THE SYNTHESIS AND EXAMINATION OF AZO DYES DERIVED FROM NOVEL COUPLERS

THESIS

Submitted in fulfilment of the
requirements for the degree of
DOCTOR OF PHILOSOPHY
by
RICHARD MARSDEN

R Marsden

Department of Colour Chemistry
University of Leeds
January 1982

ACKNOWLEDGEMENTS

The author wishes to express his sincere thanks to Dr. G. Hallas for his continual guidance, encouragement and advice throughout the course of this work. Thanks are also due to Professor I.D. Rattee, in whose department this work was carried out, and all the various staff of the department. Mr J. Stewart (and co-workers) of the Chemistry Department are congratulated on their microanalysis work, and I am indebted to Dr. D. Mason (Preston Polytechnic) for his work on basicities.

I would like to record my appreciation of the speedy and patient typing of Miss Julie Walton, and to say thanks to Jane for brightening up my life these last two years.

Finally, I am indebted to the University of Leeds for allowing a native Lancastrian to study across the border in Yorkshire.

CONTENTS

Title Page (i)

Acknowledgements (ii)

Contents (iii)

Abstract (vii)

1. INTRODUCTION

1.1. Early History of the Synthetic Dye Industry 1

1.2. Development and Improvement of Azo Disperse Dyes. 4

1.3. Early Theories of Colour and Constitution Relationships. 14

1.4. Valence Bond Resonance Theory 16

1.5. Substituent Effects in Aminoazo Dyes 20

1.6. Dipole Moment Studies 33

1.7. Protonation Equilibria of Aminoazo Dyes 36

1.8. Relationship Between pK_a Values, $C_\varepsilon/A_\varepsilon$ Ratios and Protonation Equilibria in Aminoazo Dyes 42

1.9. Application of Perturbational Molecular Orbital (PMO) Theory to Aminoazo Dyes 46

2. DISCUSSION OF RESULTS

2.1. Coupling Components 53

2.2. Electronic Absorption Spectra of Some Di- and Tri-phenylmethane Dyes 53

2.3. Electronic Absorption Spectra of the Various Azo Dyes 55

2.3.1. Neutral Solution 56

2.3.2. Acidic Solution 87

2.4. Fastness Properties of the Azo Dyes 103

CONTENTS (Cont.)

2.4.1. Light Fastness 103
2.4.2. Wash Fastness 110
2.5. Proton Nuclear Magnetic Resonance Spectra of the Azo Dyes 111
2.6. Basicity Measurements of the Azo Dyes 128

3. DISCUSSION OF EXPERIMENTAL

3.1. Preparation of Intermediates 134
3.1.1. Coupling Components 134
3.1.2. Diazo Components 134
3.1.3 Miscellaneous Preparations 134
3.2. Synthesis of Azo Dyes 139
3.2.1. Diazotisation 139
3.2.2. Azo Coupling 143
3.3. Side Reactions 148
3.4. Purification Techniques 152
3.5. Examination of the Dyes 153
3.6. Calculation of pK_a Values 154

4. EXPERIMENTAL DETAILS

4.1. General Information 158
4.2. Reaction Schemes 159
4.3. Preparation of Diazo Components 162
4.4. Preparation of Coupling Components 164
4.5. Preparation of Dyes 168
4.5.1 Diazotisation Procedures 168
4.5.2 Coupling Procedure 171
4.5.3. Nitrosation of 5-Amino-3-phenyl,1,2,4-thiadiazole and Coupling to N-Phenylpyrrolidine 172

CONTENTS (Cont.)

4.6. Miscellaneous Preparations 199

4.7. Preparation of the Dyes for Spectral Measurements 202

4.8. High Temperature Dyeings on Polyester 202

4.9. Fastness Tests 203

4.10. Measurement of pK_a Values 205

REFERENCES 206

5. APPENDIX 1. Quantitative Applications of Molecular Orbital Theory to the Spectral Properties of Dyes 213

5.1. General Considerations 213

5.2. The Hückel Molecular Orbital (HMO) Method 214

5.3. The Pariser-Parr-Pople (PPP) Self Consistent Field (SCF) Molecular Orbital (MO) Method 218

5.3.1. Configuration Interaction (CI) 222

5.4. Practical Applications of the PPP Method 223

6. APPENDIX 2. Dyed Polyester Samples

Plate 6.1. High Temperature Dyeings on Polyester of Some Dyes Derived from N-Phenylpyrrolidine (64-70; $Y=-CH_2CH_2-$) 249

Plate 6.2. High Temperature Dyeings on Polyester of Some Dyes Derived from (a) N-Phenylpiperidine (64-67; $Y=-CH_2CH_2CH_2-$) and (b) N-Phenylmorpholine (64-67; $Y=-CH_2OCH_2-$) 250

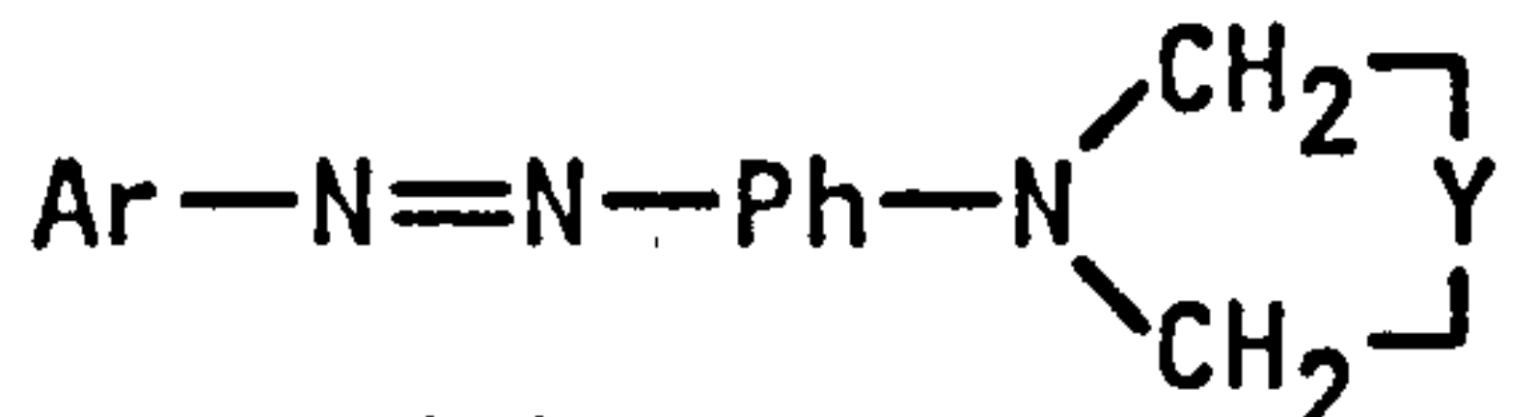
Plate 6.3. High Temperature Dyeings on Polyester of Some Dyes Derived from (a) N-Phenylthiomorpholine (64-66; $Y=-CH_2SCH_2-$), (b) N-Phenylthiomorpholine-1,1-dioxide (64 ; $Y = -CH_2SO_2CH_2-$), (c) N'-Ethyl-N-phenylpiperazine

CONTENTS (Cont.)

(64 ; Y = $-CH_2N(Et)CH_2-$), (d) N'-Acetyl-N-phenylpiperazine (64-66; Y=$-CH_2N(Ac)CH_2-$) and (e) NN-Diethylaniline(30) 251

ABSTRACT

The work presented in this thesis comprises the synthesis and examination of several series of azo dyes of general structure (I) where Y incorporates the terminal nitrogen atom in a five- or six-membered saturated heterocyclic ring system, and Ar is an aromatic carbocyclic or heterocyclic residue, often containing substituent groups. Results are interpreted in terms of the effect of Ar and Y (electronic and steric) on the conjugation of the lone pair of electrons of the terminal nitrogen atom with the rest of the system. Thus, the pyrrolidinoazo dyes $(Y{=}{-}CH_2CH_2{-})$ absorb at similar wavelengths to their *NN*-diethyl analogues whilst the corresponding piperidino dyes $(Y{=}{-}CH_2CH_2CH_2{-})$ show hypsochromic shifts of λ_{max}. The presence of a Y-heteroatom in a six-membered saturated ring increases this hypsochromic effect.



$$\mathrm{Ar{-}N{=}N{-}Ph{-}N}\begin{array}{l}\diagup CH_2\urcorner\\ \qquad\ \ Y\\ \diagdown CH_2\lrcorner\end{array}$$

(I)

Absorption bands of the mono-protonated chromogens have also been examined; in the azobenzene series it is found that variation of the terminal amino group produces a change from almost exclusive protonation at the β-azo nitrogen atom (azonium ion) to nearly quantitative protonation at the terminal nitrogen atom (ammonium ion).

Trends in the p.m.r. spectra of the dyes have been noted. Fastness properties of the dyes on polyester are given. Light fastness ratings are generally low, although the presence of a Y-heteroatom in the six-membered terminal amino ring is advantageous, resulting in values approaching those of the *NN*-diethyl counterparts. The light fastness properties of monoazo dyes are discussed generally.

Basicity values have been obtained for selected dyes of each series; pK_a is generally found to decrease as the donor capacity of the terminal nitrogen atom decreases. Somewhat surprisingly, the basicities of the 4'-substituted pyrrolidinoazobenzene types appear to be insensitive to the substituent, whereas measurements on related piperidino compounds suggest that for this series pK_a falls as the electron withdrawing strength of the 4'-substituent increases.

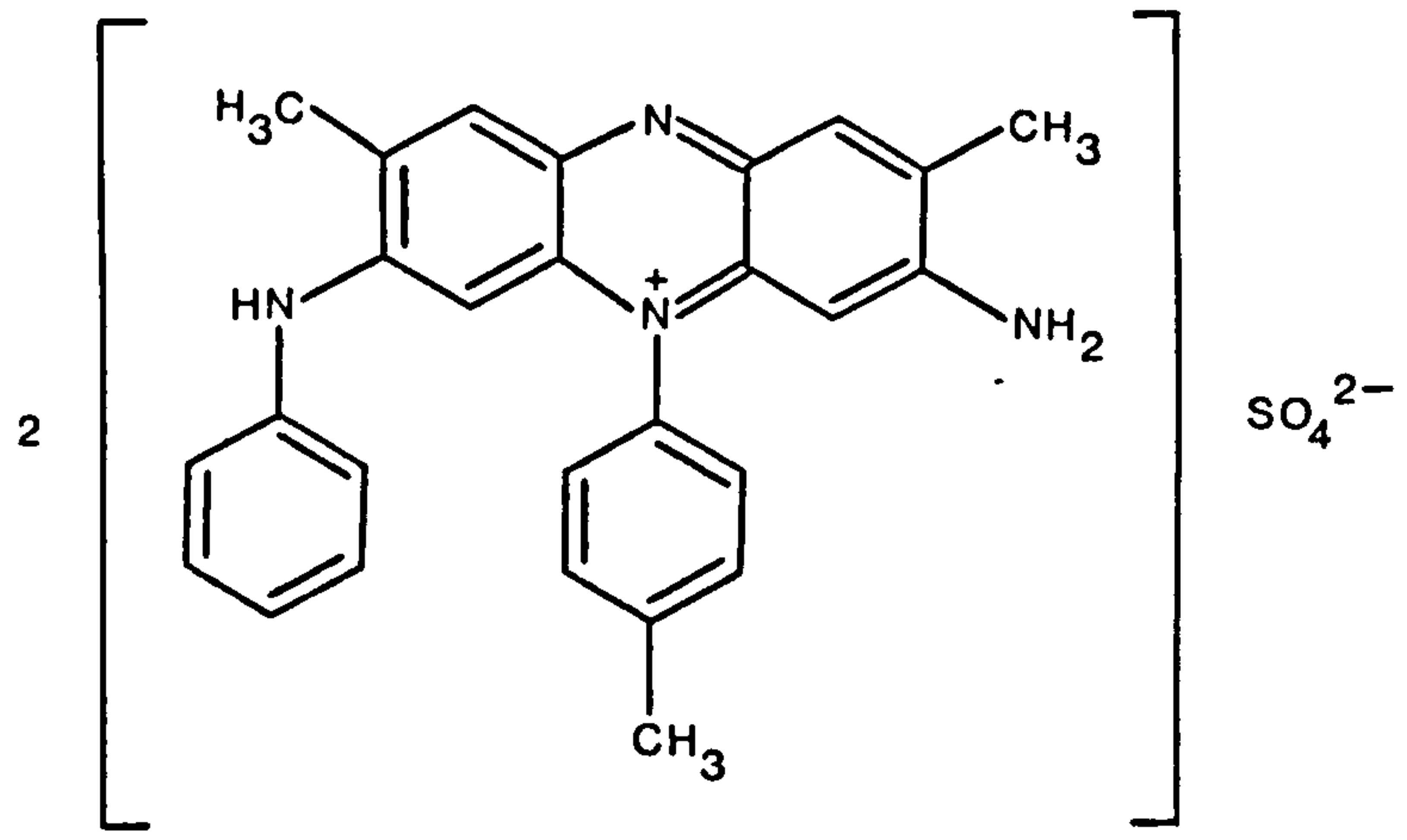
Pariser-Parr-Pople (PPP) molecular orbital calculations have been carried out for dyes of the pyrrolidino series. Good results are obtained for chromogens where Ar is carbocyclic, and also where Ar is heterocyclic after modification of certain parameters relevant to the heteroatoms of this system (it is possible that these parameters may not be of general use in other dye systems). Additional information available from this type of calculation, such as prediction of oscillator strengths, electron densities, dipole moments and transition moments, is briefly discussed.

