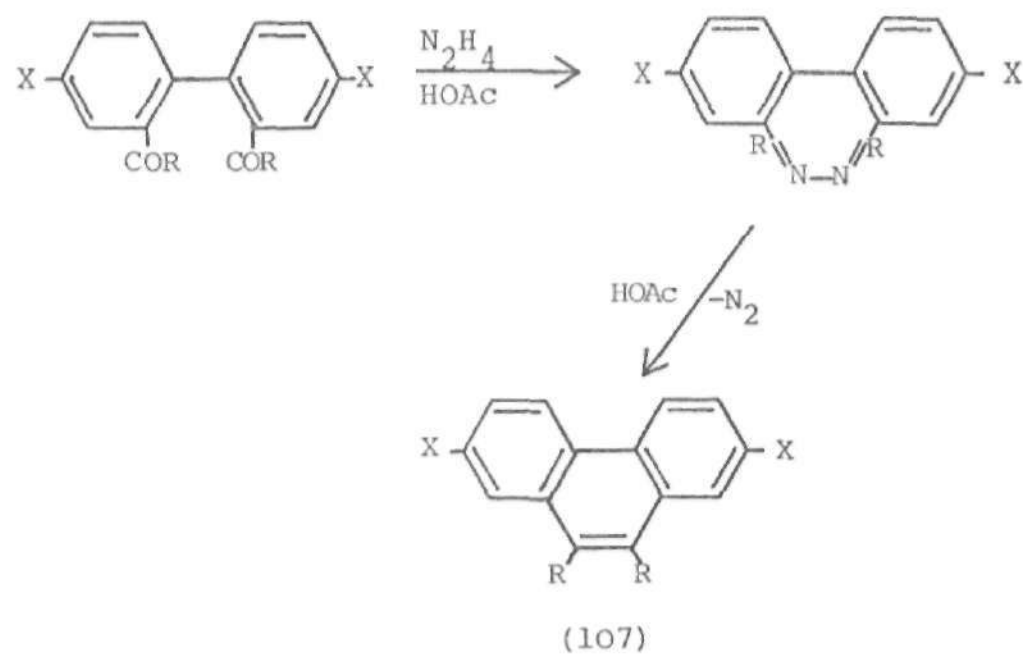


Chart 4.3. Possible route to 2,7-dinitrophenanthrene.

In order to obtain the desired compound [(107) R = H, X = NO₂], the following procedure (Chart 4.4) was attempted.

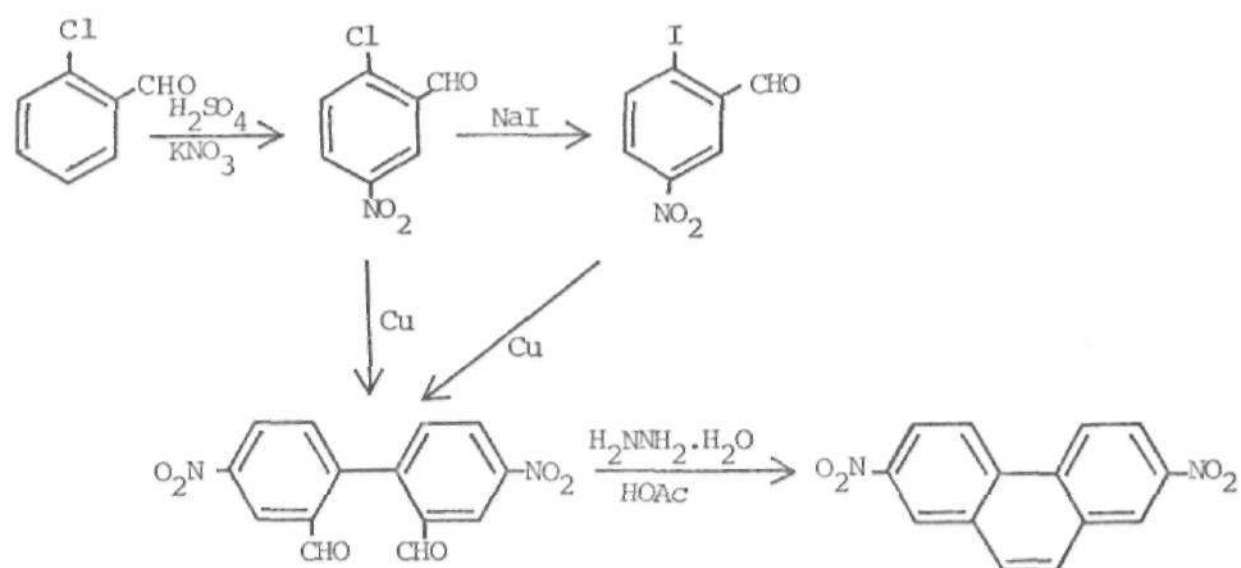


Chart 4.4. Attempted preparation of 2,7-dinitrophenanthrene.

Economically speaking, this last method compares favourably with the two described previously, as the starting material is the relatively cheap *o*-chlorobenzaldehyde. The first nitro compound was prepared by mild nitration using potassium nitrate in concentrated sulphuric acid. The conversion of the chloro compound into the corresponding iodo analogue using sodium iodide in ethanol did not proceed as smoothly as anticipated. The preparation of the iodo compound is essential because the formation of the dialdehyde in the Ullmann reaction is greatly enhanced by the loss of iodine; the established order of reactivity is $\text{Cl} < \text{Br} < \text{I}$. An attempt was made to obtain the dialdehyde from the chloro compound but, as feared, this was unsuccessful. Even though this route appears economically advantageous, it is by no means the best route to 2,7-dinitrophenanthrene. Bacon and Lindsay¹¹³ who prepared the 3,6-isomer, reported an overall yield of only 13% in four steps from the iodide. It seems likely that preparative difficulties may be overcome by delaying the nitration until the dialdehyde has been formed; this procedure was in fact followed by Bochenkov¹⁰⁷ who prepared this same compound on a very small scale.

(b) 2-Amino-7-nitrophenanthrene

An attempt was made to prepare 2-amino-7-nitro-9,10-dihydrophenanthrene according to the procedure shown in Chart 4.5. However, the reaction sequence led to the formation of 2-amino-3-nitro-9,10-dihydrophenanthrene. The tendency

towards the ortho-substitution seems to be a general pattern for phenanthrene derivatives and related compounds; an attempt to nitrate 3-acetylamino-9-bromophenanthrene gave 3-acetylamino-9-bromo-2-nitrophenanthrene. The nitration of 9-acetylamino-phenanthrene is also known to occur at the 10-position.¹¹⁴

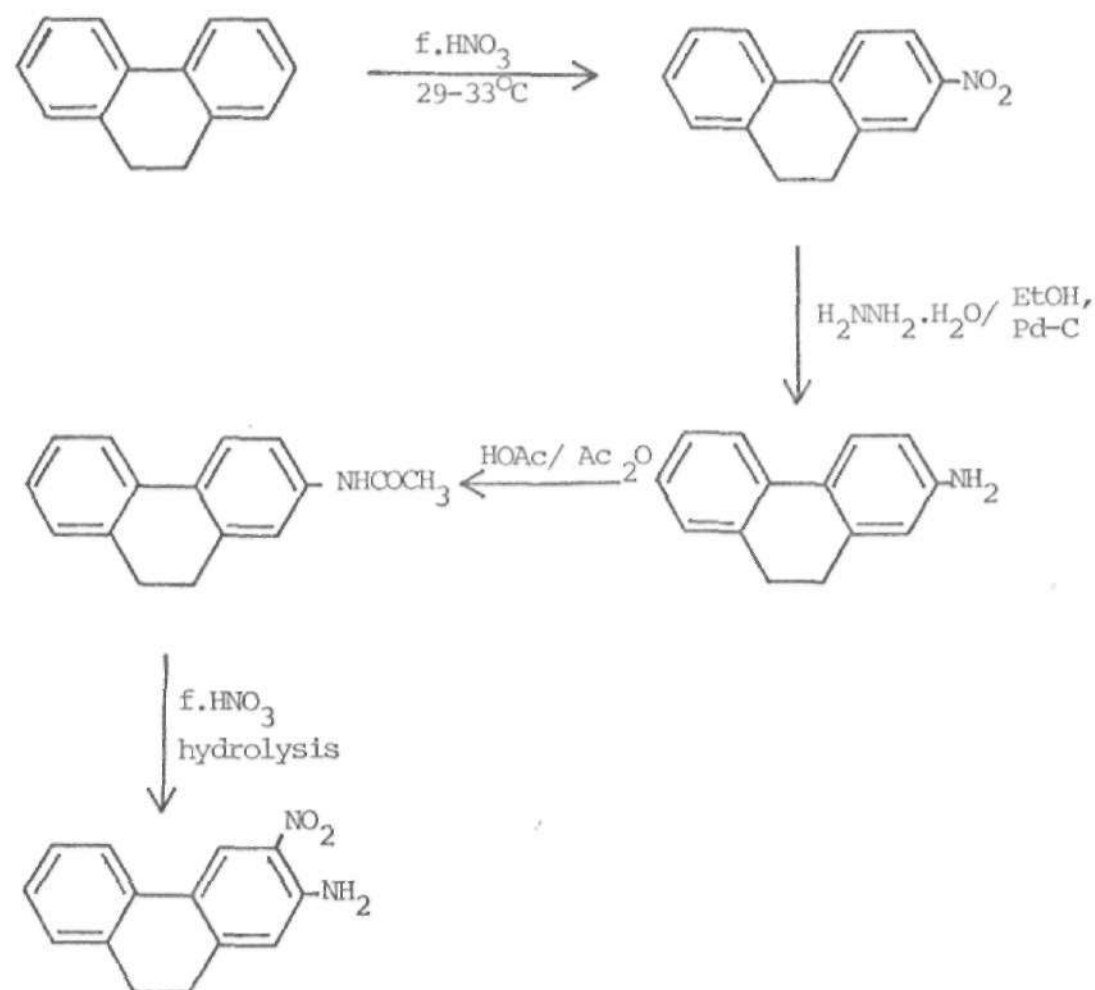


Chart 4.5. Preparation of 2-amino-3-nitro-9,10-dihydrophenanthrene.

The selective reduction of symmetrically substituted nitro groups has been reported for a number of compounds.¹¹⁵ It is generally believed that one of the nitro groups is preferentially attacked by the reducing agent and that, once the amino group has been formed, further reduction is greatly retarded or prevented altogether. There are numerous examples of selective reduction of dinitro-naphthalenes,¹¹⁶ embracing a wide spectrum of reducing agents under different reaction conditions. Although quantitative yields have been quoted for some of these reductions, very poor yields are also frequent. Attempts to reduce 2,7-dinitro-9,10-dihydrophenanthrene and the corresponding phenanthrene analogue by following Staab's procedure¹¹⁷ were unsuccessful. Staab suspended 3,6-dinitrophenanthrene in ethanol and added a solution of sodium hydrosulphide and ammonium chloride in water, followed by work-up after refluxing for half an hour. When the rather expensive solid sodium hydrosulphide was replaced by the same reagent, but prepared in situ in accordance with Hodgson's technique, reductions proceeded smoothly giving products of very high purity. In this procedure¹¹⁸ a 13% aqueous sodium sulphide solution is treated with powdered sodium hydrogencarbonate followed by the addition of methanol; the resultant thick precipitate is washed with methanol. The clear filtrate is then added dropwise to a hot solution or suspension of the dinitro compound in methanol. The crude product is usually dissolved in hydrochloric acid to give a solution from which

the free amine is obtained by neutralisation using dilute aqueous ammonia. By using this procedure, both 2,7-dinitro-9,10-dihydrophenanthrene and the corresponding phenanthrene analogue were selectively reduced to the respective nitro-amines. The identity of these compounds was confirmed by NMR (details shown in Figures 4.2 and 4.3).

The aromatisation of 2,7-dinitro-9,10-dihydrophenanthrene was achieved by refluxing the material in carbon tetrachloride containing *N*-bromosuccinimide (NBS) and a trace of dibenzoyl peroxide. Two important observations were made in this series of reactions:

- (i) aromatisation proceeded quantitatively only at the dinitro stage; an impure product was isolated when 2-amino-7-nitro-9,10-dihydrophenanthrene was treated with NBS.
- (ii) the monoreduction of 2,7-dinitro-9,10-dihydrophenanthrene took place more readily than that of the corresponding dinitrophenanthrene. The difference in reactivity may be associated with the poor solubility of the latter compound in methanol, a situation which was improved slightly by the addition of toluene.

Idoux¹¹⁹ in his reduction of dinitrobiphenyls to nitro-amines found Hodgson's technique to be particularly useful; some of his results are given in Table 4.2.

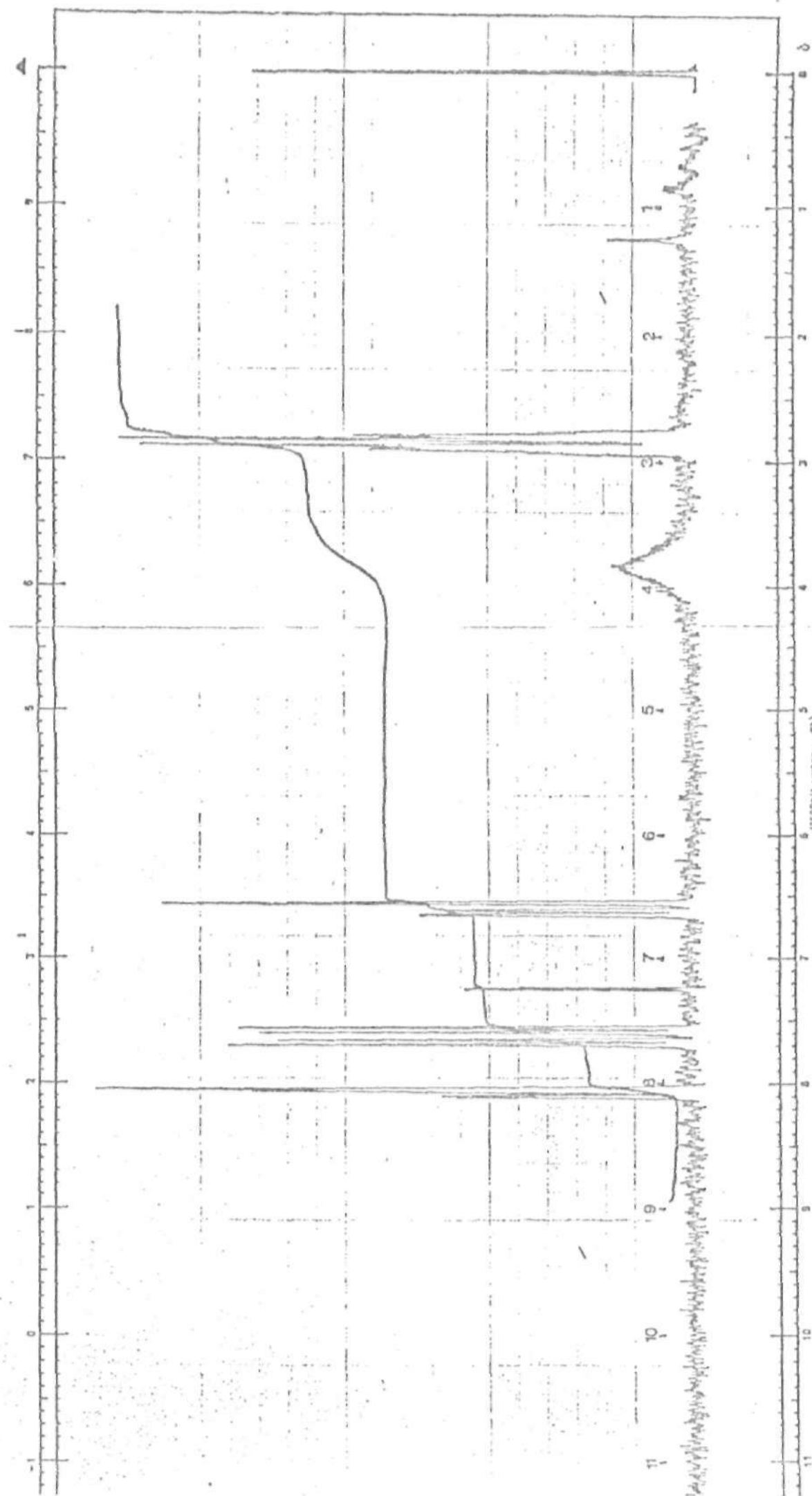


Fig. 4.2. An n.m.r. spectrum of 2-amino-7-nitro-9,10-dihydrophenanthrene.

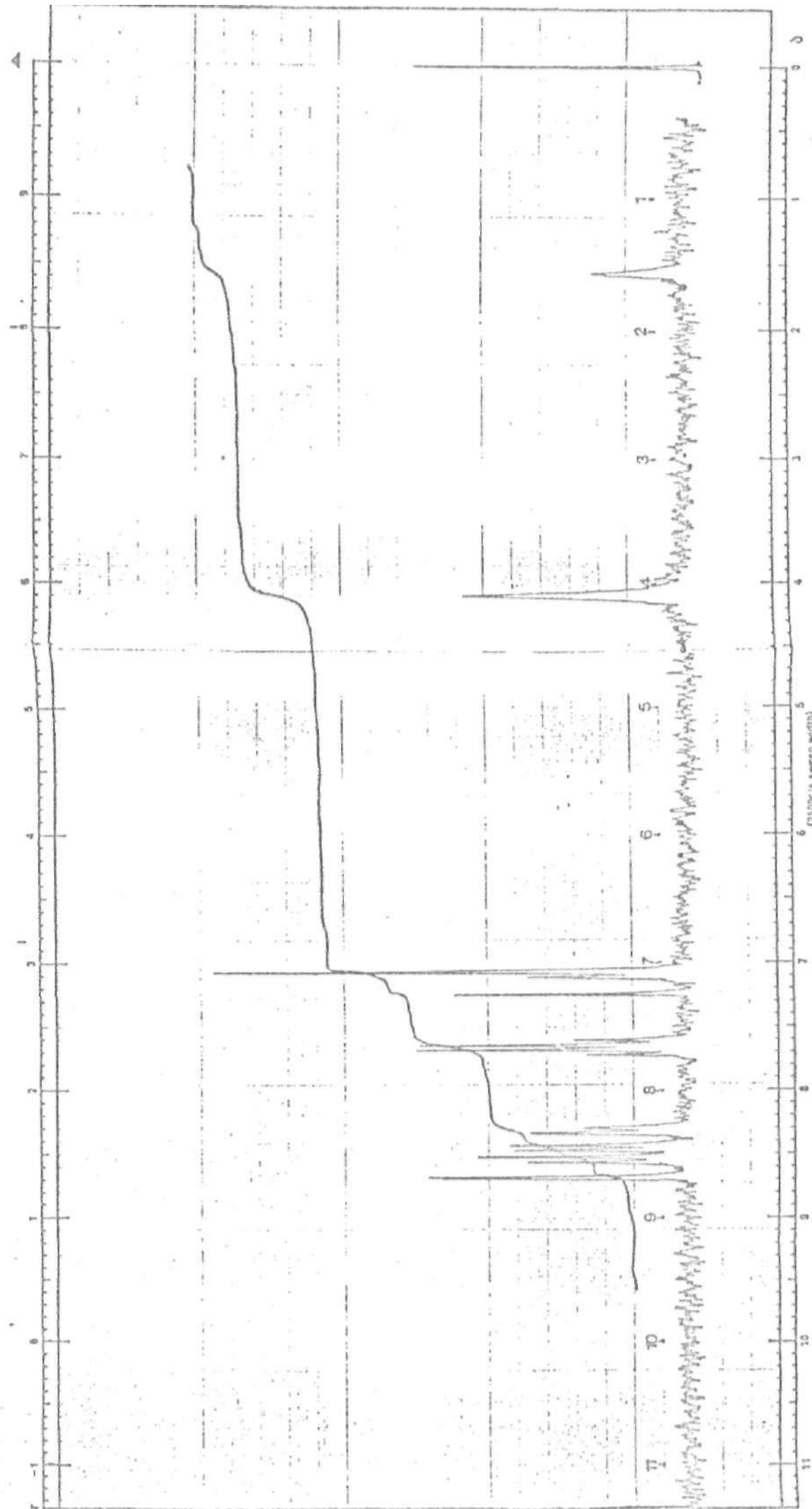


Fig. 4.3. An n.m.r. spectrum of 2-amino-7-nitrophenanthrene.

Table 4.2. Selective reduction of 4,4'-dinitrobiphenyl

<u>Run</u>	<u>Reducing agent/solvent</u>	<u>Yield(%)</u>
1	$\text{Na}_2\text{S}_x/\text{EtOH}$	35 ^a
2	$(\text{NH}_4)_2\text{S}/\text{EtOH}$	48
3	NaSH/MeOH	47
4	$\text{NaSH}/\text{MeOH-acetone}$	56
5	$\text{NaSH}/\text{MeOH-toluene}$	79 ^b

a ~ According to Ref.¹²⁰

b ~ Based on the N-acetyl derivative

The direct nitration of 9,10-dihydrophenanthrene is perhaps the most useful route to 2,7-disubstituted phenanthrenes since the parent hydrocarbon is relatively easy to prepare (Chart 4.6) and can be obtained commercially (although expensive). This route is attractive for the preparation of halonitrophenanthrenes since the nitro-amines obtained by selective reduction are easily diazotised. The main failure of the Sandmeyer reaction is usually associated with difficulties at the diazotisation stage. 2-Iodo-7-nitro-9,10-dihydrophenanthrene was prepared through the diazotisation of the nitro-amine in dilute hydrochloric acid followed by the addition of potassium iodide. Most methods found in the literature deal with symmetrical substitution and it is hardly surprising that 2-amino-7 nitrophenanthrene, prepared by selective reduction, is a new compound. Procedures leading to dihalogeno-phenanthrenes have been reported¹²¹ and from

these compounds diaminophenanthrenes can be obtained.¹²²

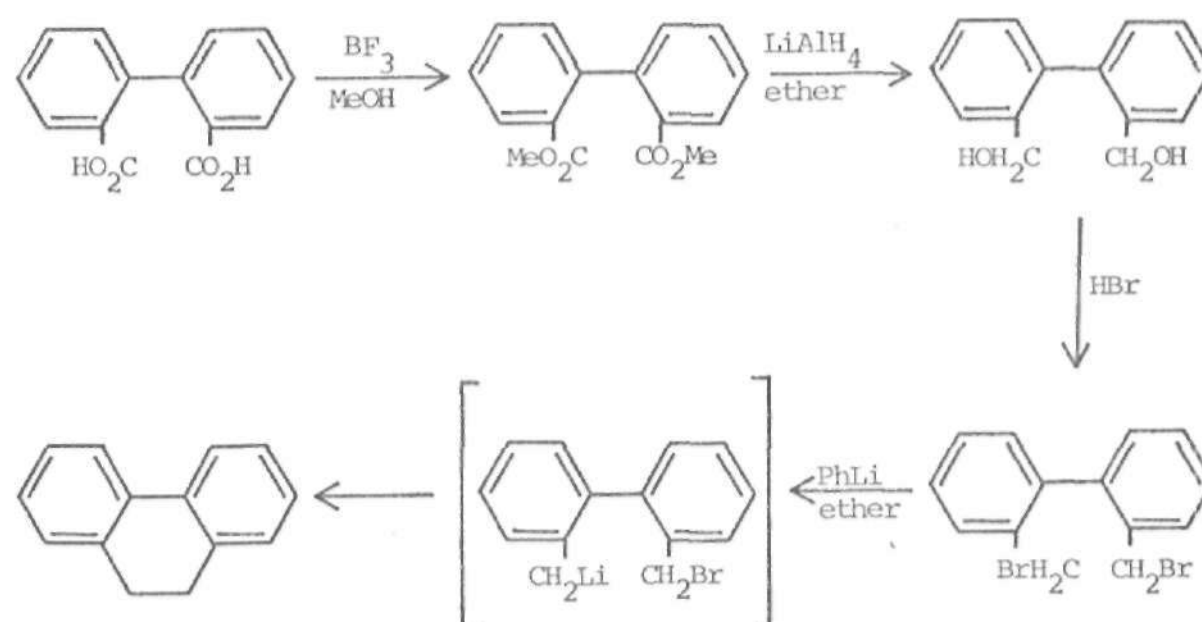


Chart 4.6. Synthesis of 9,10-dihydrophenanthrene.

2. 3,9-Disubstituted Phenanthrenes

Various 9-substituted phenanthrenes are known. In fact, one of the earliest phenanthrene derivatives with a substituent in a known orientation was phenanthrene-9-carboxylic acid (108), which was prepared by the Pschorr reaction.¹²³ The Pschorr reaction is the name given to a group of related procedures whereby polycyclic systems are formed by the union of two aryl nuclei, usually involving homolytic decomposition of a diazonium salt.

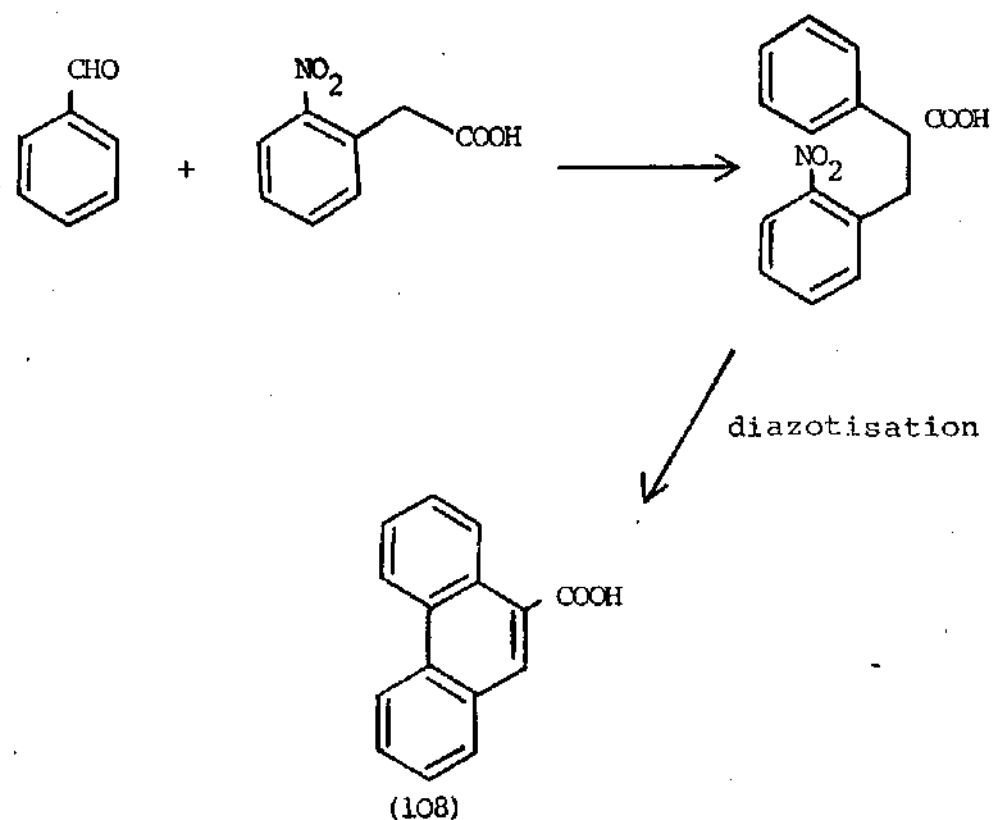


Chart 4.7. Synthesis of phenanthrene-9-carboxylic acid

If the Pschorr method is to be adopted, it is clear that a nitro-amine involving the 3,9-positions would be very difficult to prepare. 9-Bromophenanthrene was considered to be a useful alternative since it is easy to prepare on a large scale and can be used as the source of several intermediates (Chart 4.8).

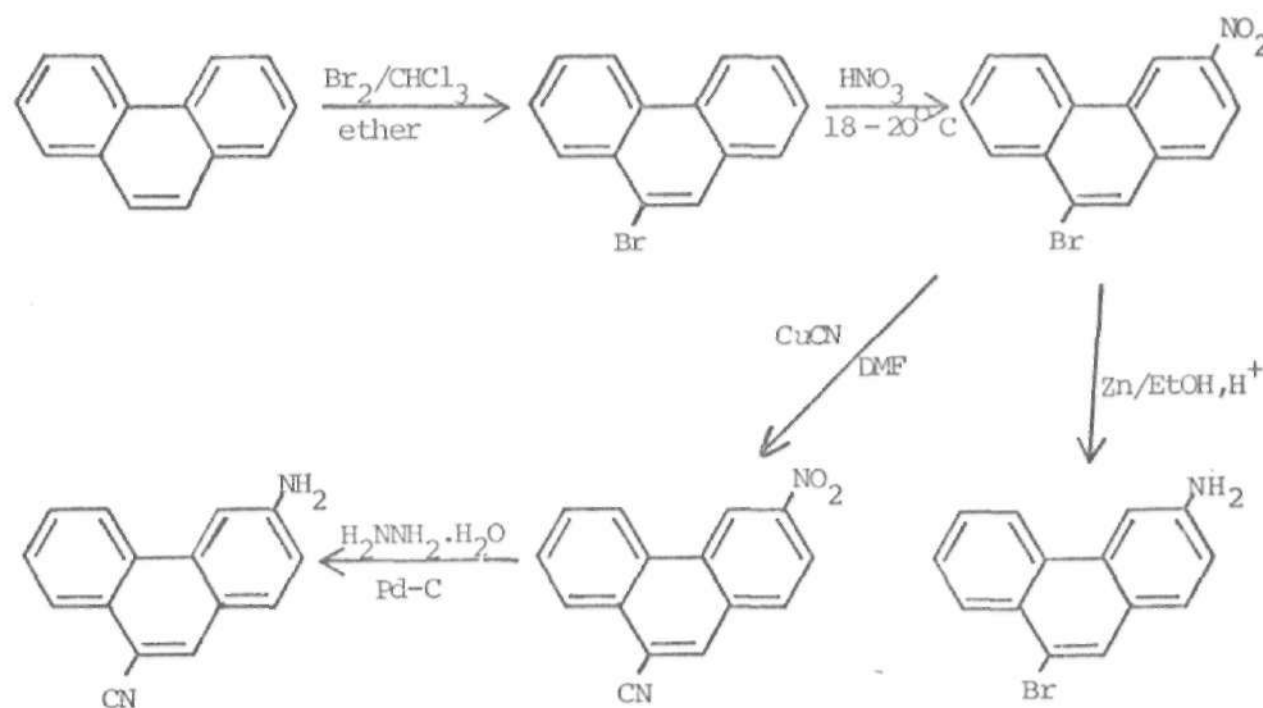


Chart 4.8. Intermediates derived from 9-bromophenanthrene.

(a) 9-Bromo-3-nitrophenanthrene and 3-amino-9-bromo-phenanthrene

9-Bromophenanthrene was obtained in high yield as described in the literature but with a slightly lower melting point. Nitration of the bromo compound using concentrated nitric acid at temperatures between 18 and 20°C afforded 9-bromo-3-nitrophenanthrene as the main product. Reasonable quantities of the nitro compound could be accumulated only after several runs, due to the poor yield. In general, substitution reactions in the phenanthrene ring are known to be accompanied by side-reactions owing to the strong tendency

towards polysubstitution. It is possible that a thorough investigation of the side products formed during the nitration would have afforded other useful isomers, but such a time-consuming approach did not appear to be worthwhile. The reduction of 9-bromo-3-nitrophenanthrene to the amine has been reported.¹²⁴ Zinc dust is added carefully to a boiling ethanolic solution of the nitro compound containing concentrated hydrochloric acid and the resultant hydrochloride amine is isolated and basified with dilute ammonia. This procedure provided the desired intermediate in reasonable yields.

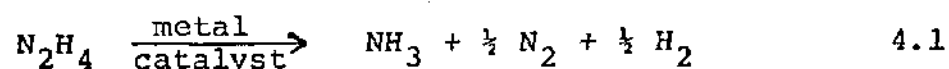
(b) 9-Cyano-3-nitrophenanthrene and 3-amino-9-cyano phenanthrene

The reaction of 9-bromo-3-nitrophenanthrene with copper(I) cyanide in refluxing dimethyl formamide (DMF) afforded 9-cyano-3-nitrophenanthrene.

An attempt to reduce the cyano compound to the corresponding amine using the technique described for 9-bromo-3-nitrophenanthrene was not fruitful. It appears that the hydrochloride of the amine is exceptionally stable. The nitro group was successfully reduced with hydrazine catalyzed by palladium charcoal.

The use of hydrazine to effect the reduction of nitro groups as well as the dehalogenation of halo compounds has been employed in a number of cases in the present work and it is appropriate to mention a few facts concerning this versatile reagent. The application of hydrazine for catalytic

reductions is widely known and is preferred to other reductive methods in a number of situations since rapid reactions take place without the use of pressure apparatus. There is some diversity of opinion concerning the decomposition of the hydrazine; different reactions have been suggested for the different hydrogenation catalysts commonly used, viz. Ni, Pd, Pt and sometimes Ru and Fe. The mode of the decomposition reaction may be written as



The exact quantities of the products will of course depend on the reaction conditions as well as on the actual catalyst used. For nitro reductions, it is generally assumed that any of the named catalysts can be employed, but Furst¹²⁵ has recommended palladium as the most suitable metal for dehalogenation purposes. The role of palladized charcoal appears to be the decomposition of hydrazine and to create more reactive sites.

(c) Hydrolysis of 3-amino-9-cyanophenanthrene

3-Amino-9-cyanophenanthrene obtained by catalytic reduction was heated for several hours with a 20% solution of sodium hydroxide in ethanol in order to convert the cyano group into the carboxyl group. The infrared spectrum of the isolated material, obtained in very poor yield, showed a broad band from 2600 to 3500 cm^{-1} , indicative of a hydroxyl group and a carbonyl stretch at 1650 cm^{-1} . Even though the

amino peaks had been submerged by the broad band described above, the disappearance of the sharp cyano peak at 2200 cm^{-1} was a further indication that the reaction did take place. The product appeared to be impure acid rather than the amide; the infrared spectrum differed greatly from that of an amide formed in an attempted amination of 9-cyanophenanthrene. This product had two bands at 3200 and 3380 cm^{-1} due to N-H stretching and one peak at 1585 cm^{-1} , which is probably due to N-H bending, in addition to a strong carbonyl stretching band at 1640 cm^{-1} . Mosby¹¹⁴ in an attempt to hydrolyze 10-nitro-9-phenanthrenecarbonitrile, used 85% phosphoric acid or 96% sulphuric acid in boiling acetic acid, but in each case the nitronitrile was unaffected. Under alkaline conditions, Mosby reported the hydrolysis of the nitro group giving 10-hydroxy-9-phenanthrenecarbonitrile. The impure product, obtained in the present attempted hydrolysis was not pursued further owing to lack of time, neither could other methods be investigated.

(d) Attempted amination of 9-bromo-3-nitrophenanthrene

An ethanolic suspension of 9-bromo-3-nitrophenanthrene to which concentrated ammonia had been added was heated to 120°C in an attempt to replace the bromine atom with the amino group. Unfortunately, the expected reaction did not take place thereby suggesting that the bromine atom is unexpectedly not as labile as chlorine since the latter is replaced under similar conditions.

(e) 3-Aminophenanthrene

The reduction of bromonitrophenanthrenes with commonly used reducing agents is known to lead to debromination. Schmidt¹²⁶ and later Austin¹²⁷ attempted the reduction of 9-bromo-10-nitrophenanthrene with tin(II) chloride, zinc and acid as well as ammonium sulphide, but in each case the aminophenanthrene was obtained. When 9-bromo-3-nitrophenanthrene was treated with hydrazine hydrate with palladium charcoal, 3-aminophenanthrene was obtained. The colourless amine had the same melting point (86 - 87°C) as that reported for the α -form of this compound in the literature.¹²⁸

(f) An alternative route to 3-amino-9-bromophenanthrene

Apart from the nitration of 9-bromophenanthrene and subsequent reduction of the nitro compound to 3-amino-9-bromophenanthrene, the latter was also prepared using a method reported by Schultz *et al.*¹²⁹ (Chart 4.9).

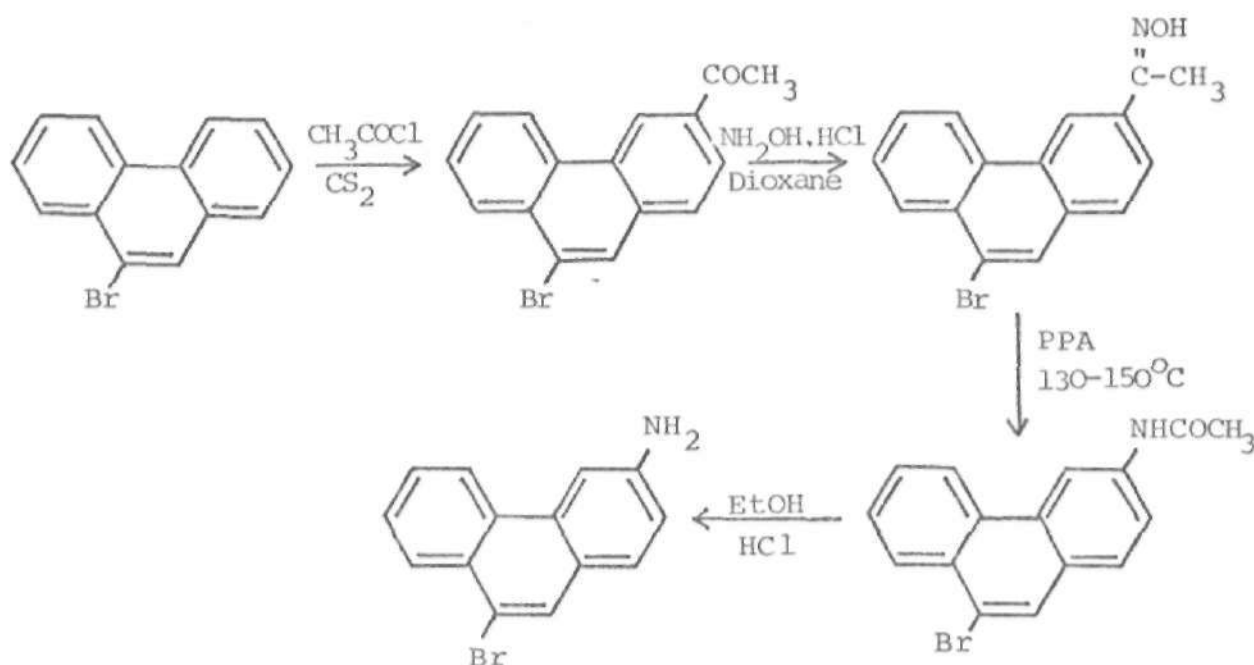


Chart 4.9. Preparation of 3-amino-9-bromophenanthrene.

Acetylation of 9-bromophenanthrene gave a product the yield and purity of which depended on the condition of the anhydrous aluminium chloride; curiously enough, purer products were obtained with less active samples of the catalyst. The conversion of the acetyl derivative into the oxime was quantitative and the infrared spectrum clearly indicated the disappearance of the carbonyl band around 1670 cm^{-1} . The oxime was treated with polyphosphoric acid (PPA) at 150°C for 10 min and then poured into water. The precipitate was filtered off and extracted with hot benzene. On evaporation of solvent, a 70% yield of 3-acetylamino-9-bromophenanthrene was obtained. Hydrolysis of the substituted amide was achieved with difficulty by refluxing the material for 24 hours in a 50:50 mixture of ethanol and concentrated hydrochloric acid followed by basification of the resulting amine hydrochloride.

(g) 3-Dimethylaminophenanthrene

3-Amino-9-bromophenanthrene offered a new route to another known compound, 3-dimethylaminophenanthrene (109).¹³⁰ The three stage process (Chart 4.10) gave the desired compound in a higher yield (70%) than that reported previously.¹³⁰ As shown in Chart 4.10, the aminobromophenanthrene was treated with an excess of methyl iodide to obtain the quaternary salt which was purified and then decomposed by refluxing overnight with methanolic sodium methoxide. The resulting product when crystallised from ethanol had m.p. $112-113^{\circ}\text{C}$ in agreement with that reported¹³¹ for 9-bromo-3-dimethylaminophenanthrene.

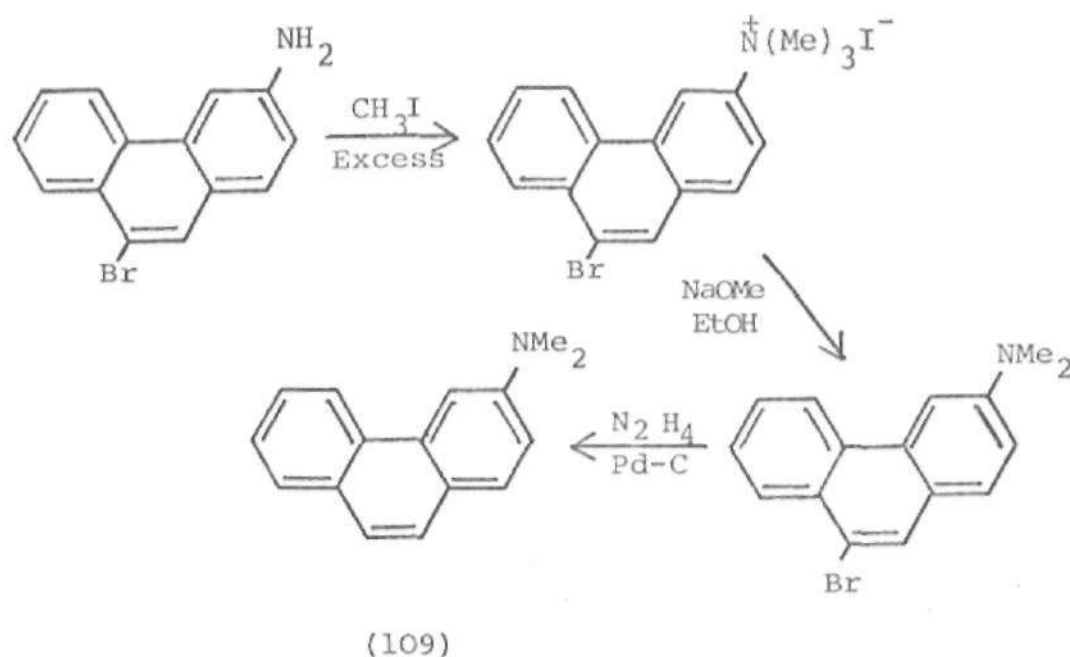


Chart 4.10. Preparation of 3-dimethylaminophenanthrene.

Two methods of debromination were attempted. In the first method, butyl-lithium was prepared as described by Hallas and Waring¹³² and added to a solution of 9-bromo-3-dimethylaminophenanthrene in ether. On work-up the product proved to be unchanged starting material. However, the second method involving the use of palladised charcoal and hydrazine was successful. 3-Dimethylaminophenanthrene was obtained as envisaged.

3. 3,6-Disubstituted Phenanthrenes

The preparation of 3,6-dinitrophenanthrene has been reported by Bacon¹¹³ and Staab¹¹⁷ in a multi-stage procedure (Chart 4.11).