To Mum and Dad

1. INTRODUCTION

1.1. Early History of the Synthetic Dye Industry[1]

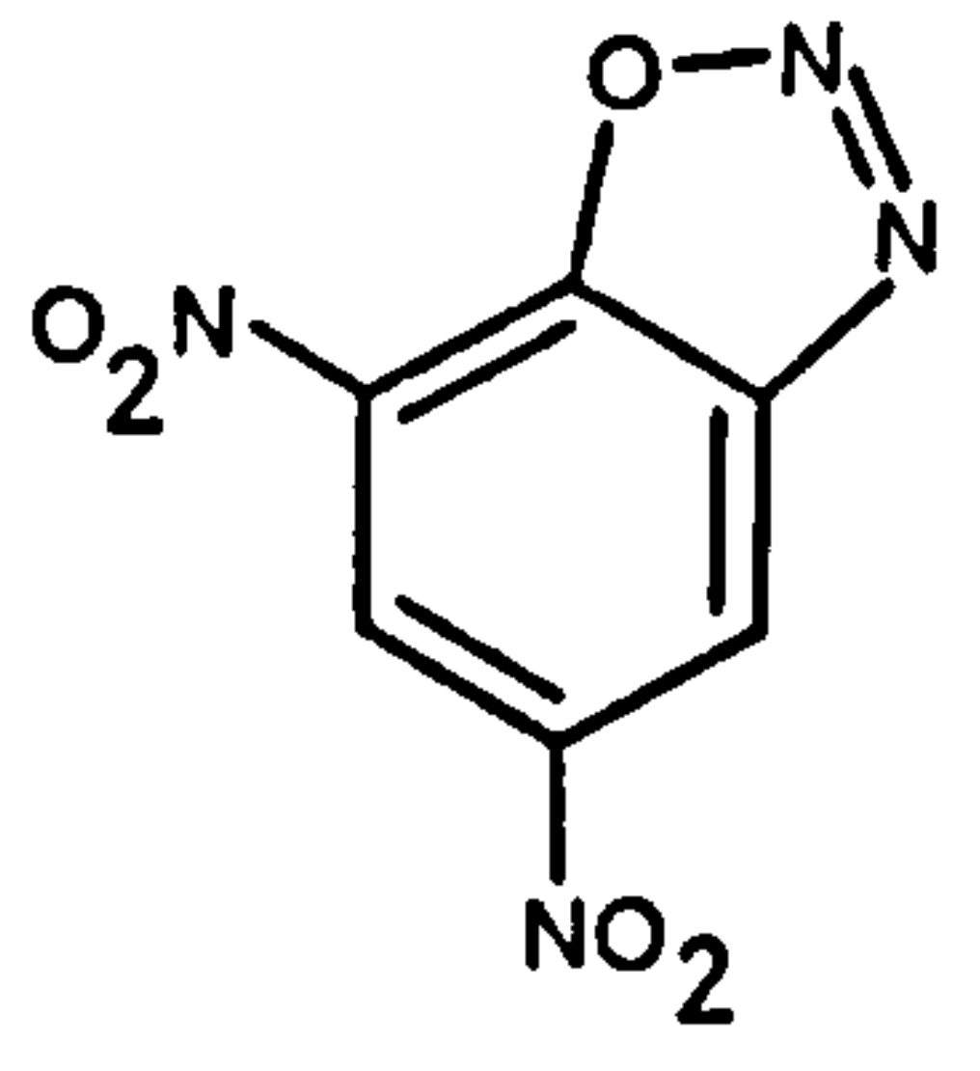
The azo dyes, characterised by the presence of one or more azo (-N=N-) groups,[2] are by far the most important of all the groups of colouring matters. These compounds span all the various dye application classes, and consequently are utilised in one form or another on all the commercial fibres in use at the present time. The history of the azo dyes dates back to the origins of the synthetic dyestuffs industry which, it is universally accepted, was launched in 1856 when William Henry Perkin,[3] attempting to synthesize quinine by the action of potassium dichromate on aniline sulphate, isolated from the unattractive black product a small amount of a violet colouring matter which dyed silk directly. Perkin called this product Mauveine; it is perhaps better known today as Perkin's Mauve(1).[4]



(1)

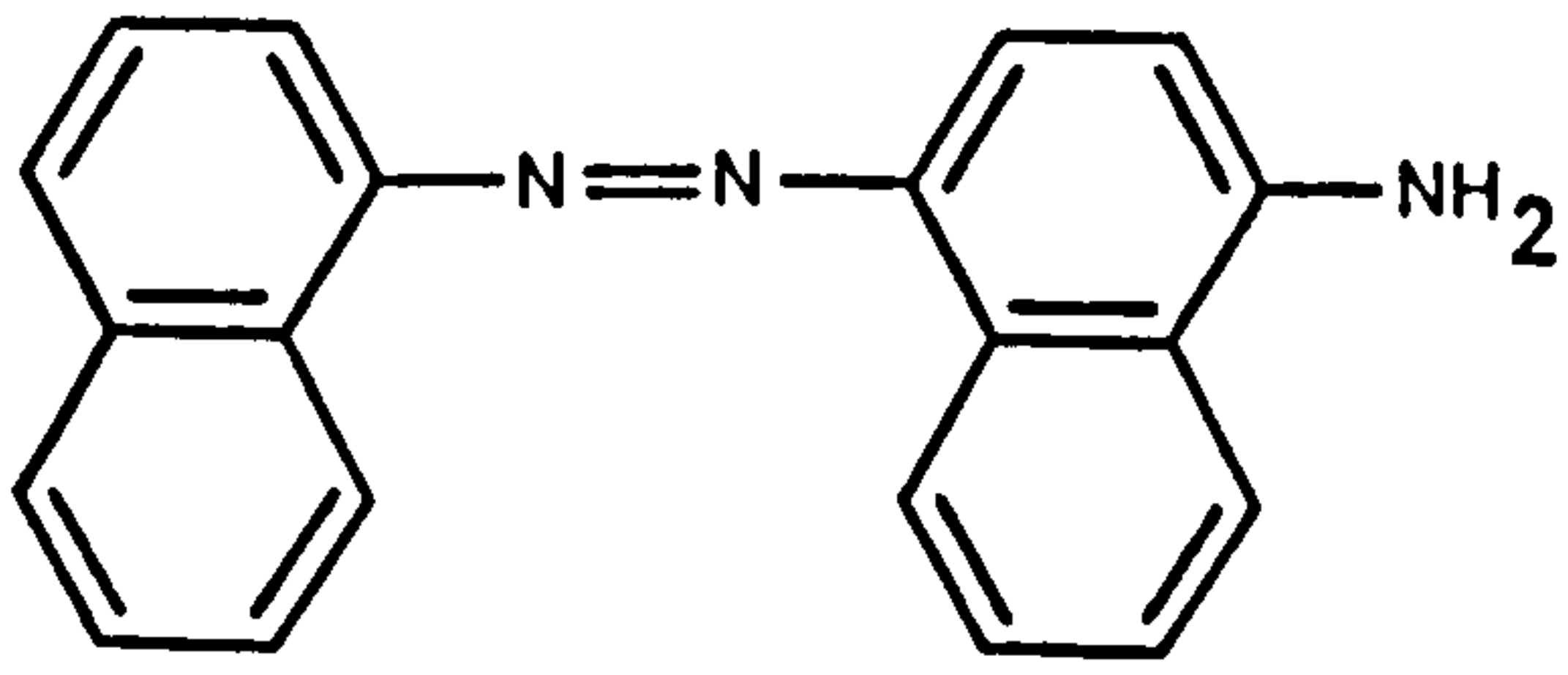
Perkin's Mauve was not the first colorant to be synthetically produced, however; as early as 1771, Woulfe prepared picric acid by the action of nitric acid on indigo and showed that it dyed silk in bright yellow shades and, five years later, Scheele prepared a dye known as Murexide by the action of nitric acid and ammonia on uric acid. Also, in 1834 Runge obtained rosolic acid, but none of these products attained any commercial significance. Perkin, however, recognised the commercial importance of his product and was able to develop its synthesis so that the dye could be used in large scale production; this began in 1857. Thus, Perkin's Mauve was the first synthetic dye to be manufactured in bulk and used for practical dyeing. The brilliant violet hue on silk immediately attracted much attention and stimulated research in the dyestuffs field.

It was in 1858 that Peter Griess[5,6] discovered the diazotisation reaction.[7,8] As the use of sodium nitrite as a source of nitrous acid was unknown until Martius' discovery in 1866,[9] Griess generated nitrous fumes by the reduction of nitric acid and reacted these with picramic acid, obtaining an unexpected product which he called a diazo compound. This material proved to be 4,6-dinitrobenzene-2,1-diazo oxide(2).[7]



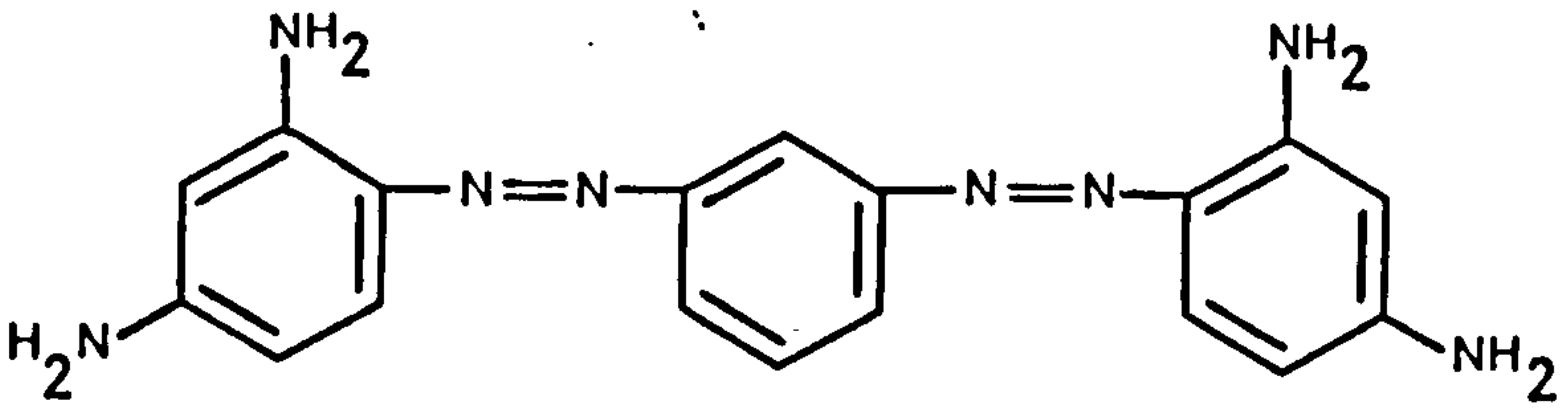
(2)

In 1859, Griess obtained aminoazobenzene by a rearrangement reaction but this was not in fact the first azo compound. Three years earlier, Perkin and Church, investigating the reduction of dinitronaphthalene, isolated 4-aminoazonaphthalene(3). These workers also reduced this compound completely, so obtaining the first naphthalenediamine and introducing what ultimately became a standard method of determining the constitution of azo compounds. Consequently, this reaction was the first definite example of the preparation of an azo compound.



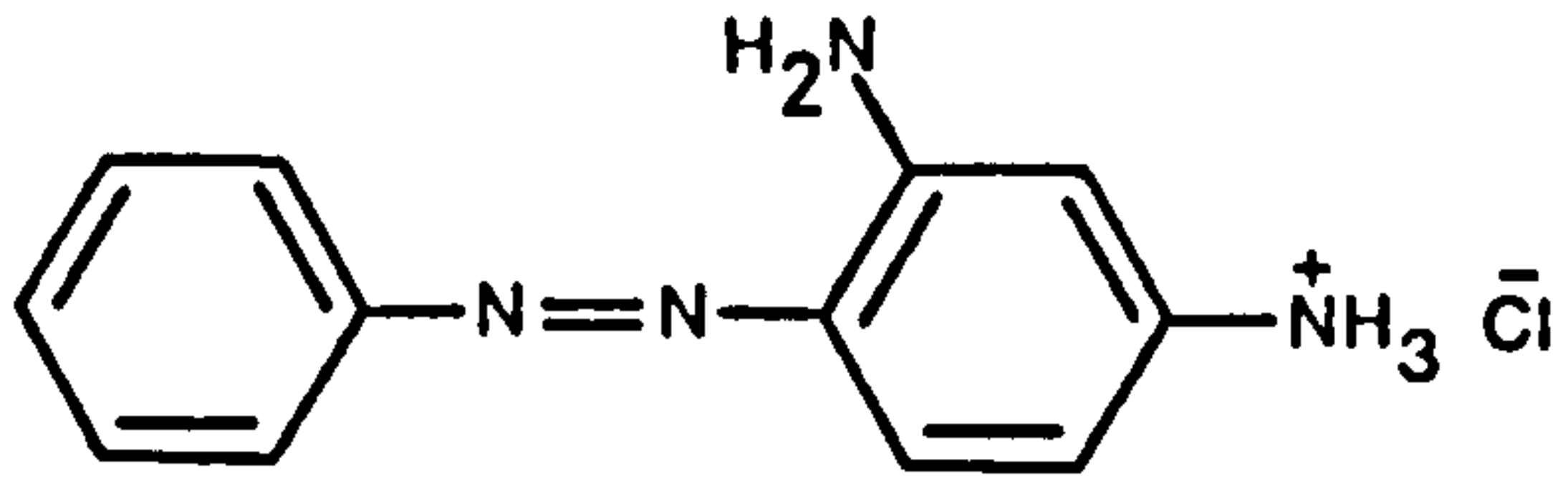
(3)

Griess eventually discovered the coupling reaction,[10] during 1861 and 1862, the first dye prepared in this way being p-phenylazo-naphthylamine, which is still in use today. About this time Griess also prepared p-hydroxyazobenzene (the first hydroxyazo dye) indirectly by treating diazobenzene with barium carbonate, and discovered the first dis-azo dye, 2,4-bisphenylazophenol. In 1870, Kekulé also prepared p-hydroxyazobenzene, this time by coupling diazotised aniline to phenol, and at the same time determined the constitution of the azo compounds. Earlier, in 1863, Roberts, Dale & Co. had marketed the first really successful azo dye, Bismark Brown (4), but the initial manufacture of an azo dye by Griess' method of



(4)

diazotisation and coupling had to wait until 1876 when Witt discovered the important basic dye Chrysoidine(4a),made by coupling benzene diazonium chloride with m-phenylenediamine.

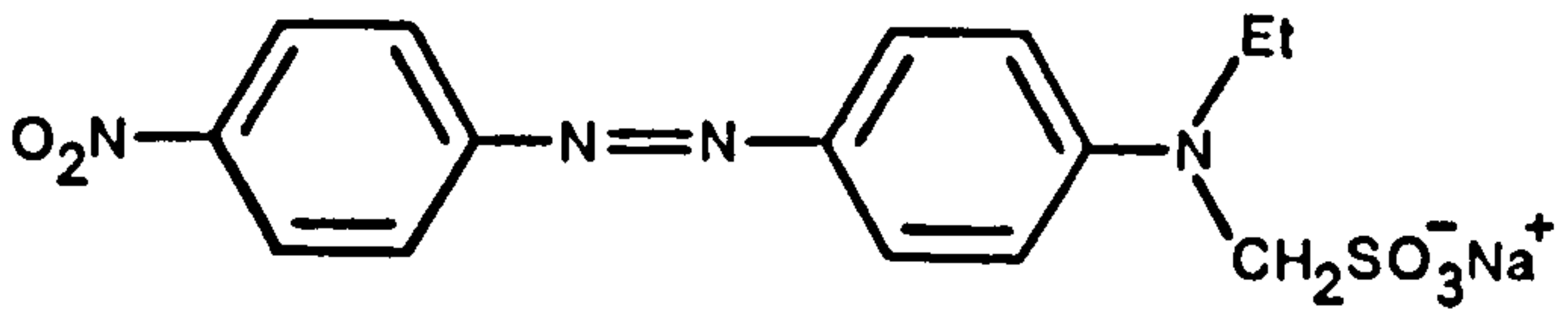


(4a)

The decisive work of Kekulé on the quadrivalence of carbon (1858) and the constitution of benzene (1865) opened up the way for the planned preparation of synthetic dyes. Towards the end of the nineteenth century, the azo dyes flourished as the range of intermediates grew[11] and, by 1885, nearly 10,000 individual coloured azo compounds were covered by patents, most of them German.