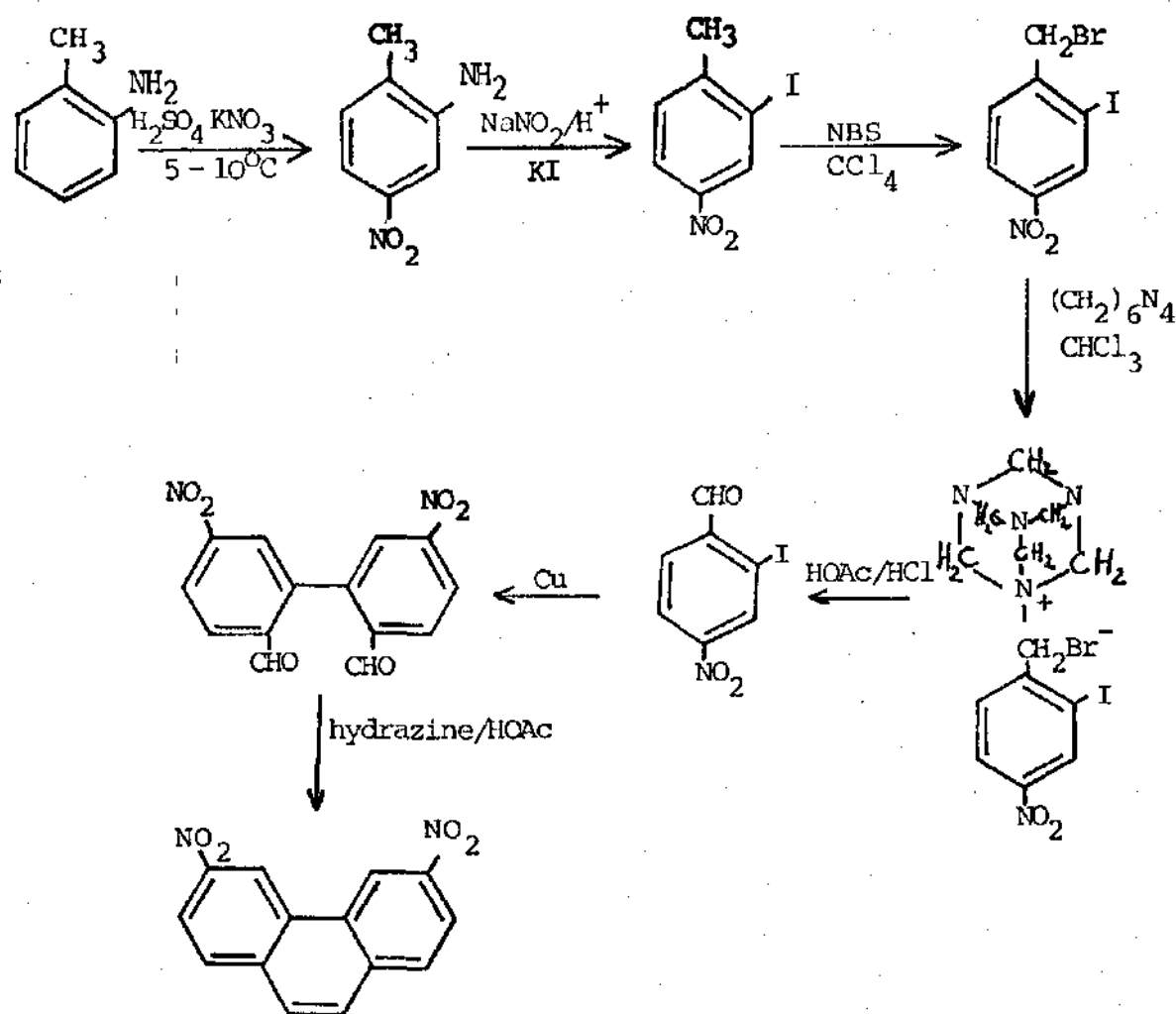


Chart 4.11. Route to 3,6-dinitrophenanthrene.

o-Toluidine was nitrated in ten times its mass of concentrated sulphuric acid by the gradual addition of finely powdered potassium nitrate to give a 63% yield of the required nitro compound, m.p. 100°C in agreement with the literature value.¹³³

Diazotisation of the amino group and subsequent treatment with potassium iodide gave the crude iodo compound as a dark oil which was treated with sodium dithionite with occasional heating on a water bath until a brown solid resulted. This

material was subjected to a prolonged distillation in steam to obtain a pure light yellow iodo compound. Although this method of purification is laborious and time-consuming, it proved to be the most suitable. Willgerodt and Kok¹³⁴ gave the melting point of their product as 58°C. The best sample obtained in the present work had m.p. 53-54°C; a similar melting range has been reported by Bacon and Lindsay.¹¹³

The direct oxidation of the methyl group in the Étard reaction¹³⁵ via the corresponding diacetate is a useful step to aldehydes whose substituents are not attacked by the oxidising agents employed or which do not influence the course of the reaction. The two oxidising agents normally used are chromium trioxide and chromyl chloride in inert solvents such as carbon disulphide or carbon tetrachloride. Aldehydes are obtained sometimes in yields exceeding 80%, although side products, namely, acids, chlorinated compounds and ketones have been observed. A typical example of the Étard reaction is the preparation of *p*-nitrobenzaldehyde (Chart 4.12).

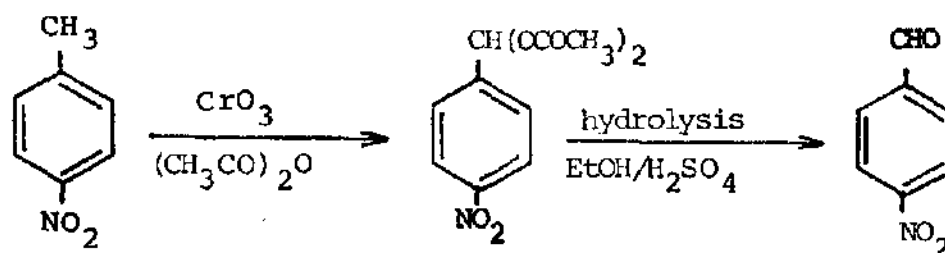


Chart 4.12. Synthesis of *p*-nitrobenzaldehyde.

The related 2-iodo-4-nitrotoluene under similar conditions did not oxidise to the expected aldehyde. It appears that

- (i) the introduction of electron withdrawing groups (e.g. NO_2), particularly in the ortho and para positions, weakens the bond between the benzene ring and the methyl group thereby rendering the formation of the addition compound very difficult; even if such a compound is formed, the original material is generally regenerated on hydrolysis;
- (ii) the introduction of bulky ortho substituents causes severe steric hindrance;
- (iii) halogenation leads to a decrease in reactivity and this is particularly pronounced for iodine; o-iodotoluene does not give the expected aldehyde, under the Étard reaction conditions, instead o-iodobenzylidene chloride has been reported as the chief product.¹³⁶

Sacks and Kempf¹³⁷ and later Mittal¹³⁸ obtained a series of dinitrochlorobenzaldehydes using p-nitrosodimethylaniline in the presence of ethanol to effect the oxidation of the methyl group. However, the more recent method used by Bacon and Lindsay¹¹³ was adopted. In this method, the side chain is brominated using N-bromosuccinimide (NBS) and the bromo compound converted into a complex salt by the action of hexamethylenetetramine (urotropin) in what is popularly known as the Sommelet reaction. The salt so obtained was added to acetic acid and heated under reflux with the addition of concentrated hydrochloric acid; a white precipitate ensued on pouring the mixture into water. Crystallisation from cyclohexane gave 2-iodo-4-nitrobenzaldehyde as fine yellow

needles, m.p. 83-84°C.

An attempt to prepare 5,5'-dinitrobiphenyl-2,2'-dialdehyde by means of activated copper bronze in the Ullmann reaction gave a product with a very low melting point, possibly an impure form of *p*-nitrobenzaldehyde. Although the possible causes of failure were not investigated fully, owing to lack of time, it is likely that the purity of the dimethyl formamide solvent used in the reaction influences the reaction much more than expected. Once the dialdehyde has been obtained, conversion into the dinitrophenanthrene using hydrazine hydrate in acetic acid takes place smoothly. However, subsequent theoretical considerations mentioned earlier in the present work made the quest for the desired nitro-amine less urgent.

4. Naphthalene Derivatives

Although routes to all the nitronaphthylamines are known, it was considered undesirable to repeat many of the procedures owing to the carcinogenic properties of the starting materials. Attention was centred around methods which avoided the use of 2-aminonaphthalene. Whenever 1-aminonaphthalene was used it was carefully converted into the acetyl derivative. In this way, 1-amino-4-nitronaphthalene and the 2-nitro isomer were prepared by nitration and hydrolysis.

Although Meisenheimer and Patzig¹³⁹ claimed the preparation of 1-amino-2-nitronaphthalene by direct amination,

it was the more recent work by Barton *et al.*¹⁴⁰ that prompted an attempt at this nucleophilic reaction. Barton and his collaborators prepared 9-amino-10-nitrophenanthrene by treating 9-nitrophenanthrene and hydroxylamine in methanol at 60°C with potassium hydroxide; moderate yields of the *o*-nitro-amine were claimed. An analogous mechanism for the amination of 2-nitronaphthalene is shown in Chart 4.13.

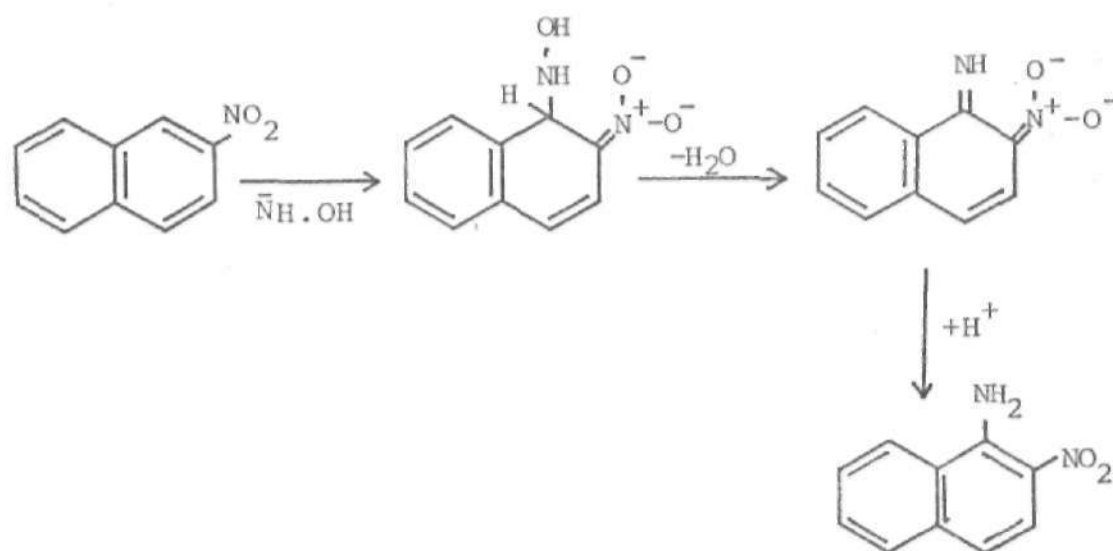


Chart 4.13. Mechanism for the direct amination of 2-nitronaphthalene.

Working at the reflux temperature, instead of 60°C as used by Barton, the mixture of 2-nitronaphthalene, hydroxylamine and potassium hydroxide in methanol gave a 50% yield of crude nitro-amine. The product was purified on alumina to give a

sample with a melting point identical to that quoted in the literature¹⁴¹ (144°C). From the proposed mechanism it appears that any strong electron acceptor in place of the nitro group would enable the reaction to take place. Unfortunately, it was not possible to prepare an appropriate compound to test this assumption. For example, 9-cyanophenanthrene would undoubtedly be affected under the stated reaction conditions.

1-Amino-5-nitronaphthalene was obtained through the selective reduction of 1,5-dinitronaphthalene in rather low yields. The reducing agent was prepared in a similar manner to that described previously for the 2,7-dinitrophenanthrene derivatives.

1-Amino-7-nitronaphthalene has been prepared by two different routes. Věselý and Dvořák¹⁴² selectively reduced 1,7-dinitronaphthalene thereby obtaining 1-amino-7-nitronaphthalene in a very low yield; Hodgson and Turner¹⁴³ obtained a purer sample with an improved yield in their selective reduction of the dinitro compound. 2-Nitronaphthalene was nitrated to give a mixture of 1,6- and 1,7-dinitronaphthalene but separation of the two components was difficult. An alternative route, due to Schroeter,¹⁴⁴ was therefore adopted.

α -Tetralone (1,2,3,4-tetrahydro-1-oxo-naphthalene) was nitrated according to Braun's method,¹⁴⁵ to give a pure sample of 7-nitrotetral-1-one. The nitrotetralone was converted into the oxime which on crystallisation had m.p. 170°C (Schroeter¹⁴⁴

gives m.p. 150°C , but Hardy, Ward and Day¹⁴⁶ who re-investigated Schroeter's method gave m.p. $167-169^{\circ}\text{C}$). The oxime was dissolved in a mixture of acetic acid and acetic anhydride and the solution was saturated with dry hydrogen chloride; basification of the reaction mixture with sodium acetate gave a red precipitate of the required nitro-amine but only in a very poor yield.

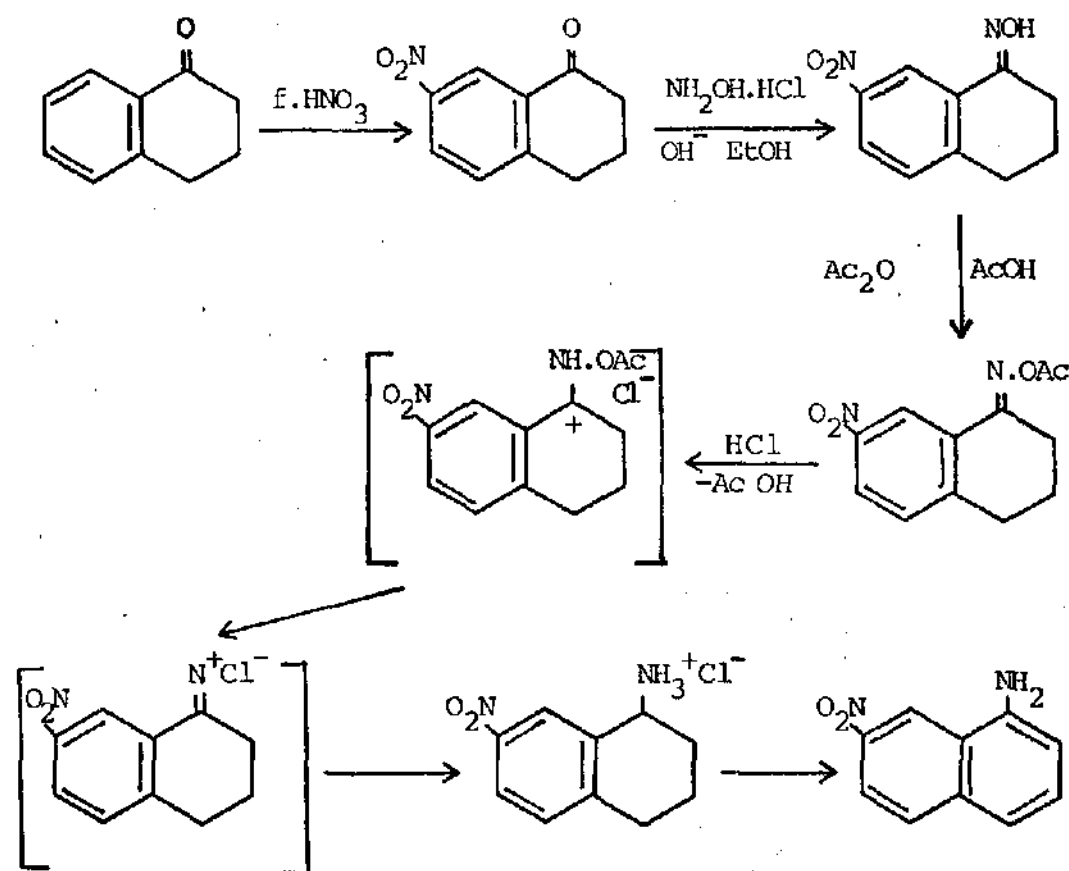


Chart 4.14. Route to 1-amino-7-nitronaphthalene.

1,3- and 2,7-Dinitronaphthalenes were prepared as reported in the literature¹⁴⁷ with the hope of obtaining 1-amino-3-nitronaphthalene and 2-amino-7-nitronaphthalene, respectively, through selective reduction. However, only small amounts could be obtained so that the rather low-yield selective reduction step was not attempted.

A mixture of 8-nitro-, 6-nitro- and 1-nitro-2-isomers was separated as reported in the literature.¹⁴⁸

Further work in the naphthalene series was discontinued as the area was becoming too restrictive, but certain intermediates obtained from ICI Manchester were used for the preparation of some azo dyes. Certain of these intermediates were used directly, but chromatographic purification was necessary in one or two cases.

II. Preparation of Couplers

Four main couplers were used in the present investigation. N,N-Diethylaniline was a BDH Analar product and was used without further purification. The other couplers used were N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline, kairolin (N-methyl-1,2,3,4-tetrahydroquinoline) and julolidine (2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizine).

N-2-Cyanoethyl-1,2,3,4-tetrahydroquinoline was prepared as described by Whitmore¹⁴⁹ (Chart 4.15).

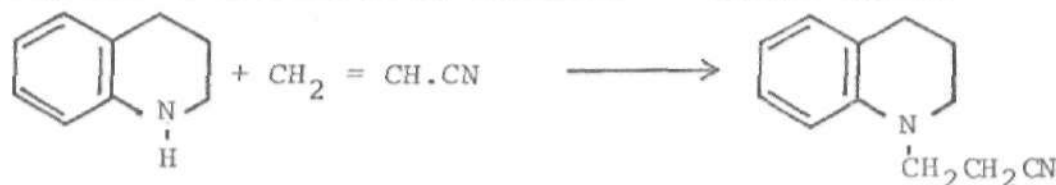


Chart 4.15. Preparation of N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline.

The almost colourless oil collected from a vacuum distillation was carefully stoppered and kept for long periods without any noticeable change in appearance.

Kairolin (N-methyl-1,2,3,4-tetrahydroquinoline) was prepared by largely following the method of Castelino,¹⁵⁰ giving the colourless quaternary salt (Chart 4.16). Dequaternization was, however, achieved through the less tedious technique of Ho.¹⁵¹ In this procedure, the ammonium salt is added to dimethylformamide (DMF) followed by the calculated amount of sodium azide (or any other suitable reagent as suggested by Ho) and the mixture heated under reflux for 2-3 h.

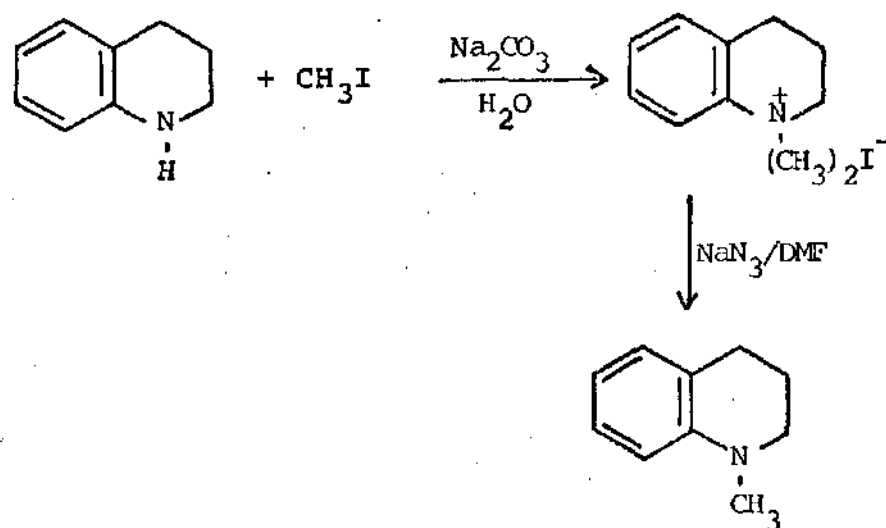
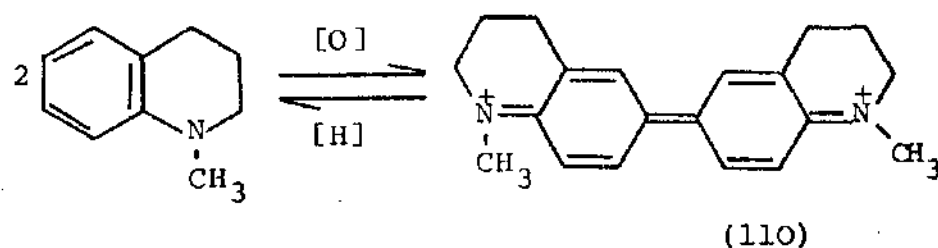


Chart 4.16. Preparation of kairolin.

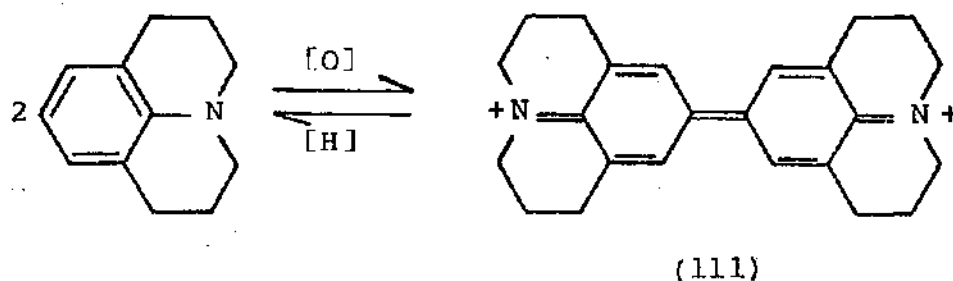
This simple method of dequaternization gives comparable yields to more time-consuming techniques found in the literature.¹⁵² Kairolin is a colourless oil when pure but yellow-brown on keeping; this behaviour can probably be associated with the

formation of an oxidative self-coupling product (110).

Similar behaviour is noted for lilolidine and julolidine.¹⁵³



Julolidine (2,3,6,7-tetrahydro-1H,5H-benzo[*ij*]quinolizine) was obtained by following the procedure of Glass and Weissberger.¹⁵⁴ As mentioned above, julolidine, a colourless solid, becomes red¹⁵³ on standing owing to the formation of compound (111).



III Preparation of Dyes

1. Diazotisation

(a) Direct Method

Although the diazotisation of most nitro-amines in the naphthalene series has been described by Hodgson,¹¹⁵ some of the reported methods are open to improvement. In general, the diazotisation of the nitro-amines proceeded more efficiently if the amine was first dissolved in acetic acid with warming

and then poured into a dilute acid solution, usually hydrochloric acid. The thick amine hydrochloride was cooled rapidly to near zero with the addition of ice. A solution of sodium nitrite in the minimum amount of water was added to the suspension with vigorous stirring. There were minor variations in the diazotisation technique depending on the amine while some derivatives, such as 1-amino-4-nitronaphthalene, were relatively easy to diazotise, others particularly those sterically hindered were not; in the case of 1-amino-2-nitronaphthalene no suitable variation of the direct route could be found. On the whole, nitro-amines from the 2,7-phenanthrene series diazotised more readily than the naphthalene nitro-amines.

(b) Nitrosylsulphuric acid Method

Sodium nitrite was added to previously cooled concentrated sulphuric acid at such a rate that brown fumes were not evolved. After the addition, the mixture was warmed gradually on a water-bath to between 65-70°C when all the sodium nitrite went into solution. The clear solution was cooled externally to zero and the polycyclic amine, usually dissolved in pyridine, was added dropwise to the nitrosylsulphuric acid paste with vigorous agitation. In some cases it was necessary to dilute the diazotisation mixture with weak acids, such as glacial acetic acid or polyphosphoric acid; dilution with water sometimes resulted in the precipitation of the amine. In almost all cases, some unreacted nitro-amine was filtered off leaving a clear diazotised solution for subsequent use.

2. Coupling

The coupler was dissolved or suspended in an acetic acid buffer, prepared by adding sodium acetate to a 1:2 mixture of acetic acid and water, with slight heating. The solution or suspension was then cooled to zero and the diazonium solution was added at such a rate that nitrous gases were not liberated. It was not always possible to control the acidity of the reaction since this depended to a large extent on the amount of acid used at the diazotisation stage.

Dyes derived from N,N-diethylaniline were generally crystalline and fairly pure. The remaining couplers gave dyes which were either resinous or oily.

3. Purification

The purity of the dye was first checked by thin layer chromatography and the amount of impurity estimated from the different bands on the plate.

In some cases a single solvent could be used as eluant in a column chromatographic treatment. More often, however, a mixture of solvents had to be employed to achieve the desired result. In the case of relatively pure dyes, the recovered product from the column was crystallised from an appropriate solvent.

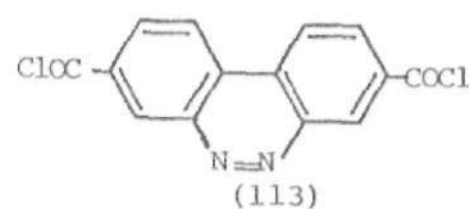
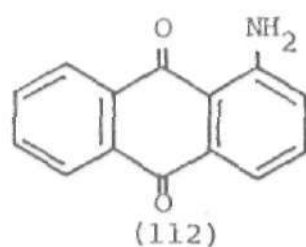
In certain cases, a preparative thin layer chromatographic plate was necessary to permit the separation of pure dye. Recrystallisation was generally achieved from light petroleum or from ethanol.

As some stages of purification did not involve all of the dye prepared, percentage yields are generally quoted for the crude dye.

IV Miscellaneous

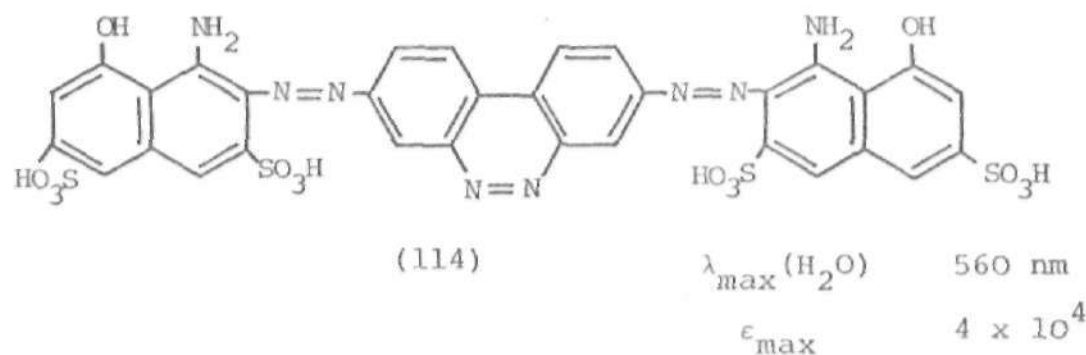
1. Dyes Derived from Benzo[c]cinnoline

Replacement of the 9,10-linkage in phenanthrene by an azo group gives 9,10-diazaphenanthrene, better known as benzo[c]cinnoline. This system was used for the preparation of vat dyes¹⁵⁵ in the early 1930s; these dyes were prepared by condensing two equivalents of 1-aminonanthraquinone (112) with acid chlorides such as (113).

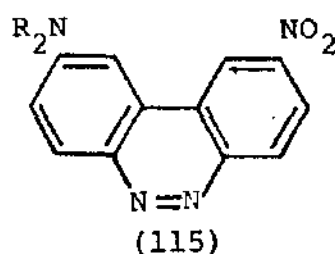


Related compounds were similarly derived from carbozole and fluorene.

A recent example of the use of the benzo[c]cinnoline system for the preparation of disazo dyes such as (114) has been reported by Krasovitskii *et al.*¹⁵⁶



Owing to the absence in the literature of simple derivatives of benzo[c]cinnoline with appropriate substituents in the 3- and 6-positions, it initially appeared worthwhile to attempt the synthesis and examination of compounds such as (115) which incorporate a fixed cis

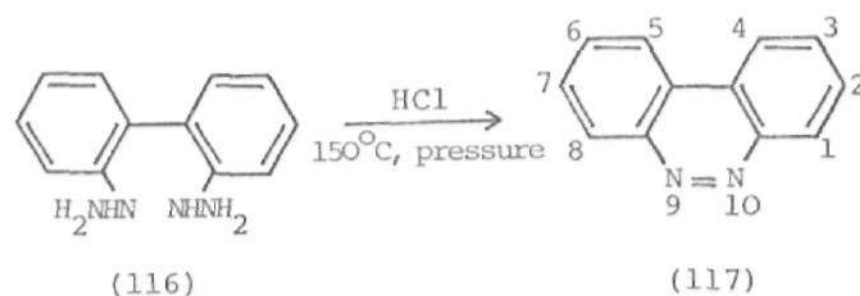


azo linkage. It was also felt that the preparation and study of suitable 2,7-disubstituted benzo[c]cinnolines would be of value.

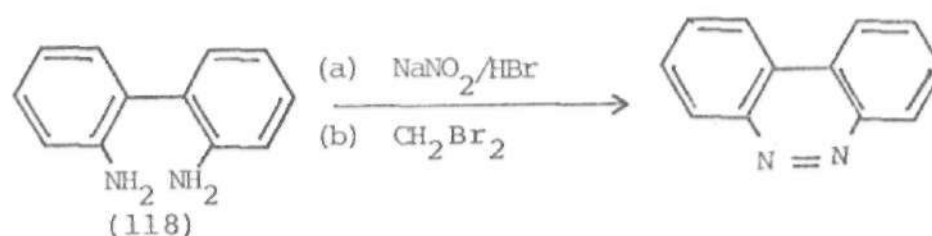
2. Routes to Benzo[c]cinnoline

Various methods of preparing benzo[c]cinnoline are known.¹⁵⁷ The most frequently used routes are briefly listed.

- (i) The reduction of 2,2'-dinitrobiphenyl using reagents such as sodium amalgam,¹⁵⁸ 'reduced iron',¹⁵⁹ Raney nickel,¹⁶⁰ zinc dust,¹⁶¹ lithium tetrahydridoaluminate(III)¹⁶² and sodium sulphide.¹⁶³
- (ii) The treatment of 2,2'-dihydrazinobiphenyl (116) with hydrogen chloride at 150°C under pressure.¹⁶⁴ The numbering for the parent structure adopted in the present work is shown in (117).



- (iii) The tetrazotisation of 2,2'-diaminobiphenyl (118) and subsequent treatment with copper(I) bromide.¹⁶⁵



- (iv) The photochemical cyclodehydrogenation of azobenzene in an acidic medium.¹⁶⁶

3. Preparation of Benzo[c]cinnoline Intermediates

Although Lewis *et al.*¹⁶⁷ have prepared several derivatives of benzo[c]cinnoline photochemically, this route was considered impracticable in the present investigation since the presence of nitro groups can lead to unwanted side reactions. Additionally, it would be difficult to obtain reasonable quantities of the desired intermediates. A synthetic approach was therefore adopted for the preparation of 2,7- and 3,6-disubstituted benzo[c]cinnolines.

Unfortunately, the direct nitration of benzo[c]cinnoline has not yet been achieved. King and King,¹⁶⁸ however, were able to nitrate the N-oxide (119) (Chart 4.17).

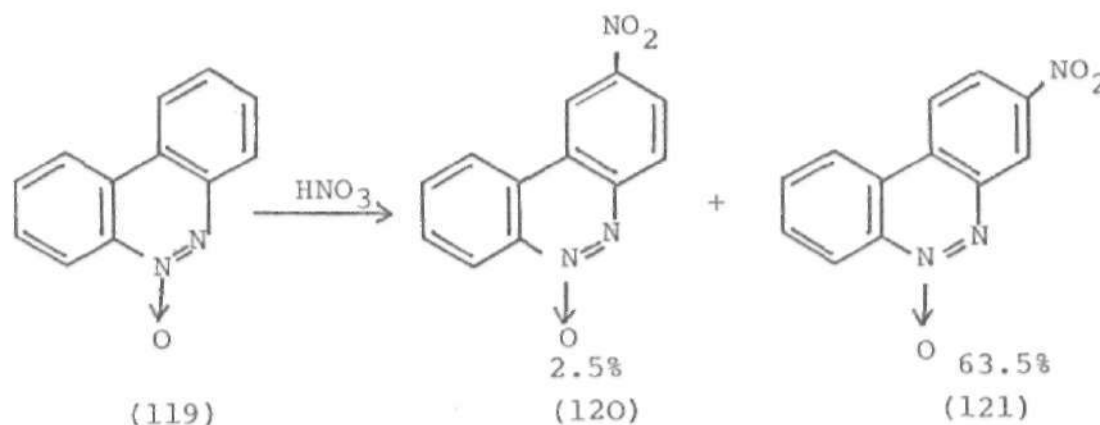


Chart 4.17. Nitration of benzo[c]cinnoline.

This route did not appear promising for the synthesis of disubstituted derivatives since, in particular, further nitration of either (120) or (121) would lead to a variety of products.

Thus, in order to prepare appropriate 2,7-disubstituted derivatives of benzo[c]cinnoline, the route shown in Chart 4.18 was adopted.

The tetranitrobiphenyl was prepared by means of an Ullmann reaction using activated copper bronze. The final stage in the reaction sequence shown in Chart 4.18 was undertaken in accordance with the findings of Ross and Kuntz.¹⁶⁹ These workers investigated both catalytically and chemically neighbouring group interaction in the reduction of 2,2'-dinitro-4,4'-bis(trifluoromethyl)biphenyl (123).

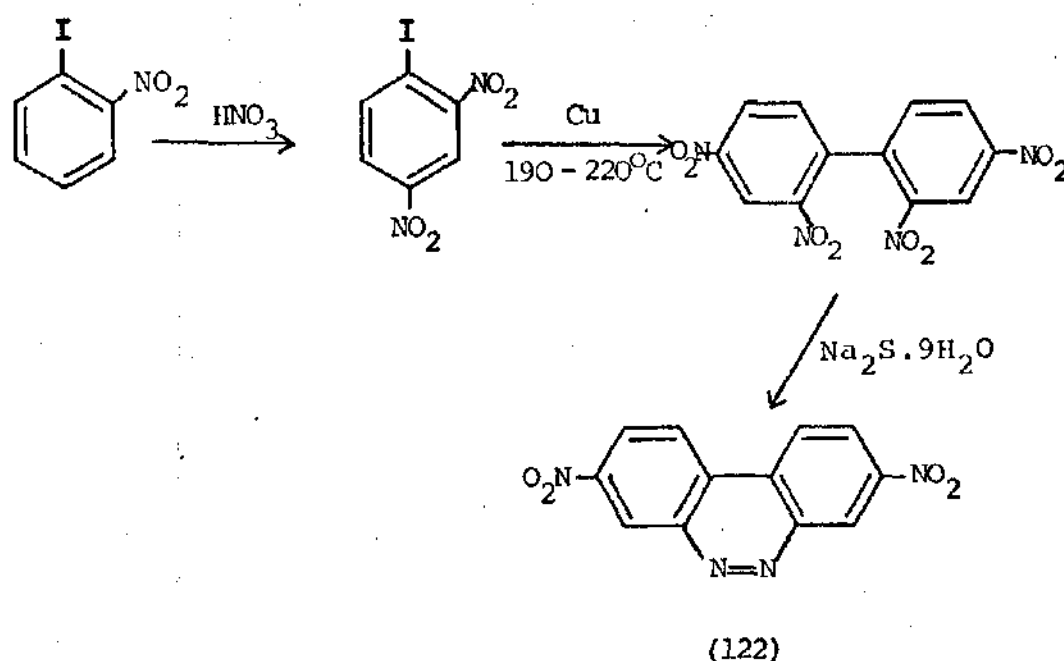
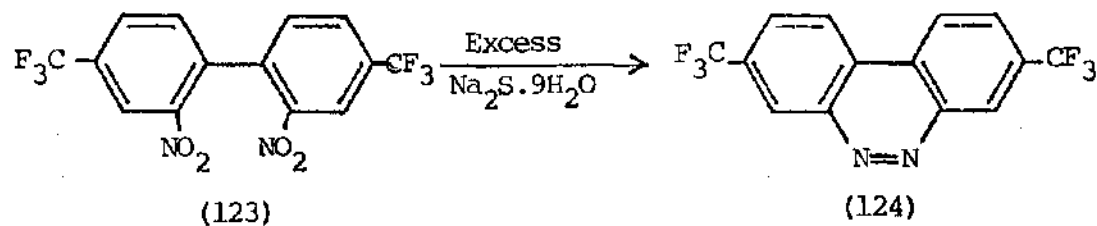


Chart 4.18. A possible route to a disubstituted benzo[c]cinnoline.



It was found possible to obtain (124) as the predominant product by varying the amount of sodium sulphide; the N-oxide and the N,N-dioxide were present as byproducts. The amount of reducing agent required was calculated per nitro group. Adaptation of this procedure to hopefully obtain compound (122) led to inconclusive results owing to the presence of a mixture of products.

The complexity of this type of reaction can be appreciated by following the postulated stages in the cata-

lytic reduction of 2,2'-dinitrobiphenyl to the diamine.¹⁷⁰
 (Chart 4.19). It is not altogether surprising that the
 presence of two additional nitro groups results in complex
 reaction mixtures.

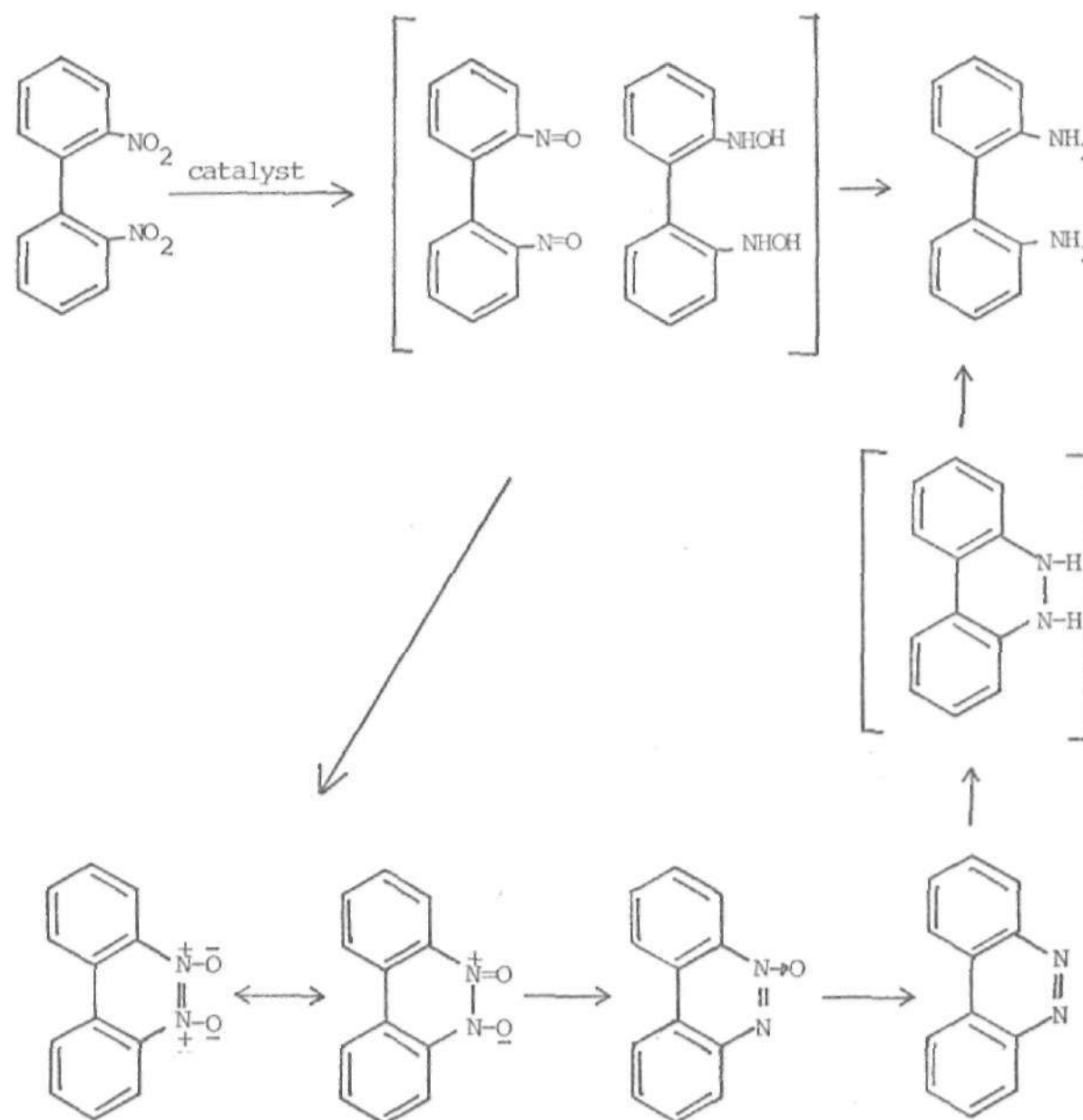


Chart 4.19. Mechanistic representation of the reduction
 of 2,2'-dinitrobiphenyl.

Bavin¹⁷¹ carried out the reduction of 2,2'-dinitro-biphenyl under different conditions and concluded that benzo[c]cinnoline, which is an intermediate product in the reaction sequence, could be obtained in yields exceeding 90% by using Raney nickel of low activity as the catalyst. Unfortunately, detailed investigations could not be carried out owing to lack of time.

The synthetic difficulties experienced in these efforts to prepare 2,7-disubstituted benzo[c]cinnolines led to the abandoning of attempts to prepare similar 3,6-disubstituted derivatives.

EXPERIMENTAL DETAILS

Notes

1. Melting points were determined using a Gallenkamp apparatus and are uncorrected. In certain cases, purity was checked by means of differential thermal analysis (DTA).
2. Visible and ultraviolet spectra were measured on a Unicam SP 800 recording spectrophotometer using the 'fast scan' mode, and a slit width of 0.02 mm.
3. Infrared absorption spectra were recorded on a Perkin Elmer 157G spectrophotometer.
4. Nuclear magnetic resonance spectra were determined at the Physico-Chemical Measurements Unit, Harwell using Varian HA 100 and HR 220 instruments.
5. Elemental analyses were carried out in the School of Chemistry at the University of Leeds.
6. Thin layer chromatographic (t.l.c.) plates were prepared from aluminium oxide 150 neutral (Type T). Chromatographic columns were prepared using woelm neutral alumina.

General Procedures

1. Preparation of 'sodium sulphide reagent' for the selective reduction of dinitro-compounds

A 13% aqueous solution of sodium sulphide nonahydrate (ca. 100 ml) was treated with sodium hydrogencarbonate (28 g) and methanol (100 ml) was added. The thick white precipitate was filtered off, washed with methanol (100 ml) and the clear filtrate used immediately for the reduction of dinitro-compounds.

2. Diazotisation of amines by the direct method

The amine (ca. 0.01 mole) was added to a 10-20% (v/v) aqueous solution of hydrochloric acid (25 ml) and warmed until it dissolved. Ice (20 g) was introduced directly to the hot solution, which was cooled rapidly to between 0 and 5°C. An equimolar solution of sodium nitrite (NaNO_2) in the minimum amount of water was added gradually to the well-stirred amine hydrochloride, maintaining the temperature at about 0°C. In some cases, a solution of the amine in glacial acetic acid was poured into one of dilute hydrochloric acid prior to diazotisation at 0°C. Stirring was continued for a maximum period of 1h, after which the unreacted amine (if any) was filtered off and the clear diazonium solution was kept at 0°C until required.

3. Preparation of Nitrosylsulphuric Acid

Sodium nitrite (ca. 1g) was added portionwise to ice-cold concentrated sulphuric acid (ca. 10 ml) with vigorous agitation. The temperature of the mixture was raised gradually (water-bath) to between 65 and 70°C and kept in this range until all the salt dissolved. The solution was cooled, usually in a salt-ice mixture, to 0°C. A solution of the amine (5 ml) to be diazotised (in an organic solution) was then introduced slowly to the thick paste which was stirred vigorously after each addition.

4. Preparation of Coupling Component Solutions for Azo-coupling

The coupler (ca. 0.01 mole) was added to a buffer, prepared as follows. Finely divided anhydrous sodium acetate was added to a 2:1 mixture of water and glacial acetic acid. The suspension of the coupler in the acidic buffer was generally warmed slightly to assist dissolution before external cooling to 0°C.

Part AGeneral IntermediatesI Naphthalene Derivatives1. 1-Amino-2-nitronaphthalene

A mixture of 2-nitronaphthalene (3 g) and hydroxylamine hydrochloride (7.5 g) in methanol (150 ml) was heated by means of an isomantle to about 50°C; a solution of potassium hydroxide (15 g) in methanol (90 ml) was added in one portion and the whole was refluxed for 8 h. The resulting orange mixture was filtered to remove unwanted material. After removal of solvent in a rotary evaporator, the orange-yellow residue was triturated with water (50 ml), filtered and dried. Crystallisation of the crude material from ethanol gave a product (1.8 g) which was further purified by column chromatography on alumina using benzene-methylene chloride (2:1) as eluant. The recovered material was crystallised from ethanol to give orange-yellow crystals of 1-amino-2-nitronaphthalene (1.5 g, 46%), m.p. 142-144°C (Lit.^{141,172} m.p. 144°C).

2. 1-Amino-2- and 4-nitronaphthalenes

1-Aminonaphthalene (30 g) in a mixture of acetic anhydride (28 ml) and acetic acid (200 ml) was heated on a water bath for 20 min. The solution was cooled to 22°C and concentrated nitric acid (5 ml, d = 1.42) was added in one portion. A further addition of the acid (10 ml) was made at 15 - 20°C over 15 min. In this way the precipitation of the acetylated form was avoided and stirring difficulties eliminated. The solution was stirred for 20 h and the yellow

solid was filtered off, washed with water and dried.

The mixture of 2- and 4-nitroaceto-1-naphthalides (40 g) was added to ethanol (125 ml) and sulphuric acid (125 ml; 50%) and then refluxed for 8 h. The free amine mixture was obtained on pouring the cold solution into water. The mixed amines (20 g) were added to a mixture of glacial acetic acid (200 ml) and concentrated hydrochloric acid (13 ml); the undissolved solid was filtered off and crystallised from ethanol to give dark yellow crystals of 1-amino-4-nitronaphthalene, m.p. 194°C (Lit.,¹⁷² m.p. 194°C).

Addition of water to the filtrate afforded a small quantity of the 2-nitro-isomer which had the same melting point as that prepared above.

3. 1,3-Dinitronaphthalene

(a) 2,4-Dinitro-1-naphthol

Finely powdered 1-naphthol (50 g) was added to concentrated sulphuric acid (100 ml) and the mixture was stirred until a clear solution was obtained. On warming the liquid (water-bath), 1-naphthol-2,4-disulphonic acid separated out; the solid was collected and dissolved in water (250 ml). The solution so obtained was cooled and slowly added to nitric acid (60 ml, $d = 1.42$), the temperature being maintained below 10°C . To complete the nitration, the mixture was heated to 100°C on a water-bath and maintained at this temperature for 15 min with vigorous stirring.

The pale yellow precipitate (60 g, 74%) of 2,4-dinitro-1-naphthol was filtered off and crystallised from ethanol as yellow crystals, m.p. 132°C (Lit.,¹⁷³ m.p. 132°C).

(b) 1-Amino-2,4-dinitronaphthalene

2,4-Dinitro-1-naphthol (32 g) was dissolved in hot diethylaniline (78 ml); to the cooled slurry was added 4-toluenesulphonyl chloride (27 g) and the mixture was stirred vigorously for about 15 min. A crystalline mass of 4-toluenesulphonyl derivative 2,4-dinitro-1-naphthol (40 g) was filtered off and crystallised from ethanol before dissolving in an excess of diethylaniline with warming. Concentrated ammonia (ca. 20 ml) was then slowly added to the solution of the ester, when part of the 1-amino-2,4-dinitronaphthalene separated out. The remainder of the amine was obtained on addition of 10% hydrochloric acid (50 ml). The 1-amino-2,4-dinitronaphthalene so obtained melted at 240°C (Lit.,¹⁷⁴ m.p. 241°C).