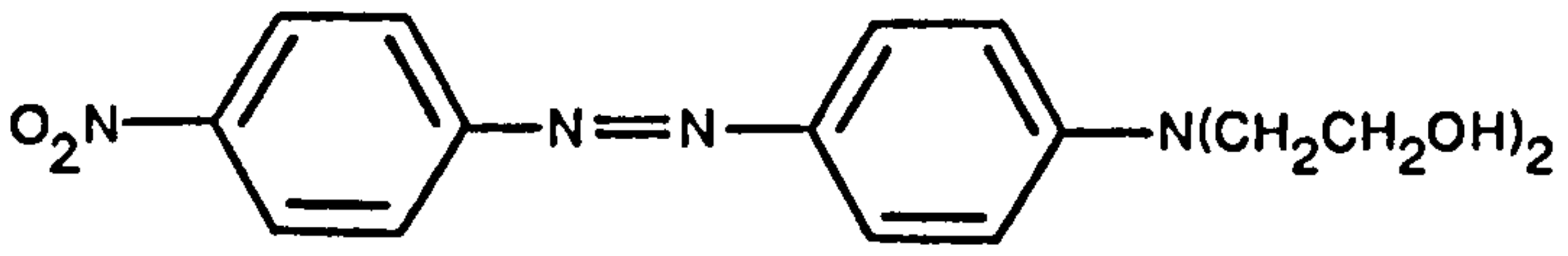
1.2. Development and Improvement of Azo Disperse Dyes

Before the First World War, almost all dyes were applied from solution in an aqueous dyebath to cotton, wool, silk and other natural fibres. The introduction of a man-made fibre, cellulose acetate, with an inherent hydrophobic nature, created a situation in which few of the then available dyes had affinity for the new fibre. As the result of an examination into the dyeing properties of cellulose acetate, Green and Saunders in 1922 discovered the Ionamines[12] (BDC) which were ω-sulphonic acids of N-alkylaminoazo compounds, such as (5), and of aminoanthraquinone derivatives. These water soluble dyes were hydrolysed in the aqueous dyebath to form the insoluble free base which underwent absorption by the fibre. Once this fact was realised, the opportunity of dyeing cellulose acetate with water insoluble dyes became

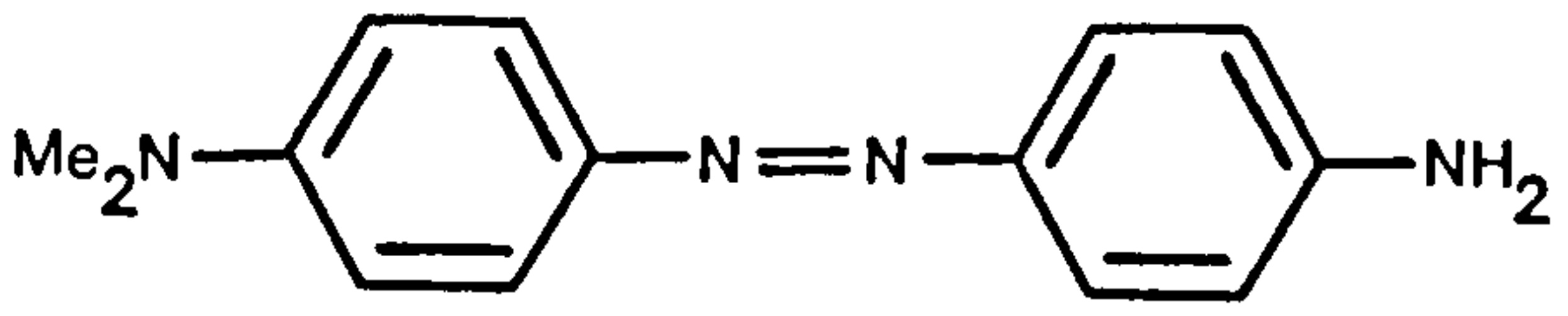


(5)

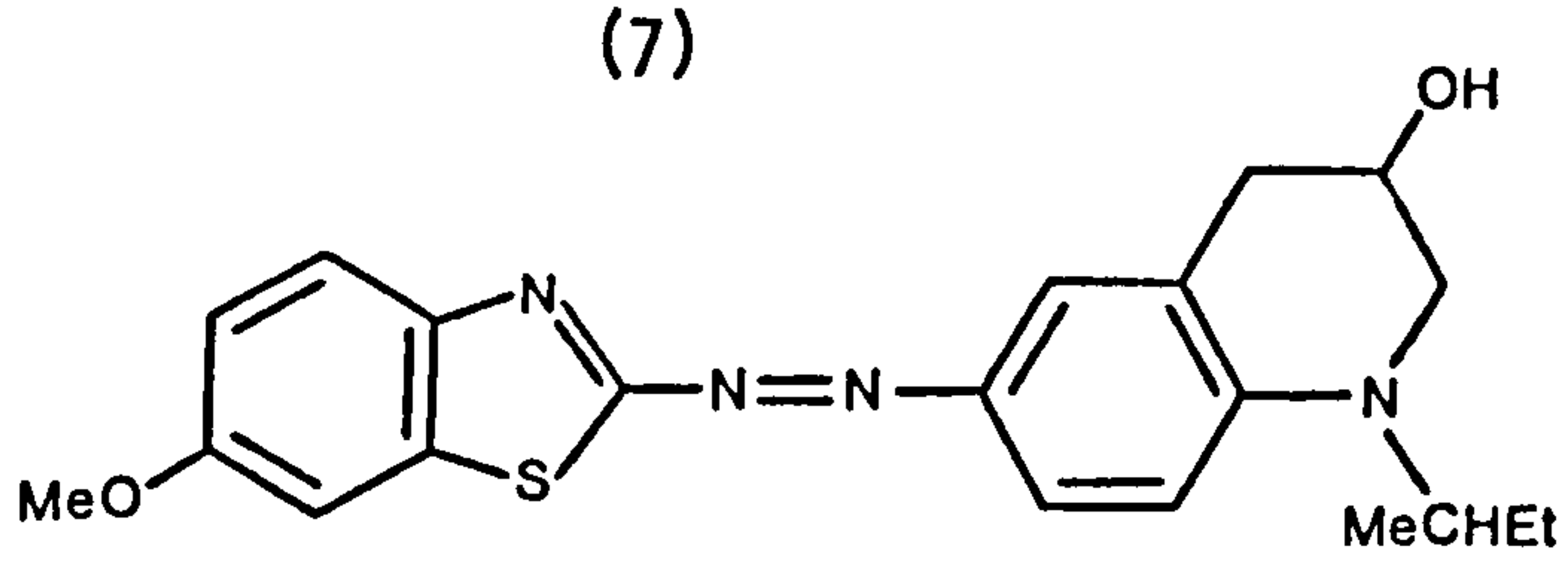
apparent, provided that these dyes were sufficiently dispersed in the dyebath. The first group of dyes of this type were the Dispersols (ICI), such as Dispersol Fast Red R(6) and Dispersol Diazo Black AS(7), so called because diazotisation of the dye on the fibre and development with hydroxynaphthoic acid gives a full blue-black coloration. The Celliton (IG) range included blue monoazo dyes, obtained both from poly-substituted anilines and also by incorporating the benzthiazole ring system as in Celliton Discharge Blue 5G(8).



(6)



(7)

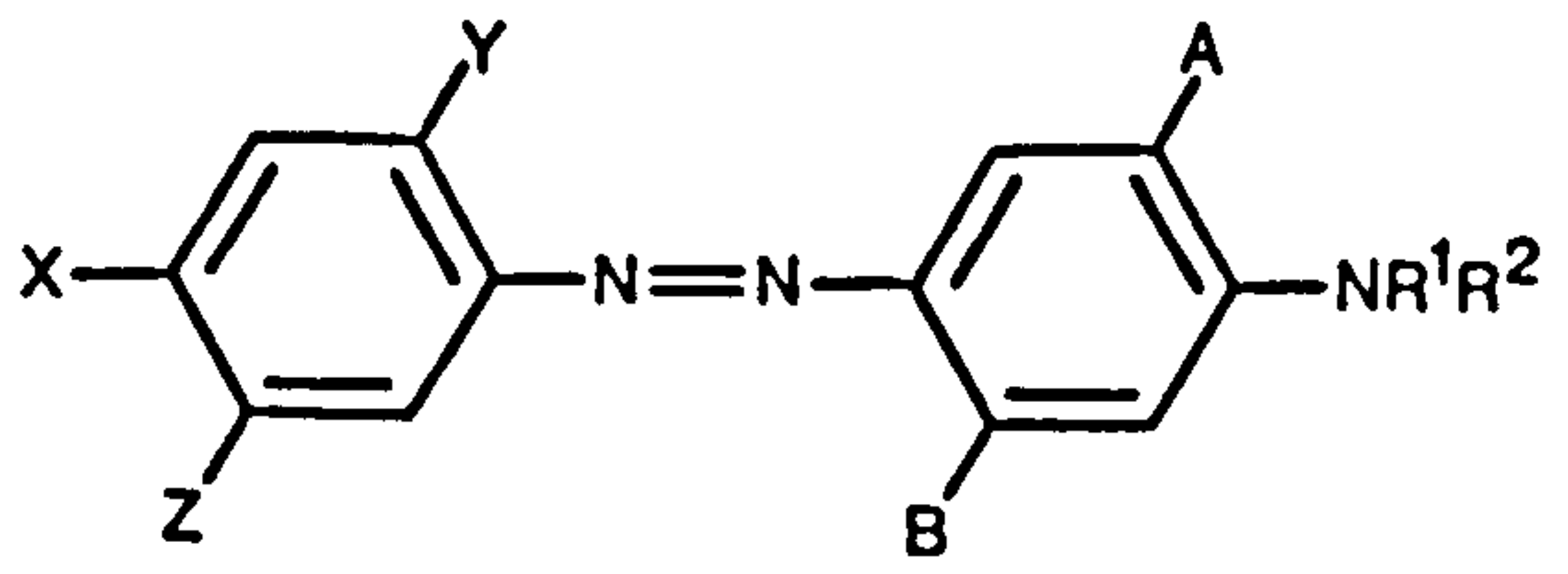


(8)

The development of nylon, first manufactured commercially in 1938 in the USA, and of acrylic fibres, developed during the 1940s, both types possessing hydrophobic characteristics, further increased the use of the disperse dyes. However, the advent of polyester fibres, discovered in 1941 and introduced commercially in 1948, prompted a particularly intensive research effort. Polyester is much more hydrophobic than cellulose acetate and is only slightly swollen by water up to the atmospheric boil which, for practical purposes, in 1950 was the maximum temperature available for dyeing. Waters[13] showed that only dyes of very low aqueous solubility had appreciable substantivity for the fibre. Hence, disperse dyes were recognised as the main type for the dyeing of this particular fibre.

The earliest recommendations were dominated by the need for acceptable colour yields in practicable dyeing times (ca. 90 min) at the atmospheric boil. Unfortunately, the fastness properties of these types were low, and the compounds were consequently superseded by dyes which had much better application properties; the dye-build-up on the fibre was increased to acceptable limits by the use of carriers at the boil and also by high-temperature dyeing at pressures such as 20lb in^{-2}.

These azo disperse dyes are of general structure (9); this type of structure has continued in use up to the present time.[14] Much of the research work carried out by dye manufacturers is concerned with ringing the structural changes in dyes of formula (9), and related compounds, in order to extend the colour range and to meet application and fastness requirements.[15-17] It has long been realised that structural



(9)

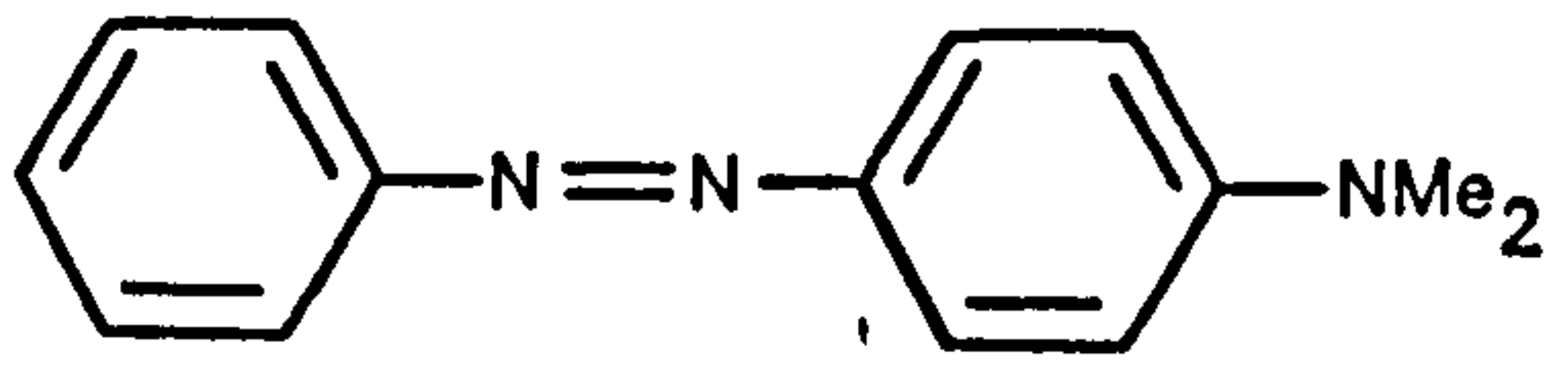
X,Y,Z = H or electron withdrawing groups

A,B = H or electron donating groups

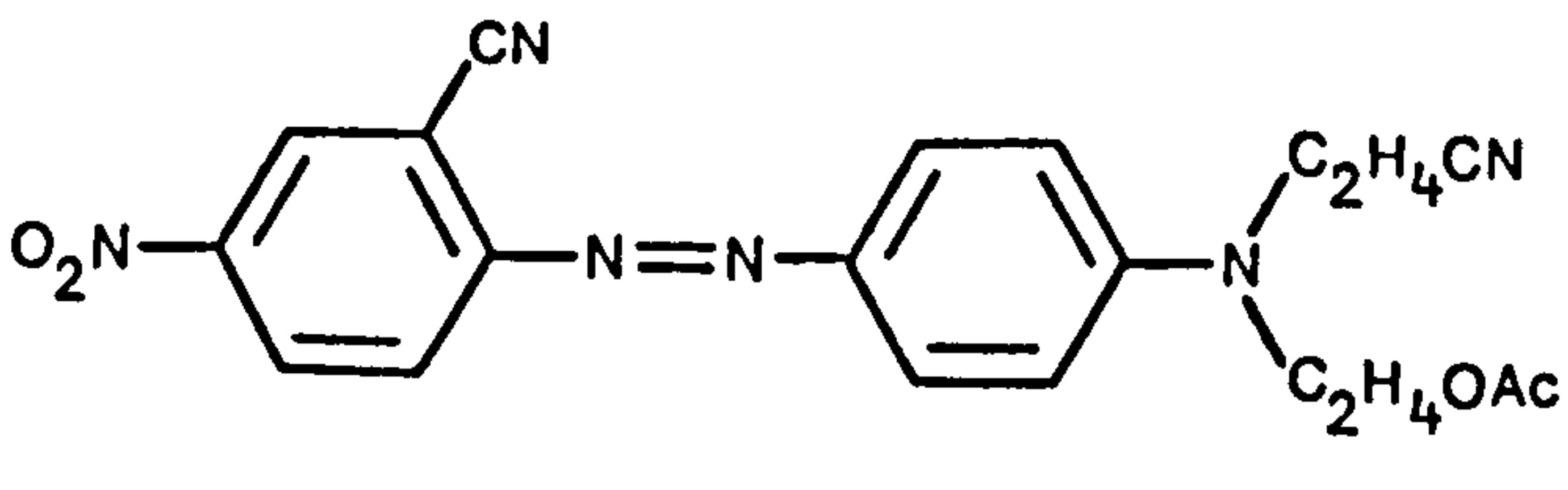
R^1, R^2 = alkyl or substituted alkyl groups

variations can improve one property at the expense of another and that inter-relationships are often complex.