(c) Preparation of 1,3-dinitronaphthalene

1-Amino-2,4-dinitronaphthalene (4.7 g) was dissolved in well-stirred concentrated sulphuric acid (18 ml, $d = 1.84$), the temperature being maintained below 0°C . A solution of sodium nitrite (1.5 g in 7 ml H_2SO_4) was then added with the temperature still below 10°C . The mixture was stirred slowly into glacial acetic acid (75 ml), the stirring was

continued for 30 min and copper(I) oxide (5 g) was added to the solution at 5°C. After 30 min the evolution of gas ceased and the mixture was poured into a mixture of ice and water to give crude 1,3-dinitronaphthalene (0.6 g), m.p. 143°C (Lit.,¹⁴⁷ m.p. 148°C).

4. 1-Amino-5-nitronaphthalene

1,5-Dinitronaphthalene (25 g) was wetted with ethanol (10 ml) and added to hot water (450 ml). The temperature of the mixture was raised to 95°C whereupon 'sodium sulphide reagent' (50 ml), prepared by the aforementioned general procedure, was added over 15 min with controlled heating and constant agitation. The resulting precipitate was filtered off, washed with water and extracted with aqueous hydrochloric acid (7%, 3 l). The extracts were combined and basified with ammonia at 0°C. The mononitro-amine (6 g, 28%) was obtained as red flakes. Crystallisation from light petroleum (b.p. 60-80°C) gave 1-amino-5-nitronaphthalene, m.p. 119 - 120°C (Lit.,¹⁴³ m.p. 119-120°C).

5. 1-Amino-7-nitronaphthalene

(a) Nitration of tetral-1-one

Tetral-1-one (25 ml) was added gradually from a dropping funnel to well-stirred fuming nitric acid (165 ml; d = 1.52); the addition was completed after 1 h and the temperature was kept at -10°C. The reddish solution was

poured onto ice, the resulting solid was filtered off and copiously washed with water. Crystallisation of the crude material from ethanol afforded yellow needles of 7-nitrotetral-1-one, m.p. 104°C (Lit.^{144,145} m.p. 106°C), $\tau(\text{CDCl}_3)$ 1.23 (1H, d, $\underline{J}_{6,8}$ 2.5 Hz, 8-H), 1.75 (1H, dd, $\underline{J}_{5,6}$ 8.5 Hz, $\underline{J}_{6,8}$ 2.5 Hz, 6-H), 2.54 (1H, d, $\underline{J}_{5,6}$ 8.5 Hz, 5-H), 6.91 (2H, t, $\underline{J}_{2,3}$ 6.0 Hz, 2 - CH_2), 7.28 (2H, t, $\underline{J}_{3,4}$ 6.0 Hz, 4- CH_2) and 7.80 (2H, m, 4- CH_2).

(b) 7-Nitrotetral-1-one oxime

7-Nitrotetral-1-one (10 g) was added to hydroxylamine hydrochloride (25 g) dissolved in water (100 ml) and sodium hydroxide (100 ml; 10%) and the mixture was warmed on a water-bath with the addition of ethanol (100 ml) until the nitrotetral-1-one dissolved. Heating was discontinued after 1 h and the excess of ethanol was distilled off. The hot mixture was cooled in ice and the resulting precipitate was collected. Crystallisation of the crude product from ethanol gave the oxime (4.8 g), m.p. 170°C (Lit.^{144,146} m.p. 150°C and $167\text{--}169^{\circ}\text{C}$, respectively).

(c) Acetylation of the oxime

The above oxime (4 g) was added to a mixture of glacial acetic acid (4 ml) and acetic anhydride (2 ml) and heated on a water-bath until solution was complete. The hot solution was poured into cold water and the precipitate

was filtered off and crystallised from ethanol to give a colourless product (3.1 g), m.p. 115°C (Lit.,¹⁴⁴ m.p. 115°C).

(d) Rearrangement of the acetylated oxime to 1-amino-7-nitronaphthalene

The acetylated oxime (3.0 g) was dissolved in a mixture of acetic acid (15 ml) and acetic anhydride (5 ml). Dry hydrogen chloride gas was bubbled through the solution for about 30 min and the solution was then warmed on a water-bath. On cooling, the resulting crystals were filtered off and washed with a solution of sodium acetate to give a red product (1 g), m.p. $130 - 131^{\circ}\text{C}$ (Lit.,¹⁴⁴ m.p. $133 - 134^{\circ}\text{C}$),

ν_{max} (KBr), $3450, 3375\text{ cm}^{-1}$ (NH_2) and $1525, 1345\text{ cm}^{-1}$ (NO_2).

6. 2,7-Dinitronaphthalene

(a) Nitration of naphthalic anhydride

A solution of naphthalic anhydride (50 g) in concentrated sulphuric acid (200 ml; $d = 1.84$) was cooled to 0°C and a mixture of fuming nitric acid (40 ml, $d = 1.52$) in sulphuric acid (50 ml, $d = 1.84$) was slowly added with constant stirring; the temperature of the nitration mixture was kept below 40°C . When all the acid mixture had been added, the reaction flask was heated to a temperature of $50 - 55^{\circ}\text{C}$ and kept between this range for about 1 h. The

mixture was cooled to 0°C and gradually added to an ice-water mixture (5 l). The resulting precipitate was collected and crystallised from toluene to give colourless needles of 3,6-dinitronaphthalene-1,8-anhydride, m.p. 214°C (Lit.¹⁴⁷ m.p. 214°C).

(b) Decarboxylation of 3,6-dinitronaphthalic anhydride

3,6-Dinitronaphthalic anhydride (20 g) was added during 5 min to boiling quinoline (40 ml) to which copper bronze (5 g) had been added. A further 5 g of copper bronze was added and the mixture was boiled for an additional 10 min. Ether (200 ml) was added to the cooled mixture and the sticky solid was filtered off and extracted in a Soxhlet apparatus with ether. The ethereal extract was shaken twice with aqueous hydrochloric acid (100 ml, 15%) to remove the quinoline and then washed with cold saturated sodium carbonate and water. The crude dinitronaphthalene, obtained in rather low yield (2 g) after removal of solvent, was crystallised from glacial acetic acid to give 2,7-dinitronaphthalene as pale yellow crystals, m.p. 234°C (Lit.¹⁴⁷ m.p. 234°C).

7. 2-Amino-1-, 6- and 8-nitronaphthalenes

Glacial acetic acid (100 ml), contained in a litre flask was immersed in an ice-salt mixture; acetylated 2-aminonaphthalene (115 g) was added followed by a dropwise addition of concentrated nitric acid (55 ml, $d = 1.42$) over

a period of 3 h. After standing for several hours, the product was filtered, and washed thoroughly with ether in a fume cupboard with careful handling. The product consisted of a mixture of 2-acetylamino-1-nitronaphthalene, 2-acetylamino-8-nitronaphthalene and 2-acetylamino-6-nitronaphthalene (ca. 120 g).

Hydrolysis of the mixture of isomers was effected by refluxing a solution of the product (120 g) in ethanol (500 ml) with concentrated hydrochloric acid (125 ml) for 4 h. The solution was then poured into cold water (3 l) and the crude 2-amino-1-nitronaphthalene was filtered off and crystallised from ethanol; yield, 60 g, m.p. 127°C (Lit.,¹⁴⁸ m.p. 127°C). The filtrate, containing the soluble hydrochloride of 2-amino-8-nitronaphthalene and 2-amino-6-nitronaphthalene was neutralised with sodium hydroxide to give an orange-red precipitate. The product (40 g) was boiled with ethanol (1 l) and filtered to remove undissolved material. After standing for a few hours, 2-amino-6-nitronaphthalene was filtered off as gold coloured crystals (8 g), m.p. 203°C (Lit.,¹⁴⁸ m.p. 203°C). The concentration of the filtrate afforded dark red crystals of 2-amino-8-nitronaphthalene (20 g), m.p. 104°C (Lit.¹⁴⁸ m.p. 103.5°C).

II 9,10-Dihydrophenanthrene and Derivatives

1. 2-Amino-7-nitro-9,10-dihydrophenanthrene

(a) 2,2'-Di(methoxycarbonyl)biphenyl

Biphenyl-2,2'-dicarboxylic acid (60 g) was added to a mixture of dry methanol (1 l) and boron trifluoride methanol complex (200 ml, 14% BF_3). After the heating under reflux for 20 h, most of the solvent was removed and the cooled solution was added to a saturated solution of sodium hydrogencarbonate. The resulting precipitate was filtered off, dried and crystallised from methanol to give whitish needles of the ester (48.5 g, 73%), m.p. 71 - 72°C (Lit.,¹⁷⁵ m.p. 74°C).

(b) 2,2'-Di(hydroxymethyl)biphenyl

A solution of the above ester (38 g) in dry ether (350 ml) was added to a refluxing solution of lithium tetrahydridoaluminate(III) (8.5 g) in dry ether (300 ml); the addition was complete in 40 min. Refluxing was continued until the vigorous evolution of gas had subsided. Water (ca. 50 ml) was introduced to the mixture, the first few drops being added with great care to decompose the unreacted lithium tetrahydridoaluminate(III). To the reaction flask was then added an aqueous solution of sulphuric acid (100 ml, 20%). Removal of ether from the organic layer afforded a residue which was crystallised from benzene to give the diol as tiny white needles (27 g, 91%), m.p. 112 - 113°C (Lit.,¹⁷⁶ m.p. 112-113°C).

(c) 2,2'-Di(bromomethyl)biphenyl

2,2'-Di(hydroxymethyl)biphenyl (20 g) was added to hydrobromic acid (1 l) at 90°C during 30 min. The mixture was then refluxed for 20 min; on cooling, a whitish precipitate was obtained. The crude solid was washed thoroughly with water, dried and crystallised from light petroleum (b.p. 60 - 80°C) to give the dibromo derivative (29.9 g, 94%), m.p. 87 - 88°C (Lit.,¹⁷⁷ m.p. 87.5°C).

(d) 9,10-Dihydrophenanthrene

Thin sheets of thoroughly cleansed lithium metal (1.5 g) were cut into small pieces and introduced into a three-necked flask containing dry ether (75 ml) under nitrogen. To the stirred suspension was slowly added bromobenzene (ca. 16 g); the reaction was initiated by adding a few drops of methyl iodide. After heating the mixture under reflux for about 2 h, a solution of 2,2'-di(bromomethyl)biphenyl (27 g) in dry ether (300 ml) was added as quickly as possible. A small amount of water was then carefully introduced to quench the reaction. The ethereal layer was separated, washed with water and dried (MgSO₄). Removal of solvent gave a residual red oil which was distilled in vacuo to give the hydrocarbon (10 g) b.p. 170°C at 10 mmHg. Crystallisation of the product from methanol (charcoal) gave long white needles of 9,10-dihydrophenanthrene, m.p. 34°C (Lit.,¹⁷⁸ m.p. 34.5 - 35°C).

(e) 2,7-Dinitro-9,10-dihydrophenanthrene

9,10-Dihydrophenanthrene (10 g) was added to acetic acid (40 ml) and heated in an oil-bath to 40°C. Fuming nitric acid (28 ml, d = 1.52) was added during 3 h, keeping the temperature between 45 and 50°C; the mixture was stirred magnetically. After 1 h, a bright yellow precipitate appeared but the mixture was stirred for a further 3 h before cooling. The resulting solid was thoroughly washed with water and dried. The crude product was extracted with methylene chloride and the insoluble residue was discarded. The filtrate was chromatographed on neutral alumina using methylene chloride as eluant, the first yellow band was collected. The residue obtained on removal of solvent was crystallised from acetic acid to afford 2,7-dinitro-9,10-dihydrophenanthrene (6 g, 40%) as pale yellow crystals, m.p. 224 - 226°C (Found: C, 61.8; H, 3.35; N, 10.05.

$C_{14}H_{10}N_2O_4$ requires C, 62.2; H, 3.7; N, 10.4%, $\tau(CDCl_3)$ 1.80 (2H, dd, J_{O} 8.5 Hz, J_{m} 2.5 Hz, 3,6-H) 1.85 (2H, d, J_{m} 2.5 Hz, 1,8-H), 2.08 (2H, d, J_{O} 8.5 Hz, 4,5-H) and 6.96 (4H, s, CH_2CH_2), ν_{max} (KBr) 1510, 1350 cm^{-1} (NO_2).

(f) 2-Amino-7-nitro-9,10-dihydrophenanthrene

2,7-Dinitro-9,10-dihydrophenanthrene (2 g) was added to a mixture of methanol (200 ml) and toluene (40 ml) and the suspension was heated on a water bath. To the suspension was carefully added during 30 min 'sodium sulphide

reagent' (50 ml), prepared by the general procedure. The resulting dark reddish solution was refluxed for a further 30 min and a small quantity of ice was then introduced into the reaction flask. The lukewarm mixture was poured onto ice and a red precipitate appeared on cooling; partial removal of the solvent resulted in a further precipitate. The crude product was washed with water and boiled with dilute hydrochloric acid (250 ml, 10%). A little undissolved solid was filtered off and the cooled filtrate was neutralised with dilute ammonia to afford a fairly pure sample of the nitro-amine (1 g, 57%). The nitro-amine was dissolved in methylene chloride and chromatographed on alumina using a benzene methylene chloride mixture (4:1) as eluant; the amine gave a strong fluorescent band on the column. The residue obtained after evaporation of solvent was crystallised from light petroleum (b.p. 60 - 80°C) to give bright orange crystals of 2-amino-7-nitro-9,10-dihydrophenanthrene m.p. 132°C (Found: C, 70.4; H, 5.05; N, 11.8. $C_{14}H_{12}N_2O_2$ requires C, 70.0; H, 5.0; N, 11.7%), $\tau(CDCl_3)$ 1.92(1H, dd, $J_{5,6}$ 8.5 Hz, $J_{6,8}$ 2.5Hz, 6-H), 1.96(1H, d, $J_{6,8}$ 2.5Hz, 8-H), 2.33(1H, d, $J_{5,6}$ 8.5 Hz, 5-H), 2.42(1H, d, $J_{3,4}$ 8.5 Hz, 4-H), 3.37(1H, dd, $J_{3,4}$ 8.5Hz, $J_{1,3}$ 2.5Hz, 3-H), 3.44(1H, d, $J_{1,3}$ 2.5Hz, 1-H), 6.15(2H, broad s, NH_2) and 7.13(4H, m, CH_2CH_2), ν_{max} (KBr) 3460, 3370 cm^{-1} (NH_2), 1500, 1340 cm^{-1} (NO_2).

2. 2-Nitro-9,10-dihydrophenanthrene

Fuming nitric acid (12 ml, $d = 1.52$) was added to a stirred suspension of 9,10-dihydrophenanthrene (8 g) in glacial acetic acid (48 ml) during 1 h, the temperature being maintained between 29 and 33°C. After a further hour, the red solution was poured into water (1 l) and left to stand overnight. The resulting precipitate was filtered off, dried, dissolved in the minimum amount of acetone and carefully precipitated by the addition of ethanol. Recrystallisation of this material from ether gave pale pink crystals of 2-nitro-9,10-dihydrophenanthrene (4.5 g), m.p. 79-81°C (Lit.,¹⁷⁹ m.p. 81 - 82°C).

3. 2-Amino-9,10-dihydrophenanthrene

2-Nitro-9,10-dihydrophenanthrene (4 g) was added to ethanol (60 ml) and the suspension was heated to 50°C. Palladium-charcoal (0.1 g) in ethanol was added in one portion to the hot mixture, followed by a gradual addition of hydrazine hydrate (4 ml). The reaction mixture was refluxed for a further 30 min, after which time excess solvent was removed under reduced pressure. Ice-water was then added to the reaction flask and the resulting white precipitate was filtered and dried to give 2-amino-9,10-dihydrophenanthrene (1.5 g) m.p. 49 - 50°C (Lit.,¹⁷⁹ m.p. 49-52°C)

Found: C, 85.9; H, 6.6; N, 6.9.

$C_{14}H_{13}N$ requires C, 86.1; H, 6.7; N, 7.1%.

4. 2-Acetylamino-9,10-dihydrophenanthrene

2-Amino-9,10-dihydrophenanthrene (0.5 g) was added to a 3:1 mixture of acetic acid (9 ml) and acetic anhydride (3 ml). The mixture was refluxed for 30 min and poured into cold water (50 ml). The suspension was left to stand for many hours before the resulting yellow solid was filtered off and dried. Crystallisation of the crude product from ethanol gave a quantitative yield of the acetyl derivative m.p. 164°C (Lit.,¹⁸⁰ m.p. 164°C).

5. Nitration of 2-acetylamino-9,10-dihydrophenanthrene

(a) Nitration of the isolated 2-acetylamino derivative

2-Acetylamino-9,10-dihydrophenanthrene (0.3 g) was added to acetic acid (3 ml) and fuming nitric acid (1 ml, $d = 1.52$) was added dropwise over 15 min. The mixture was stirred for 1.5 h and poured into ice-water. The resulting solid was filtered, dried and crystallised from ethanol to give a quantitative yield of the nitro derivative as bright yellow crystals, m.p. 177°C .

(b) Nitration of the acetylated compound in situ

2-Amino-9,10-dihydrophenanthrene (0.5 g) was added to a mixture of acetic acid (7 ml) and acetic anhydride (3 ml) and refluxed for 20 min. The solution was cooled to room temperature and fuming nitric acid (1 ml) was added to the partially precipitated mixture, keeping the temperature

below 20°C. The mixture was stirred for a further 2h. The resulting yellow crystals were removed and crystallised from ethanol to give the nitro compound, m.p. 177°C,

$\nu_{\max}$ (KBr) 1500, 1335 cm^{-1} (NO_2),
1705 cm^{-1} (C=O) and
3350 cm^{-1} (NH).

(c) Hydrolysis of the nitrated 2-acetylamino-9,10-dihydrophenanthrene

The nitroacetyl derivative (0.5 g) was added to a mixture of ethanol (10 ml) and sulphuric acid (10 ml, 50%) and refluxed for 1 h. The red solution so obtained was cooled to room temperature before adding it to ice-water. Basification of the mixture with ammonia at 0°C gave a precipitate which was filtered off and dried; the dark orange leaflets had m.p. 148°C. Further purification on alumina in benzene followed by recrystallisation from ethanol gave 2-amino-3-nitro-9,10-dihydrophenanthrene as bright orange crystals, m.p. 154°C (Found: C, 69.7; H, 5.05; N, 12.0. $\text{C}_{14}\text{H}_{12}\text{N}_2\text{O}_2$ requires C, 70.0; H, 5.0; N, 11.7%), τ (CDCl_3) 1.54 (1H, s, 4-H), 2.26 - 2.86 (4H, m, 5,6,7,8-H), 3.37 (1H, s, 1-H), 4.24 (2H, broad s, NH_2) and 7.19 (4H, s, CH_2CH_2), $\nu_{\max}$ (KBr) 1480, 1250 cm^{-1} (NO_2) and 3480, 3380, 3360 cm^{-1} (intramolecularly H-bonded NH_2).

6. 2-Iodo-7-nitro-9,10-dihydrophenanthrene

2-Amino-7-nitro-9,10-dihydrophenanthrene (0.5 g)

was diazotised according to the aforementioned general procedure. The diazonium solution was added to potassium iodide (0.4 g), dissolved in water (5 ml) with vigorous stirring giving an immediate precipitation. After stirring for 1 h, the mixture was allowed to stand at room temperature for several hours before gently warming on a water-bath until gas was no longer evolved. Sodium dithionite was added with constant agitation and occasional heating until the dark precipitate became somewhat lighter. The thick mass was crystallised from ethanol (charcoal) to give the iodo-compound (0.22 g, 31%) as small yellow crystals, m.p. 160°C ,

 ν_{max} (KBr) 1510, 1340 cm^{-1} (NO_2).7. Attempted bromination of 2-nitro-9,10-dihydrophenanthrene

2-Nitro-9,10-dihydrophenanthrene (1.13 g) in trimethyl phosphate (10 ml) was heated to 50°C and kept at this temperature while bromine (ca. 1g) in trimethyl phosphate (5 ml) was gradually added. No decolorisation of the mixture was observed and the temperature was raised gradually to 80°C and kept there for 3 h with constant stirring; the reaction vessel was protected from direct light and the heating was continued at 50°C for a total period of 20 h.

Water was then added to the mixture to give an oily product which was extracted into cyclohexane. On removal of solvent, the residue was recrystallised from a mixture of ethanol (30 ml) and benzene (10 ml). Bright yellow crystals, m.p. $78 - 80^{\circ}\text{C}$, were isolated and shown by thin layer chromatography to consist mainly of starting material.

III Phenanthrene Derivatives

1. 2,7-Disubstituted phenanthrene

(a) 2,7-Dinitrophenanthrene

2,7-Dinitrophenanthrene was prepared by two routes which, although related, differ significantly in experimental details.

Method 1

(i) 4,4'-Dinitrobiphenyl-2,2'-dicarboxylic acid

Biphenyl-2,2'-dicarboxylic acid (40 g) was added to concentrated sulphuric acid (200 ml, $d = 1.84$) contained in a 1-l flask. The mixture was externally cooled in an ice-salt mixture while fuming nitric acid (200 ml, $d = 1.52$) was slowly added from a dropping funnel during 1.5 h, the temperature being kept below 20°C . The mixture was then warmed gradually to $40-50^{\circ}\text{C}$ on a water-bath and the stirring was continued at this temperature range for 2 h. The resulting red solution was poured into ice-water (ca. 1 l) and the cream yellow precipitate was collected and crystallised

from a 1:1 mixture of ethanol-water (1.5 l) to give small crystals of the dinitro compound (44.3g, 81%), m.p. 257°C (Lit.,^{106,107} m.p. 257-258°C and 260-262°C, respectively),

$\tau[(\text{CD}_3)_2\text{SO}]$

1.31(2H, d, $\underline{J_m}$ 2.5 Hz, 3,3'-H),

1.54(2H, dd, $\underline{J_o}$ 8.5 Hz, $\underline{J_m}$ 2.5Hz, 5,5'-H) and

2.47(2H, d, $\underline{J_o}$ 8.5 Hz, 6,6'-H),

ν_{max} (KBr) 2600 - 3500 cm^{-1} (OH), 1710 cm^{-1} (CO) and 1525, 1350 cm^{-1} (NO₂).

(ii) 4,4'-Dinitro-2,2'-di(methoxycarbonyl)biphenyl

4,4'-Dinitrobiphenyl-2,2'-dicarboxylic acid (16.6 g) was added to boron trifluoride methanol complex (100 ml) in dry methanol (500 ml). The mixture was refluxed for 16 h, poured into a saturated solution of sodium hydrogencarbonate and the resulting precipitate was filtered off and dried. Crystallisation of the product from ethanol afforded very small crystals of the ester (5 g, 29%), m.p. 177°C (Lit.,¹⁰⁶ m.p. 177°C).

(iii) 4,4'-Dinitro-2,2'-di(hydroxymethyl)biphenyl

Lithium tetrahydridoaluminate(III) (1.14 g) was suspended in dry ether (25 ml) and anhydrous aluminium chloride (4 g) was added. To the suspension was added the above ester (5.4 g) in dry ether (ca. 50 ml) and the mixture was heated under reflux for 1 h. Water (15 ml) was very carefully introduced to the reaction mixture to decompose

the unreacted lithium tetrahydridoaluminate(III). After removal of the organic layer, the aqueous phase was extracted several times with ether until the final portion of solvent remained clear. Evaporation of ether from the dried (MgSO_4) organic extracts gave a residue which was boiled with water; insoluble reddish material was discarded. On cooling, the filtrate afforded bright yellow crystals of the dinitro compound (2g, 44%), m.p. $150 - 152^\circ\text{C}$ (Lit.,¹⁰⁵ m.p. $149 - 150^\circ\text{C}$).

(iv) 4,4'-Dinitro-2,2'-di(bromomethyl)biphenyl

The above diol (3 g) was added to hydrobromic acid (80 ml) and the mixture was heated to $110 - 120^\circ\text{C}$ for 1 h. On cooling the resulting solid was crystallised from ethanol to give small crystals of the dibromo compound (2 g), m.p. 140°C (Lit.,¹⁰⁵ m.p. 146°C).

(v) 4,4'-Dinitro-2'-bromomethyl-2,2'-biphenylmethyl-phosphonium bromide

The above dibromo compound (1.7 g) and triphenylphosphine (1.0 g) were added to benzene (30 ml) and refluxed for 5 h. The resulting solid was filtered off and then crystallised from a mixture of methanol (15 ml) and ether (5 ml) to give the phosphonium salt as light yellow crystals (0.66 g), m.p. 275°C (Lit.,¹⁰⁵ m.p. $275 - 277^\circ\text{C}$).

(vi) 2,7-Dinitrophenanthrene

The above phosphonium salt (0.66 g) was added to dry methanol (6 ml) followed by the dropwise addition of sodium methoxide (0.11 g) in methanol (4 ml). The mixture was stirred for 1 h, filtered and the volume of solvent was reduced to give bright yellow crystals of 2,7-dinitrophenanthrene, m.p. (DTA) 337°C (Lit.,¹⁰⁵ m.p. 333-336°C) (Found: C, 62.7; H, 3.3; N, 10.4. Calc. for $C_{14}H_8N_2O_4$: C, 62.7; H, 3.0; N, 10.9%).

Method 2

2,7-Dinitro-9,10-dihydrophenanthrene (5.40 g; 0.02 mole) was added to carbon tetrachloride (50 ml), followed by N-bromosuccinimide (3.6 g, 0.02 mole) and a trace of dibenzoyl peroxide. The mixture was refluxed for 3 h, then cooled and the resulting solid was filtered off. Solvent was removed from the filtrate, leaving a small amount of residue. The solid material was boiled in glacial acetic acid and the hot solution was filtered whereupon a cluster of yellow crystals appeared instantly; the yield was quantitative. The dinitro compound had the same melting point (337°C) as that prepared by the first route.

(b) 2-Amino-7-nitronaphthalene

2,7-Dinitrophenanthrene (1 g) was suspended in a mixture of methanol (100 ml) and toluene (20 ml). 'Sodium sulphide reagent' prepared by the general procedure (ca. 30 ml) was slowly added to the mixture with controlled heating on a

water-bath. After 1 h of refluxing, a small quantity of ice was introduced into the hot mixture but the colour did not turn orange as in the case of the corresponding dihydro compound. The solution was poured onto ice and the resulting precipitate was dissolved in hot dilute hydrochloric acid (150 ml, 10%). The cooled solution was saturated with ammonia to give pale yellow leaflets of 2-amino-7-nitro-phenanthrene (0.3 g), m.p. (DTA) 196°C (Found: C, 70.0; H, 4.45; N, 11.3. $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_2$ requires C, 70.5; H, 4.2; N, 11.76%).

2. Attempted synthesis of 3,6-disubstituted phenanthrene derivatives

(a) 2-Amino-4-nitrotoluene

2-Aminotoluene (36 g, 36 ml) was added to concentrated sulphuric acid (200 ml, $d \approx 1.84$) and cooled to 0°C . Finely powdered potassium nitrate (36 g) was gradually added (30 min) at such a rate that the temperature did not rise above 10°C . To complete the nitration fuming nitric acid (10 ml) was added and the stirring was continued for a further 45 min. The resulting viscous solution was poured onto ice and the precipitated amine sulphate was separated by draining off the excess acid. The salt was dissolved in water and treated with sodium hydrogencarbonate. The resulting precipitate was filtered off and crystallised from ethanol to give the nitroamine (32 g, 62.6%), m.p. 100°C (Lit.,¹³³ m.p. $100 - 102^{\circ}\text{C}$).

(b) 2-Iodo-4-nitrotoluene

2-Amino-4-nitrotoluene (30 g) was added to a mixture of water (500 ml) and concentrated hydrochloric acid (63.5 ml, $d = 1.8$) and warmed until solution was complete. The solution was cooled in a salt-ice mixture to below 0°C and sodium nitrite (13.8 g) in water (50 ml) was added over 15 min with constant agitation. The clear diazonium solution was slowly added to a solution of potassium iodide (50 g) in water (150 ml); a vigorous evolution of nitrogenous gases was observed. The reaction mixture was left to stand at room temperature for 1 h and then warmed on a water-bath until no more gases were evolved. The dark mass obtained after decanting the aqueous layer was treated with powdered sodium dithionite until a clear viscous oil ensued; the oil was then steam-distilled for many hours. The product from steam distillation was crystallised from ethanol to give pale yellow needles of 2-iodo-4-nitrotoluene (15.5 g, 30%), m.p. 53°C (Lit.,^{134,113} m.p. 58°C and 54°C , respectively) (Found: C, 31.8; H, 2.3; N, 5.5. Calc. for $\text{C}_7\text{H}_6\text{INO}_2$: C, 32.0; H, 2.3; N, 5.3%).

(c) 2-Iodo-4-nitrobenzyl bromide

To carbon tetrachloride (125 ml) was added 2-iodo-4-nitrotoluene (26.3 g, 0.1 mole), *N*-bromosuccinimide (17.8 g, 0.1 mole) and dibenzoyl peroxide (300 mg). The mixture was refluxed overnight, cooled and filtered. After removal of solvent from the filtrate, the residue was crystallized from light petroleum (b.p. $40 - 60^{\circ}\text{C}$) to give the benzyl compound as whitish leaflets, m.p. $82 - 83^{\circ}\text{C}$ (Lit.,¹¹³ m.p. 84°C).

(d) 2-Iodo-4-nitrobenzaldehyde

To boiling chloroform (100 ml) was introduced 2-iodo-4-nitrobenzyl bromide (20 g) and hexamethylene-tetramine (urotropin) (8 g) and the mixture was refluxed for 2 h. The resulting white salt (26 g, 90%), m.p. 182 - 183°C (decomp.), [Lit.,¹¹³ m.p. 184 - 185°C (decomp)], was filtered off and dried.

The above salt (24 g) was dissolved in acetic acid (240 ml) by boiling the mixture for 15 min. Concentrated hydrochloric acid (24 ml) was carefully added and the solution was heated under reflux for a further 10 min. The hot solution was poured into cold water (500 ml) and the somewhat oily precipitate was collected and washed with water; the filtrate yielded a further quantity of solid material on extraction with chloroform. The solid products were extracted five times with portions of boiling cyclohexane (100 ml). The volume of the combined extracts was reduced to give, on cooling, a poor yield of 2-iodo-4-nitrobenzaldehyde (2.3 g) as fine yellow needles, m.p. 83 - 84°C (Lit.,¹¹³ m.p. 84.5°C).

(e) Attempted preparation of 5,5'-dinitrophenyl-2,2'-dialdehyde

2-Iodo-4-nitrobenzaldehyde (2 g) and activated copper bronze (1.5 g) were added to dimethylformamide (15 ml) and the mixture was refluxed for 3 h under nitrogen. The solid left on removal of solvent was extracted with small

portions of cyclohexane (100 ml in all). The resulting yellow crystals, m.p. 100°C appeared to be impure 4-nitro benzaldehyde (m.p. 105°C). The desired compound has m.p. 203.5°C .¹¹³

3. 3,9-Disubstituted phenanthrenes

(a) 9-Bromophenanthrene

A commercial sample of phenanthrene (200 g) was added to a mixture of chloroform (400 ml) and ether (400ml). The suspension was stirred mechanically with external cooling in an ice-bath and bromine (ca. 180 g, 58 ml) was added dropwise over 20 min, keeping the temperature below 15°C . The temperature was then allowed to fall to zero and, after stirring for a further hour, the precipitate was removed and washed with ether (750 ml). The cream coloured dibromo adduct was transferred to a 3 l. breaker and heated on a water-bath with occasional stirring for an hour. The light coloured oil which ensued was cooled and the resulting precipitate was crystallised from light petroleum (b.p. $40 - 60^{\circ}\text{C}$), giving colourless crystals of 9-bromophenanthrene (190 g), m.p. $62-63^{\circ}\text{C}$ (Lit.,^{181,182} m.p. $61.5 - 63^{\circ}\text{C}$ and $65 - 66^{\circ}\text{C}$, respectively).

(b) 9-Bromo-3-nitrophenanthrene

9-Bromophenanthrene was nitrated by following the procedure of Braithwaite and Holt.¹²⁴ The bromo compound (40 g) was added slowly to concentrated nitric acid (400 ml,

$d = 1.42$) at $18 - 20^{\circ}\text{C}$. Stirring was continued for 10 h, the resulting solid was filtered off and washed copiously with water. The crude material was twice extracted with boiling acetone (200 ml) and the residue was crystallised from glacial acetic acid (400 ml). Long yellow needles of 9-bromo-3-nitrophenanthrene, m.p. $189 - 190^{\circ}\text{C}$ (Lit.,¹²⁴ m.p. 192°C), separated on cooling but the yield of pure product was very low (10.5 g) compared with that given in the literature.¹²⁴

(c) 3-Amino-9-bromophenanthrene

Method 1

9-Bromo-3-nitrophenanthrene (4 g) was added to boiling ethanol (1066 ml) and concentrated hydrochloric acid (133 ml) was then carefully added to the solution. Zinc powder was cautiously added to the hot mixture until the solution became permanently colourless. After filtering off the residual zinc, the volume of solution was reduced and small crystals of the amine hydrochloride appeared on cooling. The product was dissolved in a hot 50:50 mixture of ethanol and water. The solution was neutralised with dilute ammonia and the free amine was crystallised from aqueous ethanol to give pure product (2.8 g), m.p. $112 - 113^{\circ}\text{C}$ (Lit.,¹²⁴ m.p. $112.5 - 113^{\circ}\text{C}$).

(Found: C, 61.6; H, 3.65; N, 5.15.

Calc. for $\text{C}_{14}\text{H}_{10}\text{BrN}$: C, 61.7; H, 3.7; N, 5.15%).

Method 2(i) 3-Acetyl-9-bromophenanthrene

Acetyl chloride (13 ml) was added to a well-stirred suspension of 9-bromophenanthrene (35 g) in carbon disulphide (262 ml), the temperature being kept between 0 and 5°C. Anhydrous aluminium chloride (52.5 g) was gradually introduced into the mixture and the stirring was continued for 5 h during which time the temperature gradually rose to 20°C. The resulting precipitate was filtered off, and washed several times with carbon disulphide. The yellow complex was added with vigorous stirring to a mixture of chloroform (150 ml), concentrated hydrochloric acid (22.5 ml) and ice (ca. 100 g) contained in a 3-necked flask (1 l). After 1 h, the two layers were separated and the chloroform phase was washed once with dilute hydrochloric acid and twice with water. On removal of solvent, the brown crystalline residue was recrystallised from acetone (charcoal) to give colourless crystals of 3-acetyl-9-bromophenanthrene (34 g), m.p. 150°C (Lit.,¹²⁹ m.p. 150-151°C).

(ii) 3-Acetyl-9-bromophenanthrene oxime

To 3-acetyl-9-bromophenanthrene (10 g) in hot dioxane (100 ml) was added hydroxylamine hydrochloride (5 g) in aqueous sodium hydroxide (20 ml, 10%). Ethanol (ca. 40ml) was then added and the resulting clear solution was heated

for 4 h on a water-bath. Hot water (200 ml) was then added to the turbid mixture and after cooling (overnight) the oxime separated out as light brown crystals, m.p. 212°C (Lit.,¹²⁹ m.p. $212 - 213.5^{\circ}\text{C}$) (Found: C, 61.6; H, 4.2; N, 4.3. Calc. for $\text{C}_{16}\text{H}_{12}\text{BrNO}$: C, 61.1; H, 3.8; N, 4.5%).

(iii) 3-Acetylamino-9-bromophenanthrene

The oxime (3g) was added to polyphosphoric acid (90 g) and heated to $130 - 150^{\circ}\text{C}$ for 15 min before pouring into water (450 ml). The precipitate was washed thoroughly with water, dried and extracted into benzene (50 ml). Removal of solvent left a residue which on crystallisation from benzene gave small crystals of 3-acetyl-9-bromophenanthrene (1.8 g), m.p. 220°C (Lit.,¹²⁹ m.p. $220.5 - 221.5^{\circ}\text{C}$).

(iv) 3-Amino-9-bromophenanthrene

3-Acetylamino-9-bromophenanthrene (1.8 g) was added to a mixture of ethanol (20 ml) and hydrochloric acid (8 ml, 50%) and refluxed for 24 h. The solid amine hydrochloride so obtained was shaken with wet ether (60 ml) and the mixture was basified with dilute sodium hydroxide. The ethereal layer was washed with water and dried (MgSO_4). Removal of solvent gave a small residue which was crystallised from ethanol to give straw-like crystals of 3-amino-9-bromophenanthrene, m.p. 112°C (Lit.¹²⁴ m.p. $112.5 - 113^{\circ}\text{C}$).

(d) 9-Bromo-3-dimethylaminophenanthrene

A mixture of 3-amino-9-bromophenanthrene (10 g), methyl iodide (23 g), sodium carbonate (20 g) and water (100 ml) was boiled gently under reflux for 18 h. The excess of methyl iodide was then removed and the product was crystallised from aqueous ethanol to give the quaternary salt as brown granules.

Dequaternization of the salt was achieved by adding the product to dry methanol (400 ml) containing sodium methoxide (8 g) and refluxing the mixture for 24 h. The solvent was partially removed before the mixture was poured into water (1 l). The resulting precipitate was crystallised from ethanol to give long needles of 9-bromo-3-dimethylamino phenanthrene (4 g), m.p. 112 - 113°C (Lit.,¹⁸⁰ m.p. 112 - 113°C).

(e) 3-Dimethylaminophenanthrene

9-Bromo-3-dimethylaminophenanthrene (2 g) was added to ethanol (200 ml) containing palladium charcoal (0.1 g) Hydrazine hydrate (20 ml) was added over 15 min to the mixture; a vigorous reaction ensued. After 2 h of refluxing, the strongly fluorescent mixture was filtered. Removal of solvent in vacuo gave solid 3-dimethylaminophenanthrene (1 g, 70% yield), m.p. 74 - 75°C (Lit.,¹³⁰ m.p. 75 - 76°C) (Found: C, 87.15; H, 7.05; N, 6.3. Calc. for C₁₆H₁₅N: C, 87.0; H, 6.8; N, 6.3%).

(f) 3-Aminophenanthrene

A mixture of 9-bromo-3-nitrophenanthrene (1 g), 10% palladium charcoal (0.1 g) and ethanol (10 ml) was refluxed on a water-bath and hydrazine hydrate (1 ml) was added dropwise. Refluxing was continued for 10 min, the catalyst was filtered off and the solvent was removed. The residue (0.5 g, 57.5%) was crystallised from light petroleum (b.p. 40 - 60°C) to give colourless crystals of 3-aminophenanthrene, m.p. 86 - 87°C (Lit.,¹²⁸ m.p. 87°C) (Found: C, 86.7; H, 5.8; N, 7.3. Calc. for $C_{14}H_{11}N$: C, 87.0; H, 5.7; N, 7.3%).

(g) 9-Cyanophenanthrene

9-Bromophenanthrene (10 g) was heated to 230 - 250°C and copper(I) cyanide (1.5 g) was added portionwise with stirring. The temperature was raised gradually to 270 - 280°C and more copper salt (3 g) was added; it became necessary to discontinue heating as the reaction progressed owing to its exothermic nature. After 1 h the mixture was transferred to a distillation flask and the product was removed under reduced pressure. Crystallisation of the crude material from ethanol gave white crystals of 9-cyanophenanthrene, m.p. 109 - 110°C (Lit.,¹⁸³ m.p. 110°C).

(h) 9-Cyano-3-nitrophenanthrene

A mixture of 9-bromo-3-nitrophenanthrene (10 g), copper(I) cyanide (3.2 g) and dimethylformamide (30 ml) was

heated under reflux for 4 h. The partially precipitated mixture was cooled and added to a solution of iron(III) chloride (13 g) in concentrated hydrochloric acid (3 ml) and water (20 ml). The mixture was warmed to 60 - 70°C on a water-bath and stirred at that temperature for 20 min. The resulting precipitate obtained on cooling was filtered, washed thoroughly with water and dried. The crude product was crystallised from dioxane to give pale yellow needles of 9-cyano-3-nitrophenanthrene (8 g), m.p. 262°C (Lit.,¹⁸⁰ m.p. 262°C).

(i) 3-Amino-9-cyanophenanthrene

9-Cyano-3-nitrophenanthrene (6 g) was suspended in ethanol (1 l) and palladium charcoal (0.2 g, 10%) was added; hydrazine hydrate (50 ml) was slowly added and the mixture was stirred for 1.5 h. The residual catalyst was filtered off and most of the solvent was removed from the very strongly fluorescent solution. The cold solution deposited a nearly quantitative yield of long pale yellow needles of 3-amino-9-cyanophenanthrene, m.p. 189 - 190°C (Lit.,¹⁸⁰ m.p. 191°C).

Part B Dyes

I N,N-Diethylaniline Dyes

1. 4-(Phenylazo)-N,N-diethylaniline

Aniline (1.86 g) was diazotised as described by Vogel¹⁸⁴ and coupled with N,N-diethylaniline (2.98 g). The resultant product (quantitative yield) was purified on alumina with benzene as eluant, to give pure brownish yellow crystals of the dye, m.p. 96°C (Found: C, 75.9; H, 7.8; N, 16.3. $C_{16}H_{19}N_3$ requires C, 75.9; H, 7.5; N, 16.6%).

2. 4-(4-Nitrophenylazo)-N,N-diethylaniline

4-Nitroaniline (2 g) was diazotised as described by Vogel.¹⁸⁴ The clear yellow solution so obtained was coupled with N,N-diethylaniline (2.2 g) in an acidic buffer. The red crystalline product was washed with water and dried. Further purification of the crude product (3.9 g) was achieved by column chromatography (alumina/benzene) to give, on crystallisation from ethanol, dark red rhombic crystals of the dye, m.p. 108°C (Found: C, 64.8; H, 6.05, N, 18.5. $C_{16}H_{18}N_4O_2$ requires C, 64.4; H, 6.0; N, 18.8%).

3. 4-(2-Nitrophenylazo)-N,N-diethylaniline

2-Nitroaniline (2 g) was diazotised as described for 4-nitroaniline and coupled with N,N-diethylaniline (2.2 g) giving 4 g of crude dye. Chromatography afforded a product

which crystallised from ethanol to give bright red needles of the dye, m.p. 106°C (Found: C, 64.6; H, 6.4; N, 19.2. $\text{C}_{16}\text{H}_{18}\text{N}_4\text{O}_2$ requires C, 64.4; H, 6.0; N, 18.8%).

4. 4-(1-Nitro-2-naphthylazo)-N,N-diethylaniline

2-Amino-1-nitronaphthalene (1 g) was added to acetic acid (15 ml) and poured into dilute hydrochloric acid (20 ml, 10%). The mixture was heated until a clear solution was obtained. Ice was introduced to the hot solution to produce a thick precipitate of the amine hydrochloride. Diazotisation was then carried out as described in the general procedure. The filtered diazonium solution was coupled with N,N-diethylaniline (ca. 0.75 g) in a buffered solution. After stirring for 1 h, the solution was basified with sodium hydrogencarbonate (powder) and the precipitate was filtered off, washed with water and dried. The crude material (1.5 g) was chromatographed (alumina/benzene) and the resulting oil was crystallised from light petroleum (b.p. $60-80^{\circ}\text{C}$) to give golden red leaflets of the dye, m.p. 186°C (Found: C, 69.25; H, 5.75; N, 16.0. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$ requires C, 69.0; H, 5.75; N, 16.1%).

5. 4-(4-Nitro-1-naphthylazo)-N,N-diethylaniline

1-Amino-4-nitronaphthalene (0.4 g) was diazotised according to the general procedure and then coupled with N,N-diethylaniline (0.4 g). The greenish precipitate obtained

on neutralisation was filtered off, washed with water and dried. The product (0.55 g) was dissolved in the minimum amount of methylene chloride and chromatographed on alumina using benzene as eluant. Crystallisation of the residue (0.28 g) from ethanol gave green needles of the dye, m.p. 140°C (Found: C, 69.25; H, 5.8; N, 16.4. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$ requires C, 69.0; H, 5.75; N, 16.1%).

6. 4-(5-Nitro-1-naphthylazo)-N,N-diethylaniline

1-Amino-5-nitronaphthalene (1 g) was diazotised exactly as described for the other isomers and coupled with N,N-diethylaniline (0.8 g). The resulting solution was basified with sodium hydrogencarbonate to give a dark red product (1.65 g) which was chromatographed on alumina. Crystallisation of the residue from ethanol gave lustrous red cublets of the dye, m.p. $163 - 165^{\circ}\text{C}$ (Found: C, 68.7; H, 6.2; N, 15.9. $\text{C}_{20}\text{H}_{20}\text{N}_4\text{O}_2$ requires C, 69.0; H, 5.75; N, 16.1%).

7. 4-(6-Nitro-2-naphthylazo)-N,N-diethylaniline

2-Amino-6-nitronaphthalene (1.2 g) was diazotised as described above and coupled with N,N-diethylaniline (ca. 1 g) in an acid buffer at 0°C . The resulting brownish solution was stirred for 30 min and neutralised with sodium hydrogencarbonate. The resulting precipitate was filtered off, washed with water and dried. Purification of the crude

product (1.7 g) on alumina followed by crystallisation from light petroleum (b.p. 60 - 80°C) afforded bright red crystals of the dye, m.p. 214 - 216°C (Found: C, 68.7; H, 5.55; N, 15.7. $C_{20}H_{20}N_4O_2$ requires C, 69.0; H, 5.75; N, 16.1%).