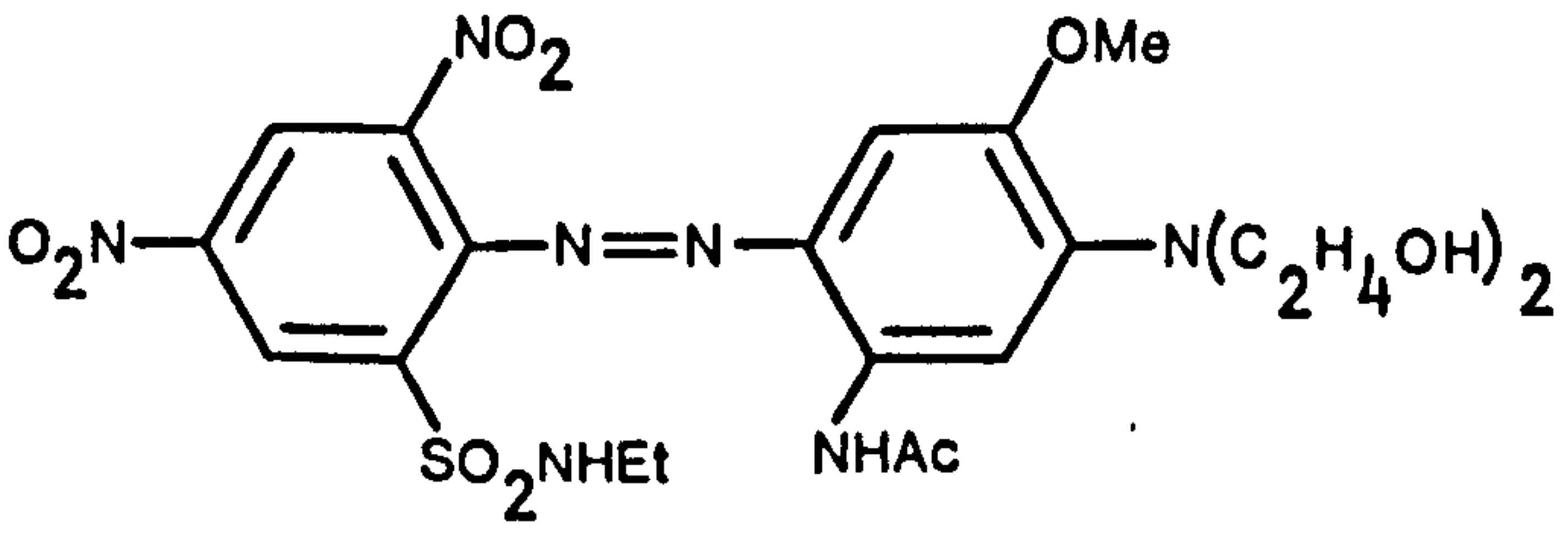
The colour of the simplest azo disperse dyes is usually yellow, as with (10).[6] Deeper colours can be obtained by variation in the number and type of substituents present, as in the case of dyes (11)[18] and (12)[19] which are red and blue, respectively, or by replacing one or both of the carbocyclic aromatic systems by heterocyclic analogues.



(10)

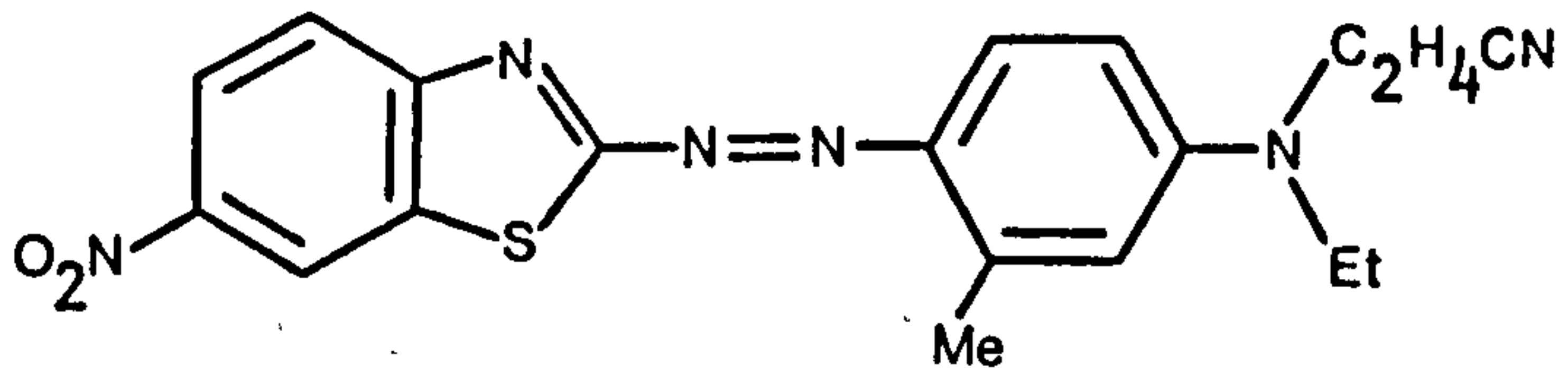


(11)

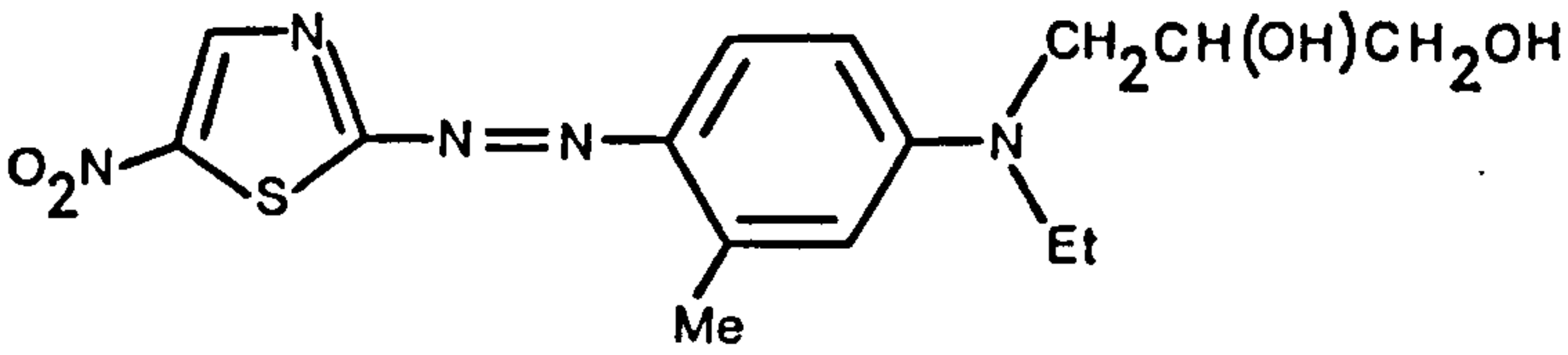


(12)

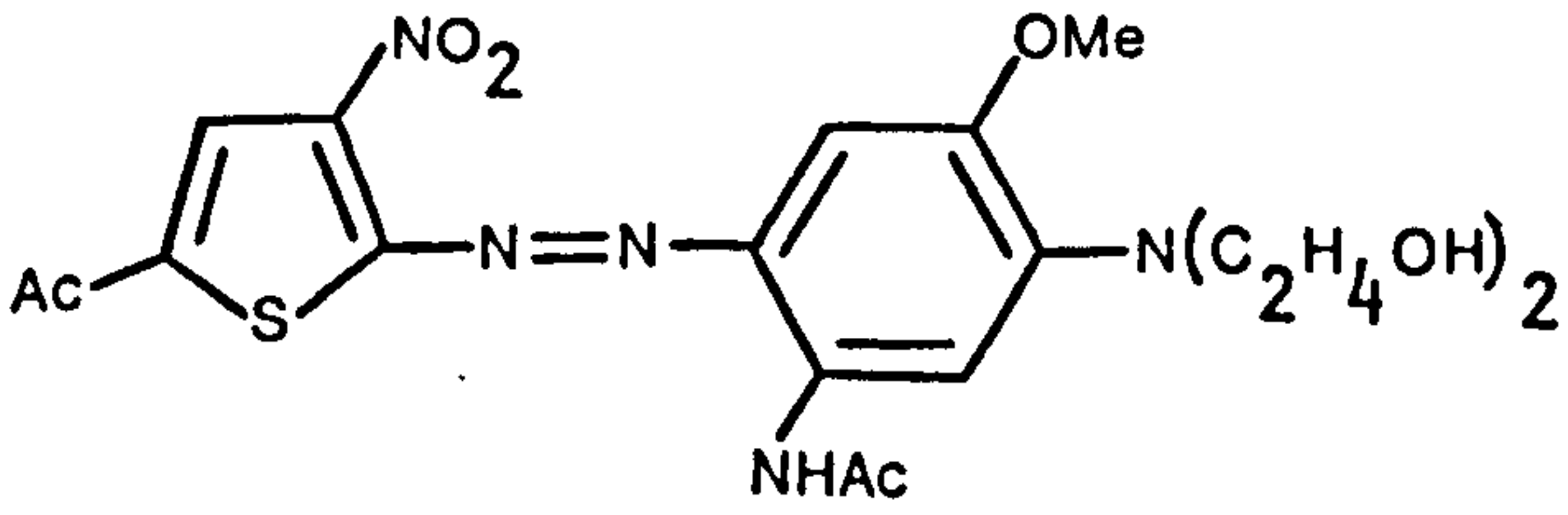
Most commonly, in the latter group, the diazo component is an appropriately substituted sulphur heterocycle, especially benzthiazole, thiazole and thiophene types, exemplified by (13),[20] (14)[21] and (15),[19] respectively. Other diazo components cited in the patent literature include those based on 3-aminopyrazoles, 5-aminoimidazoles, amino-1,2,4- and -1,3,4-thiadiazoles, 2-aminoisothiazoles and



(13)

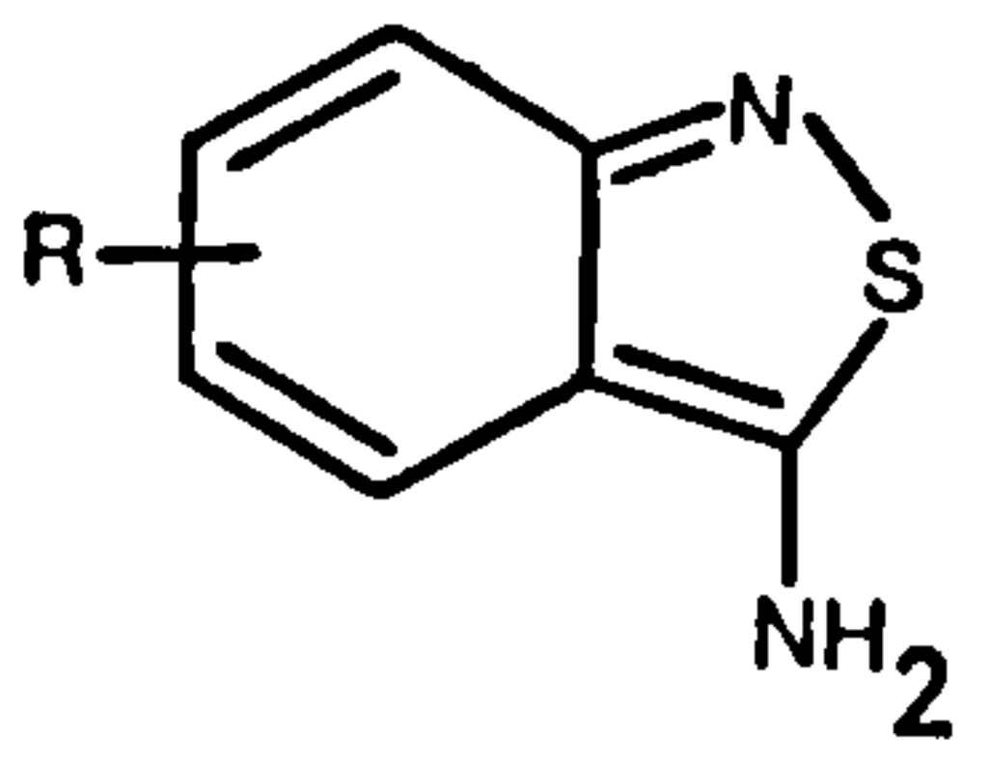


(14)



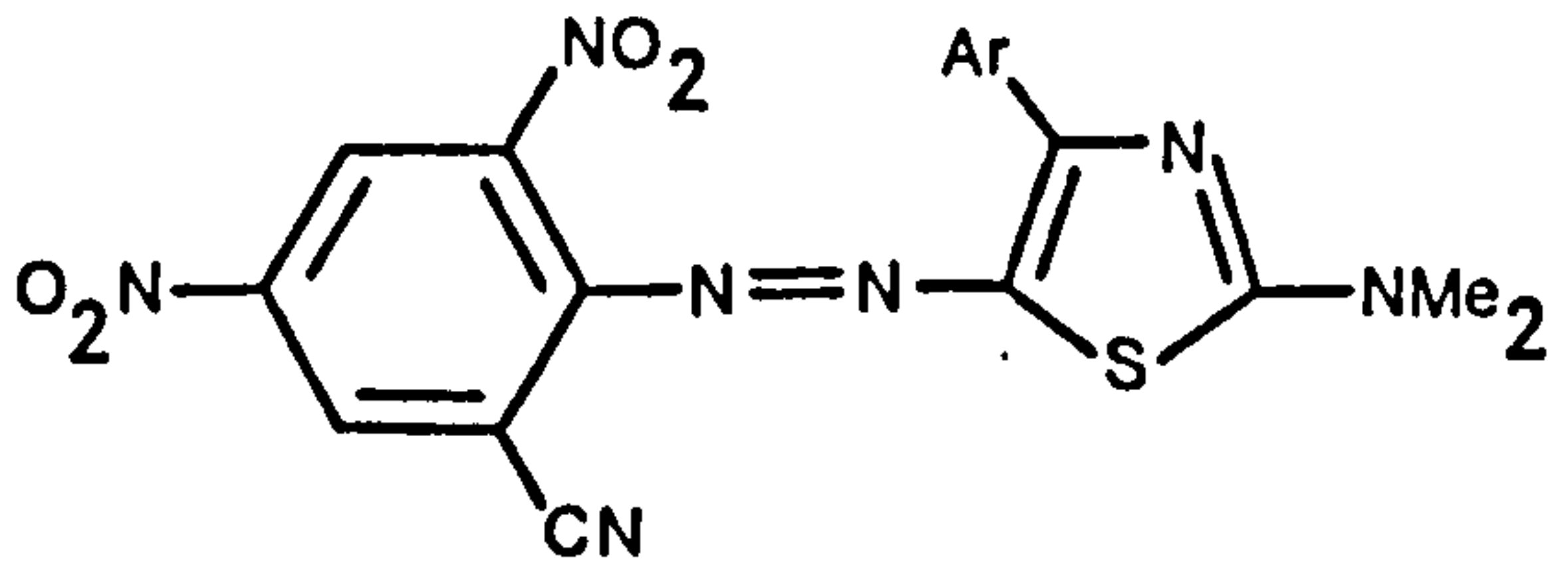
(15)

3-aminoisobenzthiazoles (16). The latter type, particularly those containing a 5-nitro group, give blues with simple coupling components, thereby exhibiting a remarkable bathochromic effect.[22] Fewer examples are known of dialkylamino heterocyclic coupling components and dyes derived therefrom; an example is provided by dye (17) which is green.[23]



(16)

Compared with their benzene analogues, these heterocyclic systems give rise to dyes which are more bathochromic, possess higher tinctorial strength and often exhibit better fastness properties.



(17)

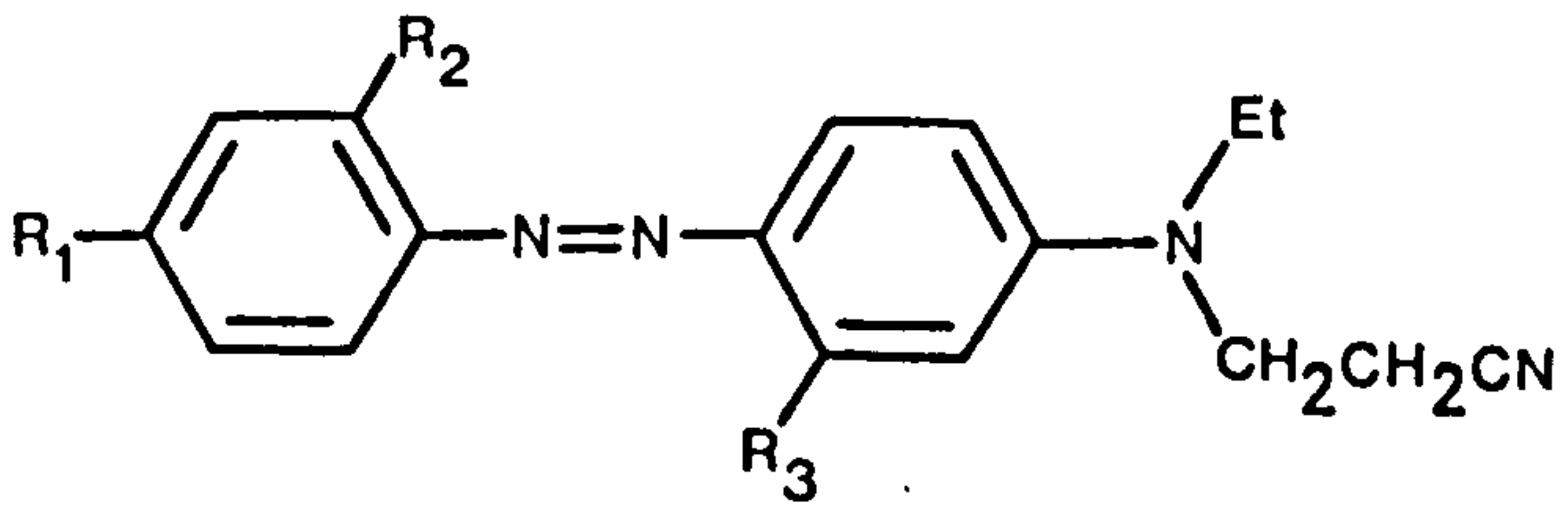
The fact that as yet relatively few of these dyes are in commercial use is mainly due to a lack of economically viable synthetic procedures. This problem will no doubt be overcome in the relatively near future.

The fastness properties of azo disperse dyes can also be changed considerably by modification of structure (9). The structure of the substrate is also a factor, and it has been found that in general the highest lightfastness occur on polyester, and the lowest on nylon, with cellulose acetate and triacetate intermediate.[24,25]

From available data it appears (Table 1.1) that lightfastness on polyester increases as the <u>para</u> substituent is made more electronegative.[20]

Similar behaviour occurs when the ortho substituent of the p-nitro dye (18) is varied,[16] although o-nitro is an exception, being 4-5 points lower than o-cyano even though the two substituents have similar electronegativities. The general trend is essentially reversed on nylon.

Table 1.1. Lightfastness Ratings of some Azo Dyes (18).[16,20]

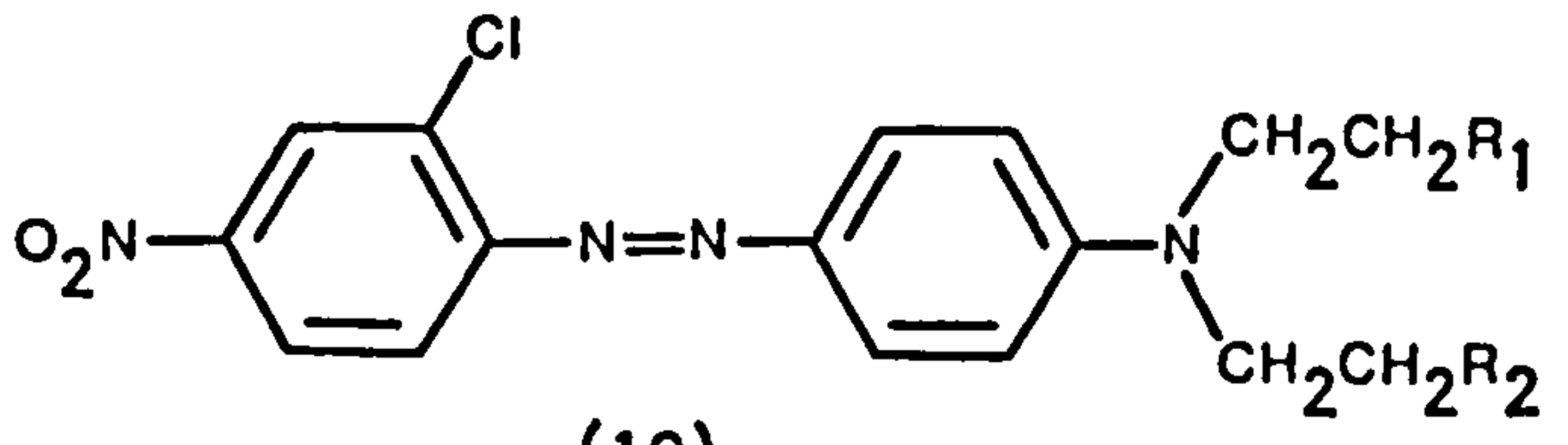


(18)

Substituents			Lightfastness	
R_1	R_2	R_3	Polyester	Nylon
H	H	Me	2	-
OMe	H	Me	2	-
SO_2NEt_2	H	Me	3	-
COMe	H	Me	4	-
SO_2Me	H	Me	4	-
NO_2	H	Me	5	-
NO_2	NO_2	H	2	1
NO_2	OMe	H	3-4	4
NO_2	Me	H	4-5	4-5
NO_2	H	H	5	4
NO_2	Cl	H	6	3-4
NO_2	CN	H	6-7	1-2

It is also apparent that the nature of the terminal alkyl groups in dyes of this type (19) is important (Table 1.2).[16] High fastness to light on polyester can be associated with the presence of one or more N-β-cyanoethyl groups, whilst the corresponding hydroxyethyl group is detrimental. It is interesting that acylation of the free hydroxy group in alkyl chains of this type causes a marked increase in the lightfastness of the dyes.[26] The introduction of an N-trifluoroethyl terminal group has recently been shown to be advantageous; dye (20; X=CF_3) was rated at lightfastness 6-7 on polyester whereas the parent dye (20; X=Me) had a value of 3.[27]

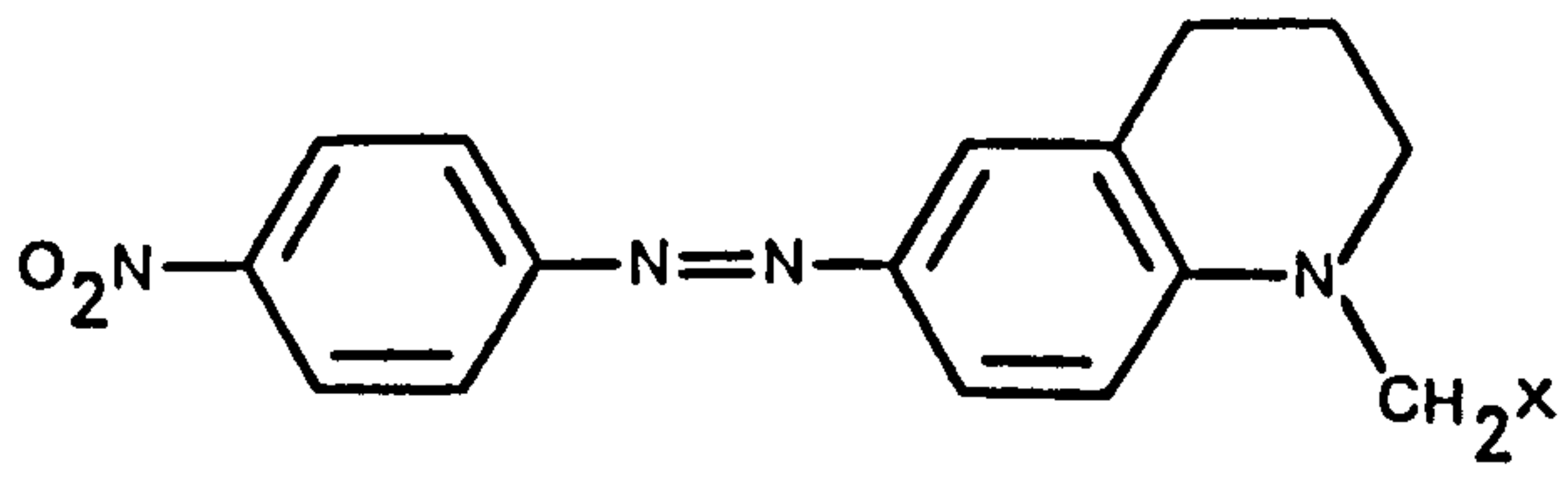
Table 1.2. Lightfastness Ratings of some Azo Dyes (19) on Polyester.[16]



(19)

R_1	R_2	Lightfastness
H	OH	3
H	H	3-4
OH	CN	4
H	CN	6
OCOMe	CN	7
CN	CN	7

Dyes containing the benzthiazole ring system generally have slightly higher lightfastness ratings on polyester compared with their benzene analogues.[20] The incorporation of a nitro group in the 6-position of the benzthiazole ring leads to greatly improved figures, but in the 4-position the same group has less effect. Incorporation of a thiazole ring into azo dyes appears to lower the lightfastness slightly; a 5-nitrothiazole derivative showed a drop of 1 point relative to its 4-nitrophenyl equivalent.[28] The 3-nitro-5-acyl-2-thienylazo dyes are reported as having similar lightfastness properties to the corresponding 5-nitrothiazole dyes.[19]



(20)

Although the photochemical degradation of aminoazobenzene disperse dyes is not a simple process,[29] certain correlations have been established. Photodecomposition rates in ethanolic solution have been linearly related to pK_a values,[30] which are claimed to be a measure of the electronegativity of the β-nitrogen of the azo group. A relationship has also been observed between the mass spectral behaviour of certain azo dyes and their lightfasness,[31] suggesting a link between the two modes of fission, electron impact and photochemical.

In addition to improving lightfastness properties, a trend has developed towards increased fastness to heat (sublimation fastness), a property which became important as new dyeing processes, such as high-temperature dyeing and thermofixation, were introduced. Heat fastness, like rate of dyeing, is dependent on the diffusion rate of the dye through the fibre infrastructure. Hence, in general, heat fastness increases with increasing relative molecular mass or polarity of the dye. The presence of hydroxy groups, which are able to form hydrogen bonds with appropriate fibres, can also be important in higher fastness to heat.[32] *N*—β—Cyanoethyl groups are beneficial to both heat and lightfastness properties.[16] The influence of nuclear substituents is less marked, although electron withdrawing groups appear to be advantageous.[16] An acylamino substituent in the 2-position is often associated with improved heat fastness,[17] as is the presence of various heterocyclic rings, such as in the benzthiazolylazo dyes.[20] Attainment of good fastness to light and thermofixation requires a careful choice of substituents.

The full range of colours and acceptable fastness properties of the azo disperse dyes are undoubtedly contributory factors in their dominance of the disperse dye market. Other equally important economic factors are:

i) the dyes are relatively cheap and generally do not require many intermediate production stages,

ii) new manufacturing plant is more versatile and requires a lower capital investment than in the case of other disperse dye classes.

The introduction of a completely new hydrophobic fibre requiring specialised disperse dyes is rather unlikely. Nevertheless, research activity will probably continue at its present pace in the near future to tailor dyes for particular application processess such as the coloration of polyester-cellulose blends[34] and transfer printing.[33] It is interesting to note that the latter process requires the dye to sublime and as such will partly reverse the underlying trend towards high sublimation fastness. Solvent dyeing[34] may or may not be commercially developed in the near future, but it is likely that research will continue into the modification of disperse dye molecules to suit any proposed solvent dyeing techniques. The increasing importance of liquid crystal technology should also encourage research into azo disperse dyes[35] and it is clear that there are still many challenges left for the azo chemist.

1.3. Early Theories of Colour and Constitution Relationships

Relationships between the colour of dye molecules and their constitution have been sought by chemists ever since the beginnings of the synthetic dye industry.

The first major generalisation was made in 1868 by Graebe and Liebermann[36] who attributed the colour of organic molecules to their unsaturation, since all the coloured compounds then known became colourless on reduction. In 1876, Witt introduced the concept of the chromophore, chromogen and auxochrome.[37] The chromophore is defined as a group of atoms in a molecule which is responsible for the colour, such as $-NO$, $-NO_2$, $-N=N-$, $>C=C<$ and $>C=O$; molecules containing chromophores are referred to as chromogens. Although some chromogens such as azobenzene are themselves coloured, a chromophoric group does not necessarily confer colour on a molecule, but rather gives it a potentiality for colour. An auxochrome is best regarded as an electron donor group,[38] and includes any substituent which possesses lone pair electrons in conjugation with a π electron system, exemplified by $-\ddot{O}R$ and $-\ddot{N}R_2$. Whilst being incapable of conferring colour on a substance by itself, the introduction of an auxochromic group into a chromogen develops the colouring power of the latter and, in general, shifts its absorption to longer wavelengths and increases the intensity. The presence of an electron donor group is an essential prerequisite for the chromogen to exhibit dyeing properties.