8. 4-(8-Nitro-2-naphthylazo)-N,N-diethylaniline

To a mixture of concentrated sulphuric acid (10 ml) and water (30 ml) was added 2-amino-8-nitronaphthalene (0.6 g) and the mixture was heated until the amine dissolved. The solution was cooled rapidly by the introduction of ice. Diazotisation was carried out in the usual way and the diazonium solution was coupled with N,N-diethylaniline (0.5 g) in an acidic buffer. After stirring for 1 h, the red solution was neutralised with sodium hydrogencarbonate; the resulting precipitate was filtered off and dried. The product (0.85 g) was dissolved in methylene chloride and chromatographed on alumina (neutral) using a 3:1 mixture of light petroleum (b.p. 60 - 80°C) as eluant. The first yellow band was discarded; the main band (red) was collected. On evaporation of the solvent, the residue (0.15 g) was dissolved in a small quantity of acetone and reprecipitated by the careful addition of ethanol to give greenish needles of the dye, m.p. 137°C (Found: C, 68.8; H, 6.05; N, 16.1. $C_{20}H_{20}N_4O_2$ requires C, 69.0; H, 5.75; N, 16.1%).

9. 4-(9-10-Dihydro-2-phenanthrylazo)-N,N-diethylaniline

2-Amino-9,10-dihydrophenanthrene (50 mg) was dissolved in pyridine (1 ml) and added gradually over 1 h to a solution of nitrosylsulphuric acid (general procedure). After the addition, the mixture was stirred magnetically for a further hour, urea (0.1 g) in water (2 ml) was then introduced followed by ice and water as the temperature rose rapidly. After another hour of agitation, the dark orange mixture was filtered; no undiazotised amine remained. The diazonium solution was added to N,N-diethylaniline (ca. 50 mg) in the same manner as described previously. The clear orange solution was neutralised with sodium hydrogencarbonate. The resulting oily product was extracted into methylene chloride and purified by preparative t.l.c. to give the dye, m.p. 156 - 158°C (Found: C, 81.0; H, 7.0; N, 12.2. $C_{24}H_{25}N_3$ requires C, 81.1; H, 7.0; N, 11.8%).

10. 4-(3-Nitro-9,10-dihydro-2-phenanthrylazo)-N,N-diethylaniline

2-Amino-3-nitro-9,10-dihydrophenanthrene (100 mg) in pyridine (2 ml) was added to nitrosylsulphuric acid as described above. The clear diazonium solution obtained after filtration was gradually added to a solution of N,N-diethylaniline (0.1 g) in an acidic buffer at 0°C. Coupling was complete after 3 h and the solution was then neutralised with sodium hydrogencarbonate; the resulting red precipitate was filtered off and dried. The crude dye (80 mg) was dissolved

in methylene chloride and purified by preparative t.l.c..

The main band was recovered and crystallised from light petroleum (b.p. 60 - 80°C) to give dark red plates of the dye, m.p. 158°C (Found: C, 71.6; H, 5.95; N, 14.1.

$C_{24}H_{24}N_4O_2$ requires C, 72.0; 6.0; N, 14.0%).

11. 4-(7-Nitro-9,10-dihydro-2-phenanthrylazo)-N,N-diethylaniline

2-Amino-7-nitro-9,10-dihydrophenanthrene (0.5 g) was diazotised by the direct method (general procedure) and coupled with N,N-diethylaniline (0.3 g). The red precipitate obtained on neutralisation was filtered off and dried. the crude dye (0.6 g) was dissolved in methylene chloride; a small amount of insoluble material was discarded. The solution was purified on alumina using benzene as eluant. On removal of solvent, the residue was crystallised from light petroleum (b.p. 60-80°C) to give bright red leaflets of the dye, m.p. 240°C (Found: C, 71.95; H, 6.0; N, 14.5.

$C_{24}H_{24}N_4O_2$ requires C, 72.0; H, 6.0; N, 14.0%),

$\nu_{\max}$ (KBr) 1510, 1335 cm^{-1} (NO_2).

12. 4-(7-Nitro-2-phenanthrylazo)-N,N-diethylaniline

2-Amino-7-nitrophenanthrene (250 mg) was diazotised by the general procedure and coupled with N,N-diethylaniline (150 mg) in an acidic buffer. The crude dye (0.3 g) was chromatographed using benzene as eluant. The recovered material

from the column was crystallised from light petroleum (b.p. 60 - 80°C) to give a dull red dye, m.p. 217°C (Found: C, 70.8; H, 5.9; N, 12.6. $C_{24}H_{22}N_4O_2$ requires C, 72.4; H, 5.5; N, 14.1%).

13. 4-(9-Bromo-3-phenanthrylazo)-N,N-diethylaniline
3-Amino-9-bromophenanthrene (1 g) was dissolved in pyridine (4 ml) and gradually added to nitrosylsulphuric acid prepared by the standard method. After stirring for 2h, polyphosphoric acid (ca. 10 ml) was added followed by an aqueous solution of urea (5 ml). Ice was added to the thick mixture to prevent the temperature from rising and the suspension was filtered to remove undiazotised amine. The diazonium solution was coupled to a suspension of N,N-diethylaniline (0.6 g) in an acidic buffer. The resulting dark resinous product was extracted into methylene chloride; insoluble material was discarded. The solution was chromatographed (alumina/benzene) and the product was treated with light petroleum (b.p. 60 - 80°C) to give the dye as a powdery red product, m.p. 124 - 126°C (Found: C, 67.05; H, 4.9; N, 9.6; Br, 18.9. $C_{24}H_{22}BrN_3$ requires C, 66.7; H, 5.1; N, 9.7; Br, 18.5%).

14. 4-(9-Cyano-3-phenanthrylazo)-N,N-diethylaniline
3-Amino-9-cyanophenanthrene (1 g) was diazotised in a manner similar to that described for 3-amino-9-bromophenanthrene and was then coupled with N,N-diethylaniline

(0.7 g). The crude dye (0.9 g) was chromatographed on alumina with benzene as eluant. The residue from the column was crystallised from ethanol to give dark red crystals of the dye, m.p. 160°C (Found: C, 79.0; H, 5.8; N, 14.8. $\text{C}_{25}\text{H}_{22}\text{N}_4$ requires C, 79.4; H, 5.8; N, 14.8%), ν_{max} (KBr) 2220 cm^{-1} (CN).

II N-2-Cyanoethyl-1,2,3,4-tetrahydroquinoline Dyes
 N-2-Cyanoethyl-1,2,3,4-tetrahydroquinoline¹⁴⁹

A solution of tetrahydroquinoline (33.3 g) in glacial acetic acid (25 g) contained in a flask fitted with a reflux condenser was heated to 125°C in an oil-bath. Redistilled acrylonitrile (25 g, b.p. 76 - 78°C) was added dropwise over 3 h and the mixture was heated under reflux for 6 h.

After cooling, the resulting brownish product was neutralised with cold saturated potassium carbonate (38 g) in water (85 ml). The brownish oily upper layer was twice extracted with methylene chloride (25 ml). Removal of solvent from the dried (Na₂SO₄) organic extracts afforded a dark brown oil which was distilled under reduced pressure to give the required product (32 g) as a pale apple-green pungent liquid, b.p. 175 - 180°C at 5 mmHg.

1. 6-(2-Nitrophenylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

2-Nitroaniline (2 g) was diazotised according to Vogel¹⁸⁴ and coupled with N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (2.7 g). The sticky product was dissolved in methylene chloride and chromatographed on alumina with benzene as eluant. The residual oil was treated with light petroleum (b.p. 40-60°C) to give red crystals of the dye, m.p. 107-108°C (Found: C, 64.6; H, 5.35; N, 20.85. C₁₈H₁₇N₅O₂ requires C, 64.5; H, 5.1; N, 20.9%), $\nu_{\max}$ (KBr) 2250 cm⁻¹ (CN), 1520, 1350 cm⁻¹ (NO₂).

2. 6-(4-Nitrophenylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

4-Nitroaniline (2 g) was diazotised as described previously and coupled with N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (2.7 g) in an acid buffer at 0°C; an immediate precipitation of dark red crystals resulted and the stirring was continued for 1 h. The product was filtered off, washed with water and dried. The crude dye (4.2 g) was purified on alumina using benzene as eluant; the first yellow band was rejected. The main band (red) was collected and the solvent was evaporated. Crystallisation of the residue from ethanol gave silvery dark red leaflets of the dye, m.p. 170 - 172°C (Found: C, 64.8; H, 5.4; N, 20.75. $C_{18}H_{17}N_5O_2$ requires C, 64.5; H, 5.1; N, 20.9%).

3. 6-(1-Nitro-2-naphthylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

2-Amino-1-nitronaphthalene (1.5 g) was added to a 1:1 mixture of hydrochloric acid and water (40 ml) and heated on a hot plate. Ice was added to the thick suspension and diazotisation was carried out by adding a solution of sodium nitrite (1.2 g in water (10 ml)). After stirring for 1 h, the diazonium mixture was filtered; some undiazotised amine remained (0.4 g). The dark yellow solution was added to a suspension of N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (1.5 g) in an acidic buffer. The reaction was stirred for 3 h

and the resulting dark green precipitate was filtered off, washed with water and dried. The crude dye (2.2 g) was purified on an alumina column using a 1:1 benzene/methylene chloride mixture as eluant; the amount of methylene chloride was gradually decreased as the column was developed. Only a small quantity of pure material was recovered from the column and this was crystallised from light petroleum (b.p. 40 - 60°C) to give small plates of the dye, m.p. 183 - 184°C (Found: C, 68.9; H, 5.2; N, 18.2. $C_{22}H_{19}N_5O_2$ requires C, 68.6; H, 4.9; N, 18.2%).

4. 6-(4-Nitro-1-naphthylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

1-Amino-4-nitronaphthalene (200 mg) was diazotised by the general procedure and coupled with N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (200 mg). The deep violet mixture was filtered and a green precipitate was recovered. Purification by chromatography (alumina/benzene) afforded an oil which on treatment with light petroleum (b.p. 40 - 60°C) gave dark green crystals of the dye, m.p. 190°C (Found: C, 68.7; H, 5.1; N, 18.15. $C_{22}H_{19}N_5O_2$ requires C, 68.6; H, 4.9; N, 18.2%).

5. 6-(5-Nitro-1-naphthylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

1-Amino-5-nitronaphthalene (0.4 g) was diazotised by the standard procedure and coupled with N-2-cyanoethyl-1,2,3,4-

tetrahydroquinoline (0.4 g) to give red platelets of the dye, m.p. 194°C (Found: C, 68.4; H, 4.9; N, 17.9. $\text{C}_{22}\text{H}_{19}\text{N}_5\text{O}_2$ requires C, 68.6; H, 4.9; N, 18.2%).

6. 6-(7-Nitro-9,10-dihydro-2-phenanthrylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

2-Amino-7-nitro-9,10-dihydrophenanthrene (200 mg) was diazotised as in the general procedure and coupled with N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (160 mg) in an acidic buffer. After stirring for 2 h, the brown precipitate was filtered off and dissolved in methylene chloride. The solution was chromatographed on alumina (neutral) with benzene as eluant. The residue was crystallised from light petroleum (b.p. $40-60^{\circ}\text{C}$) to give the dye as a red powder, m.p. 190°C (Found: C, 71.7; H, 5.55; N, 15.7. $\text{C}_{26}\text{H}_{23}\text{N}_5\text{O}_2$ requires C, 71.4; H, 5.3; N, 16.0%).

7. 6-(9-Cyano-3-phenanthrylazo)-N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline

3-Amino-9-cyanophenanthrene (0.5 g) was diazotised by the nitrosylsulphuric acid technique with the addition of polyphosphoric acid (10 ml) at the end. The filtered diazonium solution was added dropwise to N-2-cyanoethyl-1,2,3,4-tetrahydroquinoline (0.43 g) in an acidic buffer at 0°C . The sticky black product was extracted with methylene chloride and chromatographed (alumina/benzene). The product recovered

from the column was precipitated by the addition of light petroleum (b.p. 60-80°C) as red crystals, m.p. 216-218°C. Further purification was effected by means of preparative t.l.c., using a 1:1 benzene/methylene chloride mixture as eluant; the red band was collected and extracted with methylene chloride. Removal of the solvent and addition of light petroleum (b.p. 60-80°C) afforded bright red crystals of the dye, m.p. 230°C (Found: C, 78.0; H, 5.3; N, 16.4. $C_{27}H_{21}N_5$ requires C, 78.1; H, 5.1; N, 16.9%).

III Kairoline (N-Methyl-1,2,3,4-tetrahydroquinoline) Dyes

N,N-Dimethyl-1,2,3,4-tetrahydroquinoline iodide

A mixture of tetrahydroquinoline (50 g), sodium carbonate (110 g), methyl iodide (150 g), and water (400 ml) was heated under reflux for 8 h. Some solvent was distilled off and the mixture was allowed to cool; the quaternary compound which appeared was filtered off, washed with water and crystallised from ethanol to give colourless needles of the methiodide (quantitative), m.p. 174 - 176°C Lit.,¹⁵⁰ m.p. 172 - 174°C).

Kairoline¹⁵¹

A mixture of the quaternary salt (58 g) and sodium azide (13 g) in dimethylformamide (400 ml) was refluxed for 2-3 h. The mixture was poured into water (1 l), extracted with benzene (3 l) and twice washed with water. Evaporation of solvent from the dried (MgSO₄) organic layer yielded a reddish oil which was distilled under reduced pressure to give N-methyl-1,2,3,4-tetrahydroquinoline as an almost colourless oil (25 g), b.p. 78 - 80°C at 5 mmHg.

1. 6-(2-Nitrophenylazo)kairoline

2-Nitroaniline (2 g) was diazotised as described previously and coupled with kairoline (2.1 g) in an acidic buffer as in the general procedure. The relatively pure red dye was filtered off and dried; the yield was quantitative.

Purification of the crude material was carried out in the usual way to give from ethanol small shining red needles of the dye, m.p. 124°C (Found: C, 65.15; H, 5.45; N, 18.9. $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}_2$ requires C, 64.9; H, 5.4; N, 18.9%).

2. 6-(1-Nitro-2-naphthylazo)kairolin

2-Amino-1-nitronaphthalene (1 g) was dissolved in acetic acid (10 ml) with warming and poured into dilute hydrochloric acid (100 ml, 10% v/v). The diazotised solution (standard procedure) was coupled with kairolin (0.8 g) as previously described. The crude dye (0.9 g) was purified on alumina and the recovered solid was crystallised from ethanol to give brick red platelets of the dye, m.p. 206°C (Found: 70.3; H, 5.4; N, 15.6. $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$ requires C, 69.4; H, 5.2; N, 16.2%).

3. 6-(4-Nitro-1-naphthylazo)kairolin

1-Amino-4-nitronaphthalene (0.4 g) was diazotised by the direct method and coupled with kairolin (0.3 g) in an acidic buffer. The dark green product so obtained was purified on alumina and crystallised from ethanol to give dark green crystals of the dye, m.p. $136-137^{\circ}\text{C}$ (Found: C, 69.05; H, 5.4; N, 15.8. $\text{C}_{20}\text{H}_{18}\text{N}_4\text{O}_2$ requires C, 69.4; H, 5.2; N, 16.2%).

4. 6-(5-Nitro-1-naphthylazo)kairolin

1-Amino-5-nitronaphthalene (0.5 g), diazotised by the general procedure, was coupled with kairolin (0.4 g) to give a brownish product (0.6 g). Purification on alumina afforded red crystals of the dye, m.p. 174-175°C (Found: C, 69.35; H, 5.2; N, 15.85. $C_{20}H_{18}N_4O_2$ requires C, 69.4; H, 5.2; N, 16.2%).

5. 6-(6-Nitro-2-naphthylazo)kairolin

Diazotisation of 2-amino-6-nitronaphthalene (200 mg) by the general procedure and coupling with kairolin (160 mg) gave a red product which was purified by preparative t.l.c. in methylene chloride. The product was crystallised from ethanol to give brownish wool-like crystals of the dye, m.p. 209°C (Found: C, 69.4; H, 5.6; N, 16.05. $C_{20}H_{18}N_4O_2$ requires C, 69.4; H, 5.2; N, 16.2%).

6. 6-(8-Nitro-2-naphthylazo)kairolin

2-Amino-8-nitronaphthalene (0.4 g) was dissolved in acetic acid (10 ml) by warming the mixture on a hot-plate. The solution was poured into dilute hydrochloric acid (100 ml, 10%) and diazotisation was carried out in the normal way; the filtered diazonium solution was coupled with kairolin (0.3 g) in an acidic buffer. The crude dye was dissolved in methylene chloride, chromatographed on alumina and the residual solid was crystallised from light petroleum

(b.p. 60-80°C) to give dark red crystals of the dye,

m.p. 144-145°C (Found: C, 68.9; H, 5.2; N, 16.4.

$C_{20}H_{18}N_4O_2$ requires C, 69.4; H, 5.2; N, 16.2%).

7. 6-(7-Nitro-9,10-dihydro-2-phenanthrylazo)kairolin

2-Amino-7-nitro-9,10-dihydrophenanthrene (0.3 g)

was diazotised and coupled with kairolin (0.2 g). The product (0.4 g) was dissolved in methylene chloride, chromatographed on alumina and crystallised from light petroleum (b.p. 60 - 80°C) to give red plates of the dye, m.p. 254 - 256°C (Found: C, 72.2; H, 5.7; N, 13.8. $C_{24}H_{22}N_4O_2$ requires C, 72.4; H, 5.5; N, 14.1%).

IV Julolidine (2,3,6,7-Tetrahydro-1H,5H-benzo[*ij*]
quinolizine)¹⁵⁴ Dyes

Julolidine

A mixture of tetrahydroquinoline (66.5 g) and 1-bromo-3-chloropropane (400 g) was refluxed for 20 h. The reaction mixture was cooled and concentrated hydrochloric acid (50 ml) in water (500 ml) was added and the excess of 1-bromo-3-chloropropane was removed in steam. The mixture was then basified by adding sodium hydroxide (ca. 80 ml, 40%) and the product was extracted into ether (two 150 ml portions). The ethereal solution was washed with water (150 ml) and dried (NaOH). The solvent was evaporated and the residue was distilled under reduced pressure to give an almost colourless product (60 g), b.p. 170-180°C at 10 mmHg (Lit.,¹⁵⁴ b.p. 110°C/1 mmHg).

1. 9-(2-Nitrophenylazo)julolidine

2-Nitroaniline (2 g) was diazotised as described previously and added dropwise to a suspension of julolidine (2.5 g) in an acidic buffer (general procedure). The dark product (3.5 g) was extracted into methylene chloride and the solution was chromatographed on alumina with a 1:1 mixture of light petroleum (b.p. 60-80°C) and benzene as eluant. The oily residue was treated with light petroleum (b.p. 60-80°C) and the resulting crystals were removed and recrystallised from ethanol to give dark red silvery

plates of the dye, m.p. 150°C (Found: C, 66.95; H, 5.7; N, 17.2. $\text{C}_{18}\text{H}_{18}\text{N}_4\text{O}_2$ requires C, 67.1; H, 5.6; N, 17.4%).

2. 9-(1-Nitro-2-naphthylazo)julolidine

2-Amino-1-nitronaphthalene (4 g) was added to acetic acid (25 ml) and warmed; the resulting solution was added to hydrochloric acid (15 ml) in water (50 ml). The cooled suspension was diazotised by the direct method. Coupling with julolidine (3.6 g) followed by basification (NaOH) gave a dark red powder (7.5 g) which was extracted into methylene chloride. The solution was chromatographed on alumina (neutral) using a 3:1 mixture of light petroleum (b.p. $60 - 80^{\circ}\text{C}$) benzene as eluant. The residue was treated with light petroleum (b.p. $60 - 80^{\circ}\text{C}$) to give red platelets of the dye, m.p. $226 - 228^{\circ}\text{C}$ (Found: C, 71.5; H, 5.3; N, 14.4. $\text{C}_{22}\text{H}_{20}\text{N}_4\text{O}_2$ requires C, 71.0; H, 5.4; N, 15.05%).

3. 9-(4-Nitro-1-naphthylazo)julolidine

1-Amino-4-nitronaphthalene (2 g) was dissolved by warming in dilute hydrochloric acid (50 ml, 20%) and the cooled solution was diazotised by the general procedure. The filtered yellow diazonium solution was gradually added to a buffered suspension of julolidine (1.8 g). The strong violet solution was neutralised by the addition of dilute sodium hydroxide. The greenish product (3.5 g) was isolated, dried and dissolved in the minimum amount of methylene

chloride and chromatographed on alumina using benzene - light petroleum (b.p. 60 - 80°C) as eluant. The first yellow band proved to be mainly undiazotised amine. The dye recovered from the column was crystallised from ethanol to give green needles of the dye, m.p. 173°C (Found: C, 71.25; H, 5.35; N, 15.2. $C_{22}H_{20}N_4O_2$ requires C, 71.0; H, 5.4; N, 15.05%).

4. 9-(5-Nitro-1-naphthylazo)julolidine

1-Amino-5-nitronaphthalene (2 g) was diazotised in dilute hydrochloric acid by the direct method as described previously. The light yellow solution was added to a suspension of julolidine (1.8 g) in an acidic buffer. The solution was neutralised with sodium hydrogencarbonate, the solid was filtered off and dried (3.2 g). Purification on alumina afforded a product, m.p. 204-207°C (Found: C, 70.0; H, 5.2; N, 14.4. $C_{20}H_{22}N_4O_2$ requires C, 71.0; H, 5.4; N, 15.05%). The rather impure dye was dissolved in methylene chloride and subjected to preparative t.l.c. The main red band was extracted with methylene chloride; crystallisation of the residue from ethanol gave a red powder which did not have improved analysis.

5. 9-(6-Nitro-2-naphthylazo)julolidine

2-Amino-6-nitronaphthalene (1.9 g) was diazotised by the general procedure and coupled with julolidine (1.8 g)

in an acidic buffer. The dark green product (ca. 5 g) obtained on basification with sodium hydroxide was chromatographed on neutral alumina with benzene/light petroleum (b.p. 60 - 80°C) mixture as eluant; the first yellow band was discarded. Removal of solvent from the resulting red solution gave an impure product which was rechromatographed using light petroleum (b.p. 60 - 80°C) and benzene (10%) as eluant; the amount of benzene was increased progressively until two bands were separated completely. The resulting product was dissolved in a small quantity of acetone; careful addition of ethanol gave lustrous green needles of the dye, m.p. 228 - 230°C (Found: C, 70.95; H, 5.5; N, 15.15. $C_{22}H_{20}N_4O_2$ requires C, 71.0; H, 5.4; N, 15.05%).

6. 9-(8-Nitro-2-naphthylazo)julolidine

2-Amino-8-nitronaphthalene (1.5 g) was diazotised by the general procedure and coupled with julolidine (1.4 g) as described previously. The resulting dark red precipitate (3.8 g) was purified on alumina using a 3:1 light petroleum (b.p. 60 - 80°C) - benzene mixture as eluant. The residue was dissolved in a small amount of acetone; addition of ethanol gave dark red needles of the dye, m.p. 188°C (Found: C, 70.6; H, 5.35; N, 15.45. $C_{22}H_{20}N_4O_2$ requires C, 71.0; H, 5.4; N, 15.05%).