In 1892, Schütze[39] first used the terms bathochromic and hypsochromic to signify shifts of absorption bands towards longer and shorter wavelengths, respectively. Increases and decreases in the intensity of an absorption band are sometimes referred to as hyperchromic and hypochromic effects, respectively.

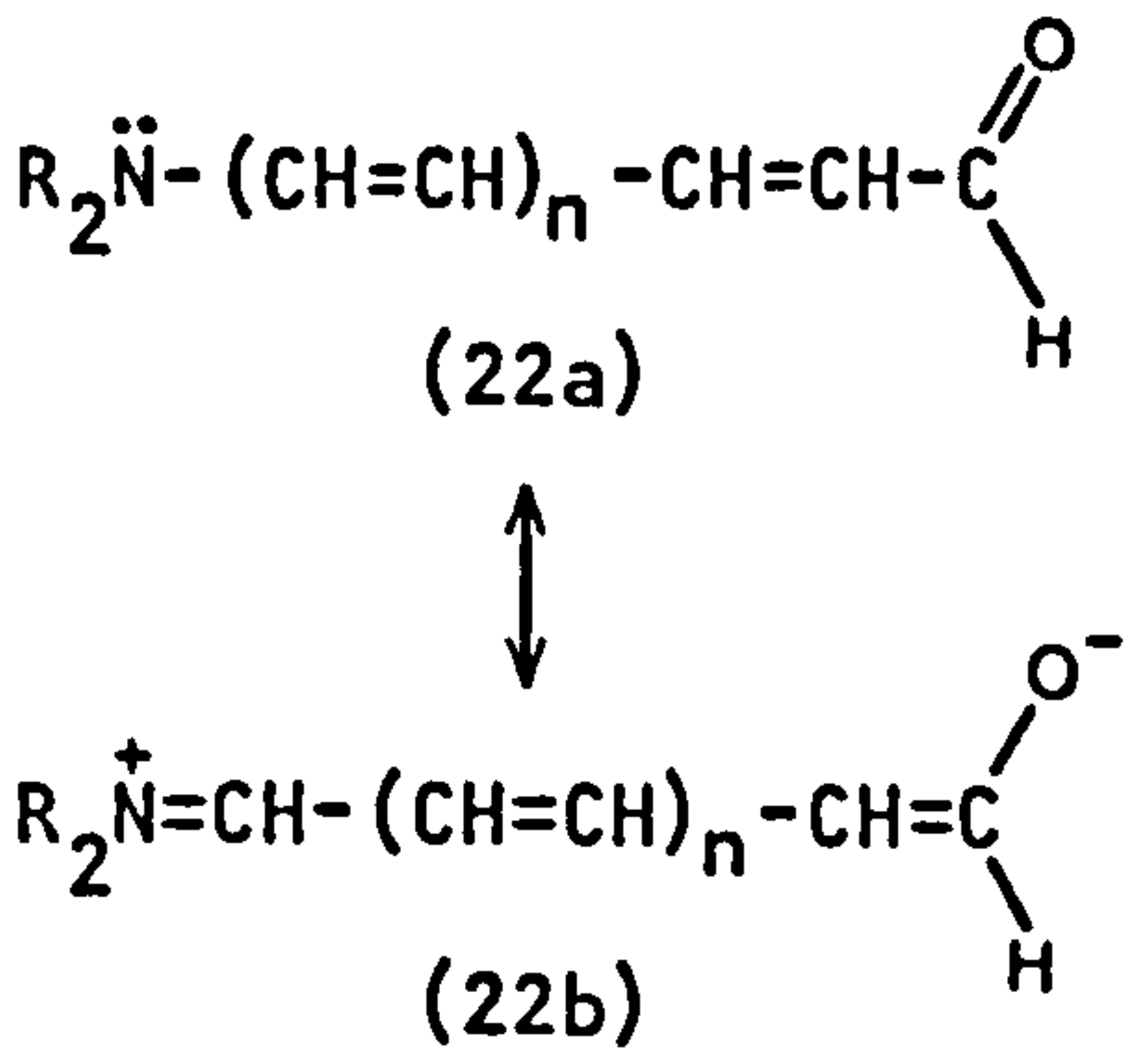
Armstrong,[40] in 1888, suggested that a quinonoid constitution is important in organic dyes. In 1907, Hewitt and Mitchell[41] noted the association between colour and conjugation. Drude,[42] in 1904, linked visible and ultraviolet absorption with the electrons in a molecule and, thirty-five years later, Lewis and Calvin[43] put forward the concept that the energy absorbed by a molecule on interaction with radiation is taken up by electronic oscillations. Previously, Dilthey and Wizinger[44] had expanded Witt's ideas by utilising the colour and constitution relationships suggested by Hantzsch,[45] von Baeyer,[46] Watson[47] and others. A dye molecule was regarded as an electron releasing, relatively basic group (the electron donor group) connected to an electron attracting, relatively acidic residue (the chromophore) by a system of conjugated double bands. The greater the respective releasing and accepting powers of the two groups and the longer the unsaturated chain joining them together, the more bathochromic is the absorption band.

In 1935, Bury[48] in considering dyes of the cyanine-type (21) suggested that the colour was due to bond oscillations between the two equivalent (degenerate) Kekulé structures (21a) and (21b) of equal energy but different charge distribution. In 1939, Pauling[49]

$$R_2\ddot{N}-(CH=CH)_n-CH=\overset{+}{N}R_2 \quad \longleftrightarrow \quad R_2\overset{+}{N}=CH-(CH=CH)_n-\ddot{N}R_2$$

(21a) (21b)

extended this argument to include neutral dyes, proposing that resonance involving high-energy, charge-separated structures such as (22b) would account for the colour of the merocyanines(22a).


(22a)

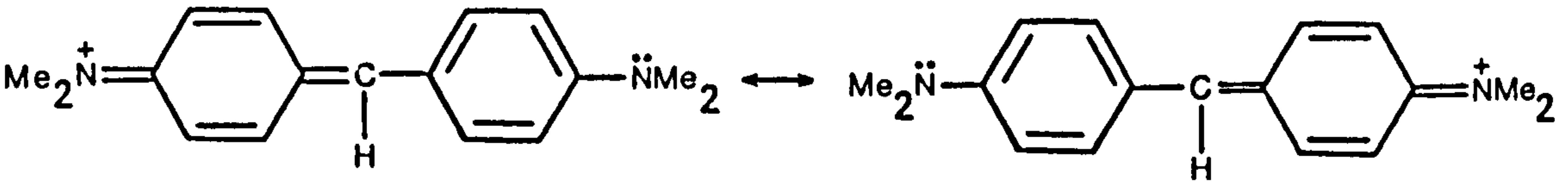
(22b)

During these developments, a better understanding of the relationship between colour and chemical constitution was dependent upon the realisation that absorption in the ultraviolet, visible and infrared regions of the electromagnetic spectrum must be treated as a single topic, coloured compounds appearing so only because the molecules happen to absorb in the region in which the human eye is sensitive (the visible region). Thus, in terms of electronic transitions, the visible absorption bands of coloured organic compounds correspond to the ultraviolet bands of colourless compounds.

1.4. Valence Bond Resonance Theory

The rapid development of quantum mechanics in the years following the pioneering work of Schrödinger in 1926 enabled the valence bond method to be used in the calculation of the electronic properties of polyatomic molecules. This method uses the concept of chemical bonds between atoms, involving electron pairs, and was first applied by Heitler and London[49a] in 1927 to the hydrogen molecule. A rigorous application of the method would entail consideration of all the possible limiting resonance structures for the molecule, of both high and low energies. However, in a simplification, only the lowest energy resonance forms are used.[50]

For instance, Michler's Hydrol Blue, a cyanine-type dye, can be regarded as a resonance hybrid of the two equivalent structures (23a) and (23b), ignoring other possible arrangements. As illustrated in Fig. 1.1(a), the wave functions of (23a), ψ_a and (23b), ψ_b, then interact



(23a) (23b)

to give two new molecular wave functions of different energy, ψ_o, by symmetric combination of ψ_a and ψ_b (1.1), and ψ^* by antisymmetric combination of ψ_a and ψ_b (1.2). The lower energy wave function ψ_o

$$\psi_o = \psi_a + \psi_b \tag{1.1}$$

$$\psi^* = \psi_a - \psi_b \tag{1.2}$$

can be equated with the ground state of the system, and has less energy than either of the contributing resonance forms, whilst ψ^* is equated with the first excited state, and has more energy than either of the contributing resonance canonicals. The wavelength of the first absorption band is then given by ΔE, the energy between the two states.

When the molecule is represented by resonance structures of differing energies, such as in (24), in which structure (24a) is more stable than (24b) due to the higher electronegativity of oxygen relative to nitrogen, interaction gives two states which have a larger separation energy, Fig. 1.1(b), than in the first instance so that a hypsochromic shift is predicted. This effect is found to obtain with (23) absorbing maximally in 98% acetic acid at 607.5 nm compared with (24) at 498 nm.[51]

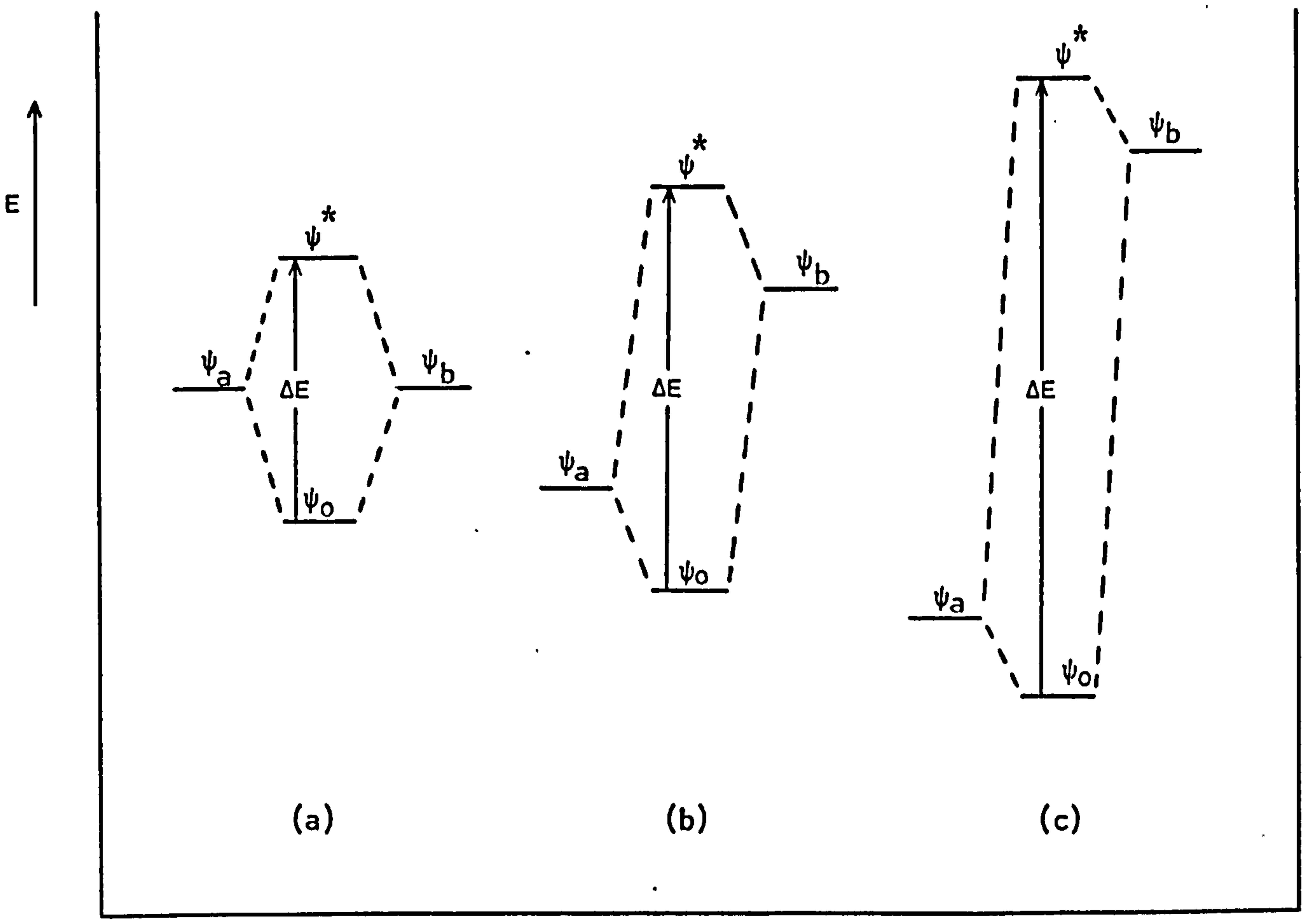
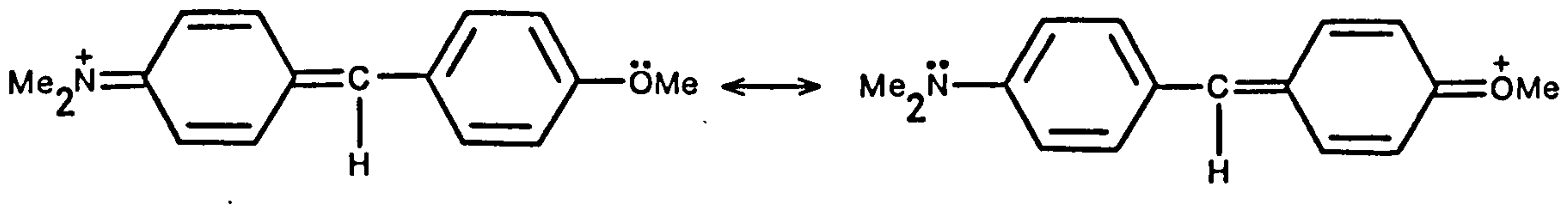
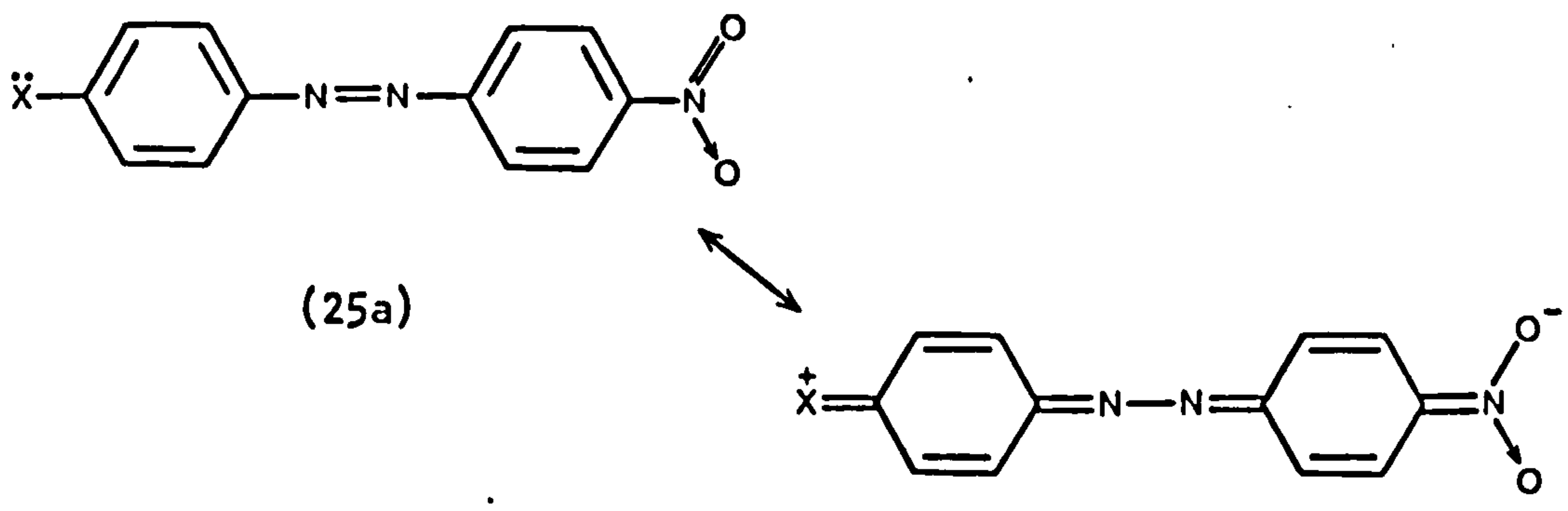


Fig. 1.1. The interaction between two classical resonance structures (a) of equal energy, and (b), (c) of unequal energy.



(24a) (24b)

In azo-type chromogens, the two major resonance canonicals differ appreciably in energy. The neutral structure, as illustrated by (25a), is more stable than that involving charge separation (25b). This situation is illustrated in Fig. 1.1(c). If X is replaced by another group which serves to destabilise the charge-separated form, then the resonance picture suggests that a hypsochromic shift will result; this



(25a)

(25b)

prediction has been confirmed experimentally. For example, when X is an amino group the chromogen absorbs at approximately 440 nm, whereas replacement with the more electronegative hydroxy group causes a shift to about 380 nm. It can be seen from Fig. 1.1(c) that the wave functions ψ_a and ψ_o for (25) are relatively close in energy terms, compared with (23) and (24), so that the resonance form (25a) can be regarded as the ground state of the molecule. Similarly, (25b) is taken to represent the excited state.

Use of these structures can account qualitatively for the solvatochromic effects of azo dyes in different solvents. An increase in solvent polarity will tend to stabilise the charge-separated excited state more than the neutral ground state (Fig. 1.2) resulting in a bathochromic shift.[52] Thus, for example, dye (25; $X{=}NEt_2$) absorbs at 460 nm in cyclohexane and 490 nm in ethanol, exhibiting a characteristic positive solvatochromism.

The depiction of (25a) and (25b) as ground state and excited state structures, respectively, in azo dyes is vindicated somewhat by the results of dipole moment measurements on a series of <u>para</u>-substituted 4-<u>NN</u>-dimethylaminoazobenzene dyes, which indicate that the contribution of charge-separated structures such as (25b) to the ground state of the dyes does not exceed 7%.[53]

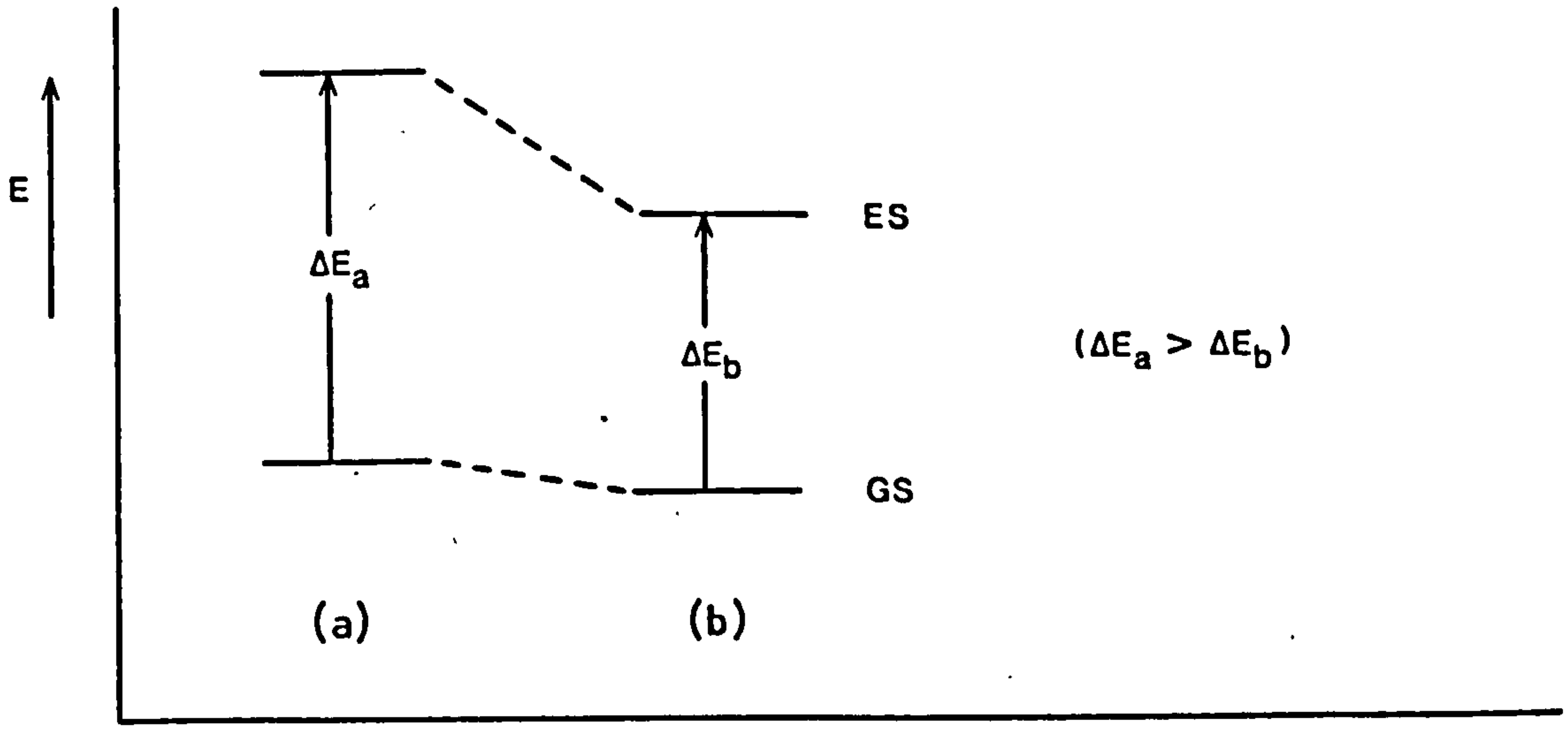


Fig. 1.2. Change in energy levels on moving from (a) a non-polar to (b) a polar solvent for a system in which the ground state (GS) is less polar than the excited state (ES).

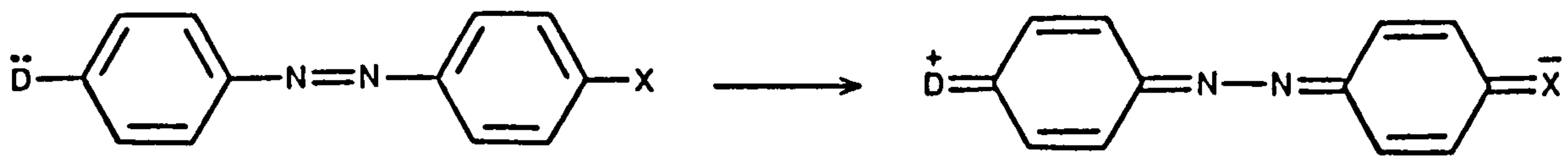
1.5. Substituent Effects in Aminoazo Dyes.[14,54]

Azo dyes have been classified as donor-acceptor chromogens[54] (26)

D-A-N=N-B

(26)

where A and B are carbocyclic residues and D is the donor group. As all azo dyes exist preferentially in the trans configuration under normal conditions, all discussions and data will pertain to the trans isomers, unless otherwise specified. Tables 1.3-1.5 show that changes in D, A and B give rise to considerable variations in maximum wavelength of absorption (λ_{max}). Closer examination reveals general trends which can often be explained qualitatively by reference to structures (27a) and (27b) which, as already pointed out with (25) in section 1.4, correspond



(27a)

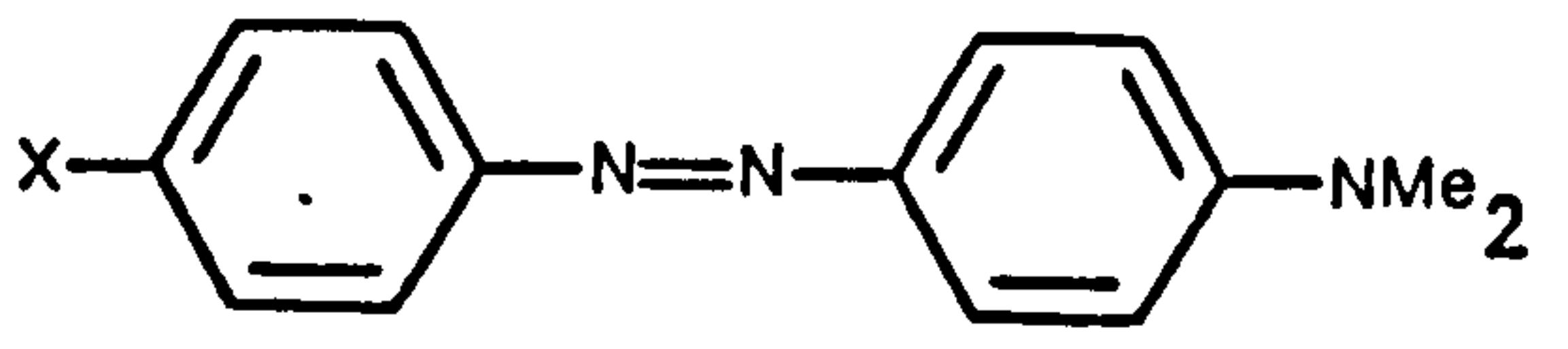
(27b)

to the ground state and excited state of the chromogen, respectively. Factors which bring the two structures closer together in energy terms lead to bathochromic shifts of λ_{max}. Consequently, the stronger the electron donor group D and the electron withdrawing group X, the more stabilised is the excited state relative to the ground state, and the more bathochromic is the shift. In 4,4'-disubstituted systems of type (27), it is usually found that, for a given series of dyes, the wavelength shift produced by an acceptor substituent X is approximately related to the appropriate Hammett σ constant.[18,54-57] The deepest coloured dyes have electron donor substituents in ring A and electron withdrawing substituents confined to ring B.

Resonance considerations suggest that structures of the type (27b), in which the negative charge is delocalised onto the electron acceptor group X, should only be important when X is ortho or para to the azo linkage; meta-substituents should act only through inductive effects which will stabilise the excited state less leading to hypsochromic shifts relative to ortho- and para-analogues. This situation is observed experimentally, for example, with the cyano-substituted 4-NN-diethylaminoazobenzenes (Table 1.5). The 2'- and 4'-cyano derivatives have similar λ_{max} values whereas the 3'-isomer shows a hypsochromic shift of about 20 nm; the dicyano-substituted chromogens also show the expected order of shifts. The cyano group is particularly suitable for this type of measurement, since its rod-like shape minimises any steric interference of the type shown in Fig. 1.3.[65a] Such steric effects are apparent when two substituents are present ortho to the azo group in the same ring and are maximised by spherical substituents.[66]

In general, steric crowding in a molecule is most often relieved by bond rotation to give a non-planar system. Rotation is much easier

Table 1.3. Visible Absorption Spectra of some 4'-Substituted Derivatives of 4-NN-Dimethylaminoazobenzene (28) in Neutral and Acidic Solutions.[55]



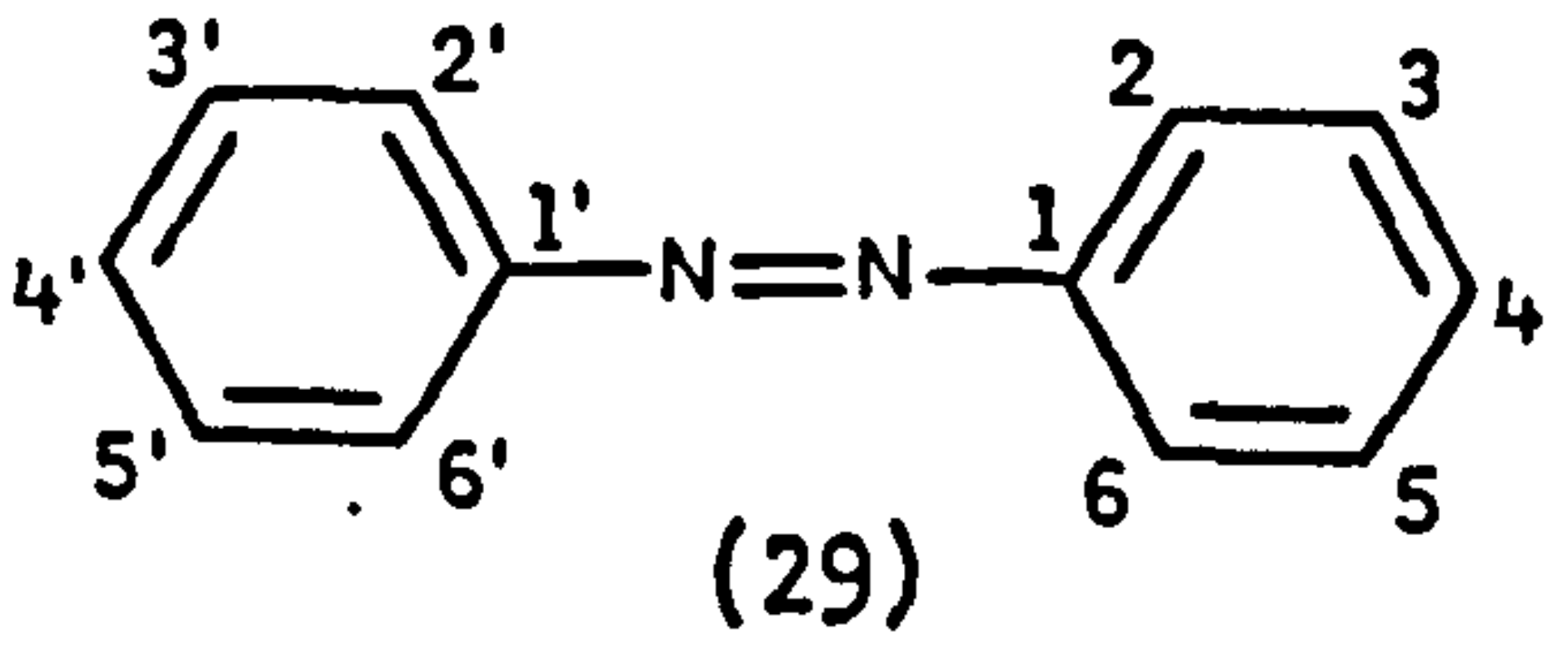
(28)

No.	X	λ_{max}/nm (ethanol)	λ_{max}/nm (ethanolic HCl[a])	$\Delta\lambda$/nm	σ_p[b]
1	NMe_2	450	664	214	-0.83
2	NH_2	410	610	200	-0.66
3	OMe	407	555	148	-0.27
4	OEt	405	552	147	-0.24
5	SMe	420	555	135	0.00
6	Me	407	533	126	-0.17
7	C_6H_5	422	544	122	+0.01
8	H	407	518	111	0.00
9	F	407	518	111	+0.06
10	I	422	528	106	+0.18
11	Cl	417	522	105	+0.23
12	Br	419	523	104	+0.23
13	OCF_3	419	512	93	+0.35
14	SCN	433	516	83	+0.52
15	SCF_3	432	514	82	+0.50
16	CF_3	427	505	78	+0.54
17	Ac	447	517	70	+0.52
18	SO_2Me	445	505	60	+0.72
19	NO_2	475	508	33	+0.78
20	SO_2CF_3	476	500	24	+0.93

[a] Two volumes of ethanol and one volume of hydrochloric acid, d. 1.19

[b] Ref. 58

Table 1.4. Visible Absorption Spectra of some Donor-substituted Azobenzene (29) Derivatives in Ethanol.