Part CMiscellaneousPreparation of activated copper bronze¹⁸⁴

Copper bronze (25 g) was treated with a 2% solution of iodine in acetone (250 ml) over a period of 10 min. The grey mixture was filtered and the resulting solid was stirred with a 1:1 mixture of concentrated hydrochloric acid and acetone (125 ml). The activated copper bronze was filtered off, washed thoroughly with acetone and dried under vacuum. Best results were obtained if the copper bronze so activated was used immediately.

1. 2,4-Dinitroiodobenzene

Concentrated nitric acid (180 ml; $d = 1.42$) was added gradually to concentrated sulphuric acid (220 ml) and the mixture was cooled externally in an ice-bath. o-Nitroiodobenzene (25 g) was introduced into the mixture with constant stirring; the temperature rose to 40°C . When the addition was completed and the temperature rose no more, the reaction mixture was warmed on a water bath to about 60°C and stirred at this temperature for 30 min. The solution was then poured into ice-water. The resulting yellow precipitate (30 g, 60%) was filtered off and dried. Two crystallisations of the crude product from ethanol gave the dinitro compound as bright yellow crystals, m.p. $85 - 86^{\circ}\text{C}$ (Lit.,¹⁸⁵ m.p. 88°C).

2. 2,2',4,4'-Tetranitrobiphenyl

2,4-Dinitroiodobenzene (14 g) was added to a wide-mouthed conical flask and the contents were heated cautiously to 190°C on an oil-bath. Activated copper bronze (ca. 15 g) was added in small portions to the melt which was stirred mechanically. After the addition of the copper bronze (2 h), the temperature was gradually raised to 220°C and was kept there for a further 2 h. The half-baked mixture was then emptied into clean sand to prevent it settling in the flask. The cooled sand mixture was added to a large thimble and the product was extracted into benzene in a Soxhlet apparatus. The solvent was boiled down and the yellow product so obtained was crystallised from benzene to give the tetranitro compound as yellow prisms (3.6 g, 46%) m.p. 163 - 164°C (Lit.,¹⁸⁶ m.p. 163°C) (Found: C, 43.05; H, 2.0; N, 16.6. Calc. for $C_{12}H_6N_4O_8$: C, 43.1; H, 1.8; N, 16.8%).

3. Attempted preparation of 4,4'-dinitrobenzo[c]cinnoline

A suspension of 2,2',4,4'-tetranitrobiphenyl (3 g) in ethanol (100 ml) was heated on a water-bath to between 55 and 60°C. An aqueous solution of sodium sulphide nonahydrate (8 g in 40 ml of water) was added within 30 min. The mixture was refluxed overnight, and the dark red slurry was poured into water. The dark precipitate so obtained (1.5 g) was extracted into hot methylene chloride. After removal of solvent, the yellow-orange residue was crystallised from

ethanol to give material which melted at 208°C (Found: C, 55.6; H, 4.5; N, 19.5. $\text{C}_{12}\text{H}_6\text{N}_4\text{O}_4$ requires C, 53.3; H, 2.2; N, 20.7%).

4. 1,5-Diaminonaphthalene

A mixture of commercial 1,5-dinitronaphthalene (2 g), iron dust (6 g), iron(II) sulphate (0.6 g) and water (20 ml) was refluxed for 3 h and then cooled in an ice-water mixture with continuous agitation. The resulting precipitate was filtered off and extracted into boiling ethanol (25 ml) with the addition of charcoal. The filtrate on cooling afforded 1,5-diaminonaphthalene (0.6 g) as colourless needles, m.p. 190°C (Lit.,¹⁸⁷ m.p. 190.5°C) (Found: C, 76.1; H, 6.4; N, 18.0. Calc. for $\text{C}_{10}\text{H}_{10}\text{N}_2$: C, 76.0; H, 6.3; N, 17.7%).

REFERENCES

1. P. Griess, Ann., 106, 123 (1858).
2. P. Griess, Compt. Rend., 77, 49 (1859).
 P. Griess, Ann., 113, 334 (1860).
 P. Griess, Ann., 137, 85 (1886).
3. K.H. Saunders, "The Aromatic Diazo Compounds and Their Technical Applications", Edward Arnold, London, 1949, p.50.
4. E. Fischer, Ann., 190, 99 (1877).
- 5.(a) P. Griess, Phil. Trans. 154, 668 (1864).
 (b) E. Bamberger, Ber., 30, 506 (1897).
6. J.M. Tedder, Tetrahedron, 1, 270 (1957).
7. J. Griffiths, "Colour and Constitution of Organic Molecules", Academic Press, 1976.
8. E. Mitscherlich, Ann., 12, 311 (1834).
- 9.(a) Ger. Pat. 65,402, FBY.
 (b) U.S. Pat. 2,713,576, Rohm and Haas Co.
 (c) A.P. Terentiev and J.D. Mogiljanskij, Doklady Akad. Nauk. U.S.S.R., 103, 91 (1955).
10. T. Zincke and H. Bindewald, Ber., 17, 3026 (1884).
- 11.(a) S. Hünig and K.H. Fritsch, Ann., 609, 143 (1957);
 ibid., 172 (1957).
 (b) S. Hünig and H. Balli, Ann., 609, 160 (1957).
 (c) S. Hünig and G. Köbrich, Ann., 617, 181 (1958);

idem, ibid., 203 (1958); idem, ibid., 210 (1958);
idem, ibid., 220 (1958).

(d) S. Hünig, Angew Chemie Intern. Edit. 1, 640 (1962).

12. S. Hünig, R.D. Rauschenbach, and A. Schütz, Ann., 623, 191 (1959).
13. K. Venkataraman, "The Chemistry of Synthetic Dyes", Academic Press, Vol. III, New York, 1971, p.258.
14. H. Noether, Thesis, Marburg University, 1957.
15. H. Zollinger, "Azo and Diazo Chemistry", Interscience Publ., 1960, p.24.
16. J.H. Ridd, Quart. Rev., 15, 418 (1961).
17. E. Knoevenagel, Ber., 23, 2995-2998 (1890).
18. H.H. Hodgson and J. Walker, J. Chem. Soc., 1620 (1933).
19. C. De Milt and G. van Zandt, J. Amer. Chem.Soc., 58, 2044 (1936).
20. S. Krishna and R.L. Bhatia, Proc. 15th Indian Sci. Cong., 152 (1928).
21. J.A. Cade and A. Pilbeam, Chem. and Ind., 1578 (1959).
- 22.(a) U.S. Pat. 2,659,719, Eastman Kodak Co.
 (b) U.S. Pat. 2,683,708, Eastman Kodak Co.
 (c) U.S. Pat. 2,790,791, Eastman Kodak Co.
23. C.K. Ingold, "Structure and Mechanism in Organic Chemistry", 2nd Edit., G. Bell and Sons, London, 1969, p.372.

24. U.S. Pat. 2,773,864, General Aniline.
25. H.H. Hodgson and E. Marsden, J. Soc. Dyers and Colourists, 60, 16 (1944).
26. R. Pütter, Angew Chem., 63, 188 (1951).
27. H. Zollinger, Helv. Chim. Acta., 38, 1597 (1955).
28. K. Venkataraman, "The Chemistry of Synthetic Dyes", Academic Press, Vol. I, New York, 1952, p.432.
29. C.C. Barker and G. Hallas, J. Chem. Soc. (B), 1068 (1959).
30. R.W. Castelino and G. Hallas, J. Chem. Soc. (B), 793 (1971).
also K.L. Ng, M.Sc. Dissertation, University of Leeds, 1976.
31. Colour Index, 3rd Edit., Vol. 4, 1971, The Society of Dyers and Colourists, Bradford; The American Association of Textile Chemists and Colourists, Lowell, Mass., U.S.A.
32. Thorpe's Dictionary of Applied Chemistry, 4th Ed., Vol. IV, Longmans, London, p.195.
33. C. Graebe and C. Liebermann, Ber., 1, 106 (1868).
34. O.N. Witt, Ber., 9, 522 (1876).
35. R. Nietzki, Verhandlugen des Verein zum Beförderung des Gewerbfleisses, 58, 231 (1879).
36. H.E. Armstrong, Proc. Chem. Soc., 27 (1888).

37. J.T. Hewitt and H.V. Mitchell, J. Chem. Soc., 91, 1251 (1907).
38. See, however, A.C. Sircar, J. Chem. Soc., 109, 757 (1916).
39. J. Stieglitz, Proc. Natl. Sci. U.S., 9, 303 (1923).
40. G.S. Hartley, Nature, 140, 281 (1937);
Idem, J. Chem. Soc., 633 (1938).
41. A. Hantzsch and A. Werner, Ber., 23, 11 (1890);
A. Hantzsch, Ber., 27, 1702 (1894).
42. J.M. Robertson et al., Proc. Roy. Soc., A154, 187 (1936).
43. A.H. Cook, D.G. Jones and J.B. Polya, J. Chem. Soc., 1309 (1936).
44. R.L.M. Allen, "Colour Chemistry", Thomas Nelson and Sons, London, 1971.
45. R. Kuhn and F. Bär, Ann., 516, 143 (1935).
46. A. Burawoy, A.G. Salem, and A.R. Thompson, J. Chem. Soc., 4793 (1952).
47. G.M. Badger and R.G. Buttery, J. Chem. Soc., 614 (1956).
48. V.V. Perekalin and M.V. Savostyanova, Zhur. Obsch. Khim., 21, 1329 (1951).
49. H.E. Fierz-David, L. Blangey, and E. Merian, Helv. Chim. Acta, 34, 846 (1951).
50. See below
50. A. Hantzsch and F. Hilscher, Ber., 41, 1171 (1908);
50. I. Y. Bershtein and O. F. Ginzburg, Russ. Chem. Rev., 41, 97 (1972).

51. A. Hantzsch, Ber., 52, 509 (1919).
52. F. Kehrmann and S. Hempel, Ber., 50, 856 (1917).
53. C.R. Bury, J. Amer. Chem. Soc., 57, 2115 (1935).
54. M.T. Rogers, T.W. Campbell and R.W. Maatman, J. Amer. Chem. Soc., 73, 5122 (1951).
55. I.M. Klotz, H.A. Fries, J.Y. Chen Ho and M. Mellody, J. Amer. Chem. Soc., 76, 5136 (1954).
56. W.S. McGuire, T.F. Izzo and S. Zuffanti, J. Org. Chem., 21, 632 (1956).
57. H.H. Jaffé, J. Chem. Phys., 21, 415 (1953).
58. L. Pentimalli, Tetrahedron, 5, 27 (1959).
59. E. Sawicki, J. Org. Chem., 21, 605 (1956);
ibid., 22, 365, 621, 1084 (1957).
Also G.E. Lewis, Tetrahedron, 10, 129 (1960);
G.M. Badger, R.G. Buttery and G.E. Lewis, J. Chem. Soc.,
1888 (1954).
60. P.P. Birnbaum et al., Trans Faraday Soc., 49, 735
(1953).
61. A. Wohl, Bull. Soc. Chim., 6, 1312 (1939).
62. L.M. Yagupol'skii and L.Z. Gandel'sman, J. Gen. Chem.
USSR, 35, 1259 (1965).
- 63.(a) L.P. Hammett, "Physical Organic Chemistry", McGraw-
Hill, New York, 1940.

63. E. Hoyer, R. Schickfluss, and W. Steckelberg, Angew. Chem. Internat. Edit., 12, 926 (1973).
64. B. Roozpeikar, Ph.D. Thesis, University of Leeds, 1976.
65. I. Bridgeman and A.T. Peters, J. Soc. Dyers and Colourists, 86, 519 (1970).
66. G. Hallas and D.R. Waring, J. Chem. Soc. (B), 979 (1970).
also
G. Hallas, K.N. Paskins, and D.R. Waring, J.C.S. Perkin II, 2281 (1972).
67. G. Hallas, J.D. Hepworth and D.R. Waring, J. Chem. Soc. (B), 975 (1970);
G. Hallas and R.M. Potts, J.C.S. Perkin II, 59 (1974).
68. E.R. Ward, B.D. Pearson and R.R. Wells, J. Soc. Dyers and Colourists, 75, 484 (1959).
69. K. Ueno and S. Akiyoshi, J. Amer. Chem. Soc., 76, 3667 (1954).
70. W.R. Brode and D.R. Eberhart, J. Org. Chem., 5, 157 (1940).
71. J.H. Richards and S. Walker, Tetrahedron, 20, 851 (1964).
72. G. Hallas and K.L. Ng, J. Soc. Dyers and Colourists, 93, 284 (1977).

73. E.S. Stern and C.J. Timmons, "An Introduction to Electronic Absorption Spectroscopy in Organic Chemistry", 3rd Edit., Edward Arnold, London, 1970.
74. Ref. 73, p.44.
75. Ref. 7, p.76.
76. H.E. Schroeder and S.N. Boyd, Text. Research J., 27, 275 (1957).
77. C.H. Giles, Text. Research J., 33, 527 (1963).
78. G.S. Egerton and A.G. Morgan, J. Soc. Dyers and Colourists, 86, 242 (1970).
79. J.N. Murrell and A.J. Harget, "Semi-empirical Self-consistent-field Molecular Orbital Theory of Molecules", Wiley-Interscience, London, 1972.
80. W. Heitler and F. London, Z. Physik, 44, 455 (1927).
81. J. Sherman, J. Chem. Phys., 2, 488 (1934).
82. W.T. Simpson, J. Chem. Phys., 16, 1124 (1948).
83. (a) E. Hückel, Z. Phys., 70, 204 (1931).
(b) E. Hückel, ibid., 72, 310 (1931).
84. (a) E. Hückel, Z. Phys., 76, 628 (1932);
idem, ibid., 83, 632 (1933).
85. G.W. Wheland and D.E. Mann, J. Chem. Phys., 17, 264 (1949).
86. N. Muller, et al., J. Amer. Chem. Soc., 76, 4770 (1954).

87. M. Goeppert-Mayer and A.L. Clar, J. Chem. Phys.,
6, 645 (1938).
88. D.P. Craig, Proc. Roy. Soc., A200, 474 (1950).
89. C.C.J. Roothaan, Rev. Modern Phys., 23, 69 (1951).
90. R. Pariser and R.G. Parr, J. Chem. Phys., 21, 466
(1953).
91. J.A. Pople, Trans. Faraday Soc., 49, 1375 (1953).
92. Ref. 7, p.42 and 43.
93. University of Leeds, 1975.
94. University of Leeds, 1977.
95. PROCESSING, A169, 413 (1939).
96. AFRICANA
BINDERY, J. Phys. Chem. (Frankfurt),
CIRCULATION
DOCUMENTS
97. RARE BOOKS "Organic Chemistry",
REFERENCE, 1975, p.55.
SERIALS
98. THESE, 32-40 (1961).
99. LIGHT READING (1965).
ART REFERENCE
100. Signature, 66, 567 (1966).
101. pan, 32, 1357 (1959).
102. ion Spectra and Geometry
Molecules, New York, 1967.
- 103(a) A. Burger and E. Mosettig, J. Amer. Chem. Soc., 57,
2731 (1935).

- (b) Ibid., 58, 1857 (1936).
104. D.H. McDaniel and H.C. Brown, J. Org. Chem., 23, 425 (1958).
105. H.J. Bestmann, H. Haerberlein and W. Eisele, Chem. Ber., 99, 28 (1966).
106. R. Kuhn and O. Albrecht, Lieb. Ann., 455, 289 (1927).
107. V.N. Bochenkov, Zhur. Org. Khim., 12, 2355 (1976).
108. J.W. Krueger and E. Mosettig, J. Org. Chem., 3, 341 (1939).
109. H.C. Gull and E.E. Turner, J. Chem. Soc., 491 (1929).
110. R.K. Callow and J.M. Gulland, J. Chem. Soc., 2424 (1929).
111. J. Schmidt and E. Heinle, Ber., 44, 1488 (1911).
112. See ref. 105.
113. G.R. Bacon and W.S.L. Lindsay, J. Chem. Soc., 1375 (1958).
114. W.L. Mosby, J. Org. Chem., 24, 421 (1959).
115. N. Donaldson, "The Chemistry and Technology of Naphthalene Compounds", London, 1958.
116. H.H. Hodgson and D.E. Hathway, J. Soc. Dyers and Colourists, 63, 231 (1947).
117. H.A. Staab et al., Ber., 101, 829 (1968).
118. H.H. Hodgson and E.R. Ward, J. Chem. Soc., 1188 (1949).
119. J.P. Idoux, J. Chem. Soc.(C), 435 (1970).

120. D.W. Sherwood and M. Calvin, J. Amer. Chem. Soc., 64, 1350 (1942).
121. J. Schmidt and R. Mezger, Ber., 40, 4562 (1907).
122. B.M. Krasovitskii et al., Ukr. Khim. Zhur., 21 (5), 614 (1955).
123. R. Pschorr, Ber., 29, 496 (1896).
124. R.S.W. Braithwaite and P.F. Holt, J. Chem. Soc., 2304 (1959).
125. A. Furst, R.C. Berlo and S. Hooton, Chem. Rev., 65, 51 (1965).
126. J. Schmidt and G. Ladner, Ber., 37, 3573 (1904).
127. P.C. Austin, J. Chem. Soc., 1760 (1908).
128. M.J.S. Dewar and T. Mole, J. Chem. Soc., 2556 (1956).
129. J. Schultz, M.A. Goldberg, E.P. Odras, and G. Carsch, J. Org. Chem., 11, 307 (1946).
130. E. Mosettig and J.W. Krueger, J. Amer. Chem. Soc., 58, 1311 (1936).
131. R.M. Potts, Ph.D. Thesis, University of Leeds, 1977.
132. G. Hallas and D.R. Waring, Chem. and Ind., 620 (1969).
133. J.B. Cohen and H.D. Dakin, J. Chem. Soc., 81, 1333 (1902).
134. C. Willgerodt and B.R. Kok, Ber., 41, 2077 (1908).
135. A. Etard, Compt. Rend., 84, 127 (1877).

136. W.H. Hartford and M. Darrin, Chem. Rev., 58, 35 (1958).
137. F. Sacks and R. Kempf, Ber., 25, 1224 (1902).
138. D.S. Mittal, J. Indian Chem. Soc., 19, 408 (1942).
139. J. Meisenheimer and E. Patzig, Ber., 39, 2541 (1906).
140. J.W. Barton, A.R. Grinham and K.E. Whitaker, J. Chem. Soc. (C), 1384 (1971).
141. A.P.J. Hoogeveen, Rec. trav. chim., 50, 39 (1931).
142. V. Věselý and K. Dvořák, Bull. Soc. Chim., France, 33, 319 (1923).
143. H.H. Hodgson and E.E. Turner, J. Chem. Soc., 318 (1943).
144. G. Schroeter, Ber., 63, 1308 (1930).
145. J. v. Braun, Ann., 451, (1926).
146. A. Hardy, E.R. Ward and L.A. Day, J. Chem. Soc., 1979 (1956).
147. H.H. Hodgson and S. Birtwell, J. Chem. Soc., 433 (1943).
148. C.R. Saunders and C.S. Hamilton, J. Amer. Chem. Soc., 54, 636 (1932).
149. F.C. Whitmore et al., J. Amer. Chem. Soc., 66, 725 (1944).
150. R.W. Castelino, Ph.D. Thesis, University of Leeds, (1970).

151. T.L. Ho, Synthetic Communications, 3(2) 99 (1973).
152. N.D.V. Wilson and J.A. Joule, Tetrahedron, 24, 5493 (1968).
153. P.A.S. Smith and T.Y. Yu, J. Org. Chem., 17, 1286 (1952).
154. B.D. Glass and A. Weissberger, Org. Synth., 26, 40 (1946).
155. F. Ullmann and P. Dieterle, Ber., 37, 23 (1904).
156. See ref. 122.
157. C.F.H. Allen, "The Chemistry of Heterocyclic Compounds", Interscience. Publ., New York, 1958, p.371.
158. G. Wittig and O. Stichnoch, Ber., 68, 928 (1935).
159. P.Z. Slack and R. Slack, Nature, 160, 437 (1947).
160. J.L. Everett and W.C.J. Ross, J. Chem. Soc., 292 (1949).
161. J. Radell, L. Spialter and J. Hollander, J. Org. Chem., 21, 1051 (1956).
162. G.M. Badger, J.H. Seidler and B. Thompson, J. Chem. Soc., 3207 (1951).
also
J.F. Corbett and P.F. Holt, J. Chem. Soc., 3646 (1960).
163. S. Sako, Bull. Chem. Soc. Japan, 9, 393 (1934).
164. E. Tauber, Ber., 29, 2270 (1896).
165. J.J. Dobbie, J.J. Fox and A.J.H. Gauge, J. Chem. Soc., 99, 1615 (1911).

166. G.E. Lewis and R.J. Mayfield, Aust. J. Chem., 19, 1445 (1966).
167. G.E. Lewis and J.A. Reiss, Aust. J. Chem., 21, 1097 (1968).
168. F.E. King and T.J. King, J. Chem. Soc., 824 (1945).
169. S.D. Ross and I. Kuntz, J. Amer. Chem. Soc., 74, 1297 (1952).
170. R.E. Buntrock and E.C. Taylor, Chem. Rev. 68, 209 (1968).
171. P.M.G. Bavin, Can. J. Chem., 36, 238 (1958).
172. H.H. Hodgson and J. Walker, J. Chem. Soc., 1205 (1933).
173. G.T. Morgan and E.D. Evans, J. Chem. Soc., 115, 1128 (1919).
174. F. Ullmann and W. Bruck, Ber., 41, 3932 (1908).
175. D. Vörländer and F. Meyer, Ann., 320, 138 (1901).
176. D.M. Hall, M.S. Lesslie and E.E. Turner, J. Chem. Soc., 711 (1950).
177. J. Kenner and E.G. Turner, J. Chem. Soc., 99, 2101 (1911).
178. G. Schroeter, H. Müller and J.Y.S. Huang, Ber., 62, 645 (1929).
179. See ref. 108.
180. See ref. 131.

181. M.A. Goldberg, E.P. Odras and G. Carsch, J. Amer. Chem. Soc., 69, 260 (1947).
182. C.A. Dornfield, J.E. Callen and G.H. Coleman, Org. Synth. Coll. Vol. III, E.C. Horning, Ed., John Wiley and Sons, Inc., New York, 1955, p.134.
183. E. Mosettig and J. van de Kamp, J. Amer. Chem. Soc., 54, 3328 (1932).
184. A.I. Vogel, "A Textbook of Practical Organic Chemistry", 3rd Edit., London, 1970.
185. Körner, Gazz. Chim. Ital., 4, 323 (1874).
186. F. Ullman and J. Bielecki, Ber., 34, 2177 (1901).
187. H.H. Hodgson and J.S.Whitehurst, J. Chem. Soc., 202 (1945).