(29)

Substituents	λ_{max}/nm($10^{-4}\varepsilon$)	Substituents	λ_{max}/nm($10^{-4}\varepsilon$)
None	318(2.14)[a]	4-NMe_2	408(2.75)[a]
2-NH_2	417(0.63)[b]	4-NMeEt	411(2.82)[a]
3-NH_2	417(0.13)[b]	4-NEt_2	415(2.95)[a]
4-NH_2	385(2.45)[a]	4-$N(C_2H_4CN)_2$	382(1.95)[d]
4-OH	349(2.63)[a]	4-$N(C_2H_4Cl)_2$	397(2.57)[e]
4-OMe	343(-)[c]	4-$N(C_2H_4OH)_2$	407(2.95)[d]
4-SMe	362(2.40)[a]	2,4-diNH_2	411(2.09)[f]
4-NHAc	347(2.34)[a]	2,4-diO^-	473(-)[g]
4-NHMe	402(2.57)[a]	3,4-diO^-	501(-)[g]
4-NHEt	405(2.63)[a]	2,5-diO^-	572(-)[g]

[a] Ref.59

[b] Ref.60

[c] Measured by author.

[d] Ref.18

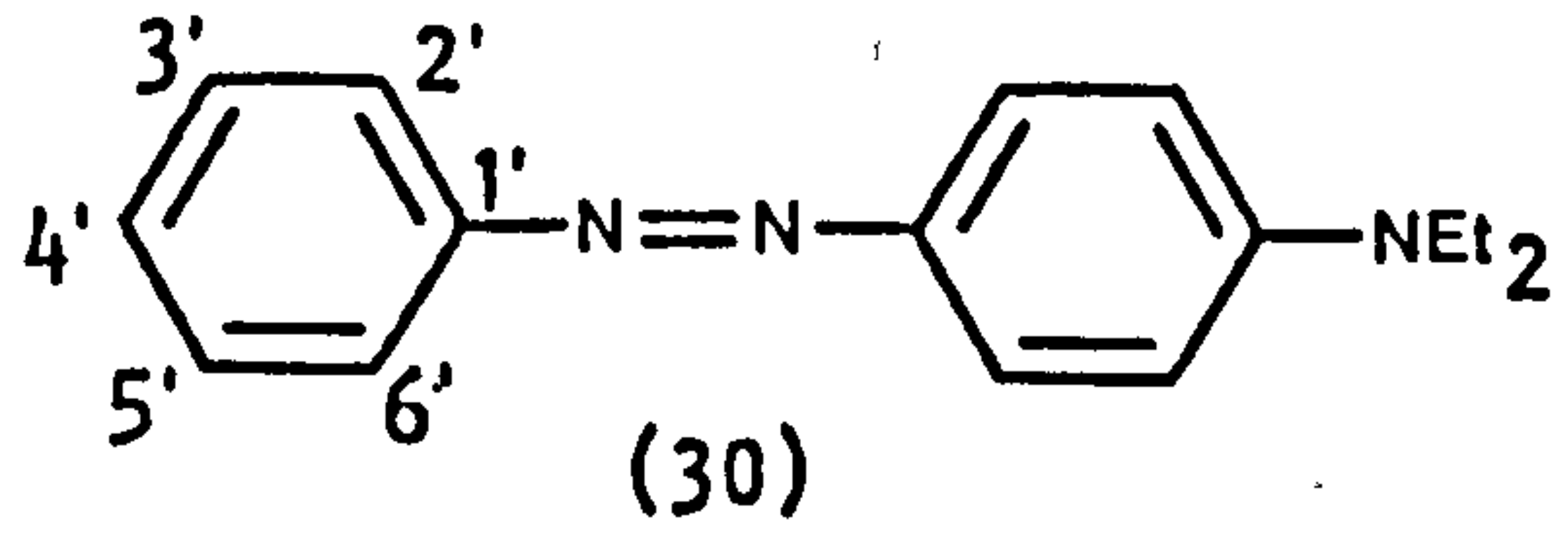
[e] Ref.61

[f] Ref.62

[g] Ref.63

energetically about an essential single bond than about an essential double bond. It is generally true that a bond of low π-bond order (essential single bond) in the ground state of a molecule has a high π-bond order (essential double bond) in the excited state. Hence, steric hindrance

Table 1.5. Visible Absorption Spectra of some Cyano- Derivatives of 4-_NN_-Diethylaminoazobenzene (30) in Ethanol.[64]



(30)

Substituents	λ_{max}/nm($10^{-4}\varepsilon$)	Substituents	λ_{max}/nm($10^{-4}\varepsilon$)
4'-CN	466(3.24)	3',5'-diCN	478(3.39)
3'-CN	446(2.82)	2',5'-diCN	495(3.63)
2'-CN	462(3.02)	3',4'-diCN	500(3.89)
2',4'-diCN	513(3.98)	2',4',6'-triCN	562(4.68)
2',6'-diCN	503(3.31)		

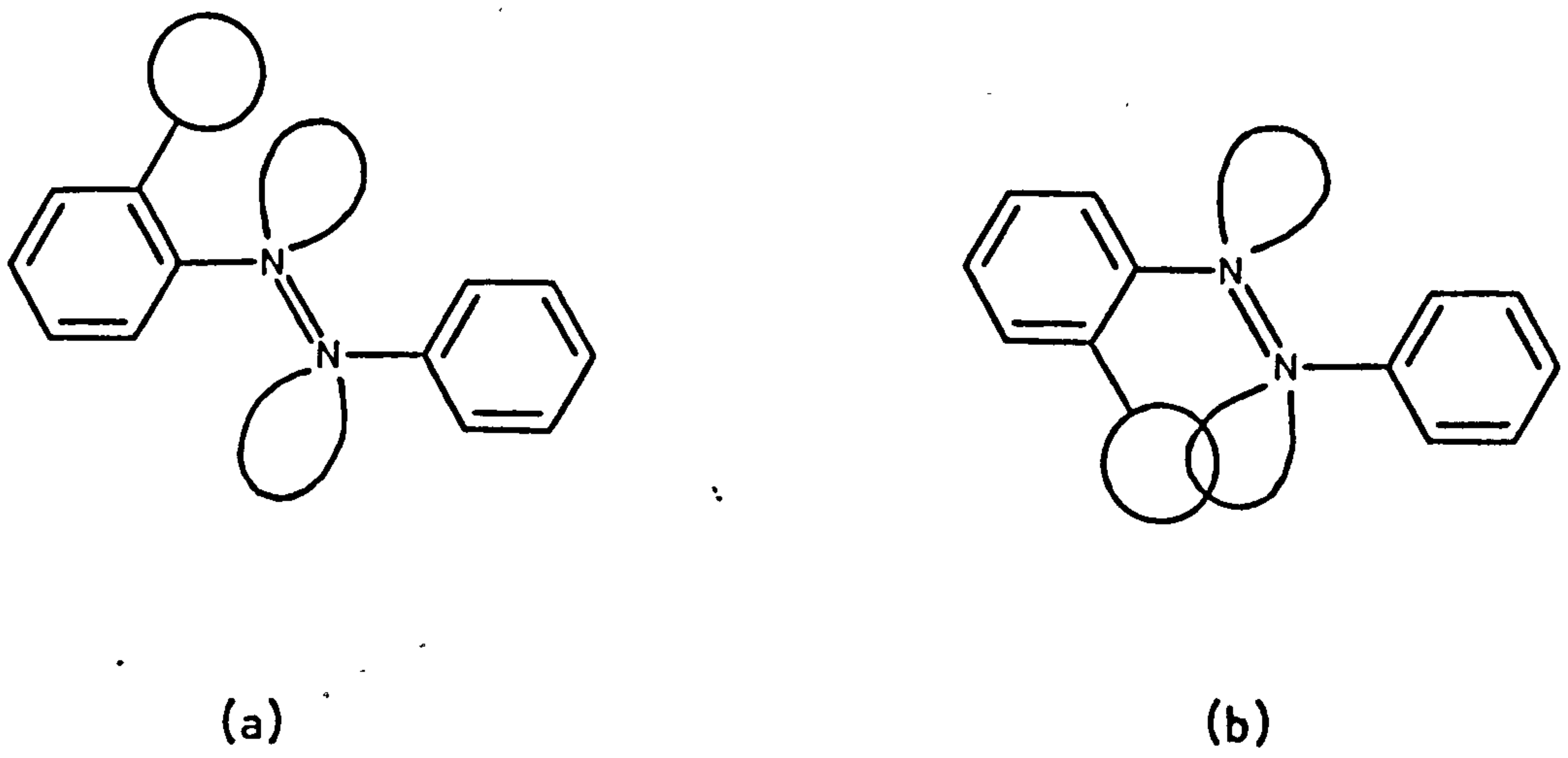


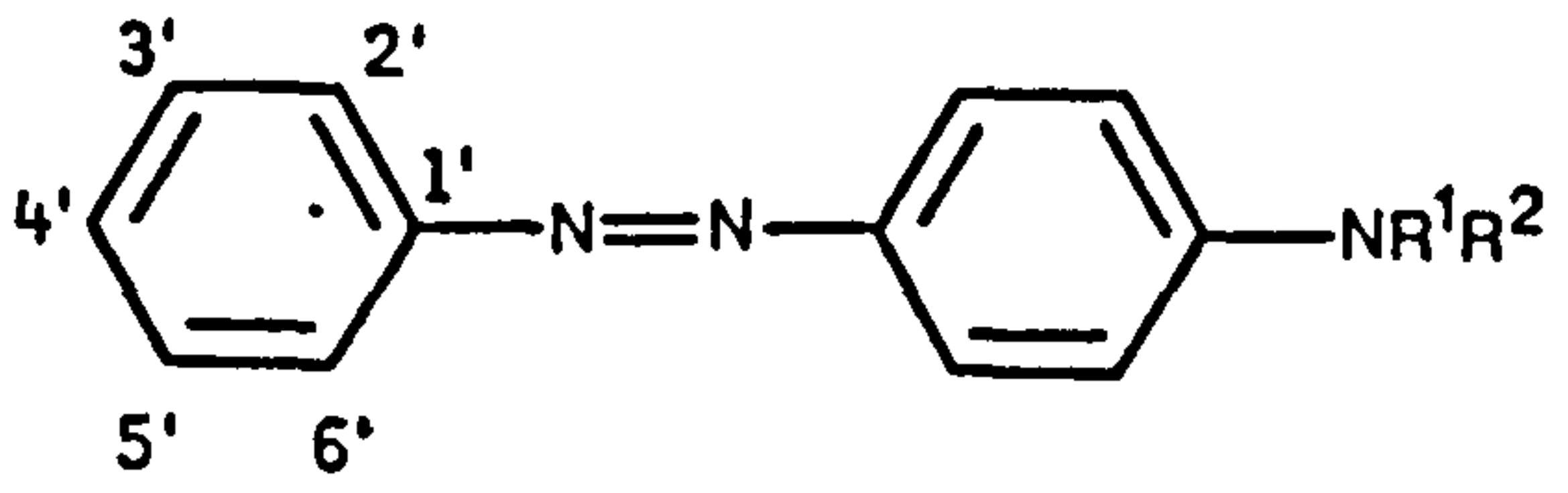
Fig. 1.3. Alternative conformations for an _ortho_-substituted azobenzene.

will destabilise the excited state more than the ground state, thereby causing a hypsochromic shift.[65b] This situation is invariably the case in azo dyes, as illustrated in Tables 1.6 and 1.7. One spherical substituent has little effect on λ_{max} (although a small drop in intensity may be observed) since the dye can assume conformation (a), Fig. 1.1. In the case of a planar group, such as nitro, the substituent can itself rotate out of the molecular plane,[66] thereby preserving the overall planarity of the benzene rings of the dye. Thus, although a hypsochromic shift is observed, the loss of absorption intensity is not great (for example, Table 1.6; 2'-NO_2). Similar arguments to explain the mild steric effect apply in cases where two planar groups are present in ortho positions (for example, Table 1.7; X=Y=NO_2). However, the introduction of a second spherical substituent causes a dramatic hypsochromic shift and marked loss of intensity (for example, Table 1.7; X=Y=Me) due to the enforced crowding between this group and the lone pair of electrons of the α-azo nitrogen atom.

Two cyano groups positioned ortho to the azo group show no obvious steric interaction and, in fact, each CN group added (in an ortho or para position) increases the λ_{max} value by a similar amount; other workers have noted this additivity relationship.[64,68]

The effects of electron donor groups in the acceptor ring are not easily explained by resonance theory. It is found that both bathochromic and hypsochromic shifts can occur as illustrated by the closely related julolidine (32)[56] and lilolidine (33)[57] dyes. The methoxy-substituted dye (34b) shows little change from the parent dye; when X=NMe_2 (34c), however, a marked bathochromic shift is observed, but such substitution leads to a symmetrical contrapolarised system.[69] It appears that an electron donor in a conjugating position (ortho and/or para) modifies the overall

Table 1.6. Visible Absorption Spectra of some *ortho*-Substituted Azo Dyes (in Ethanol) to Illustrate the Effect of One *ortho*-Substituent.

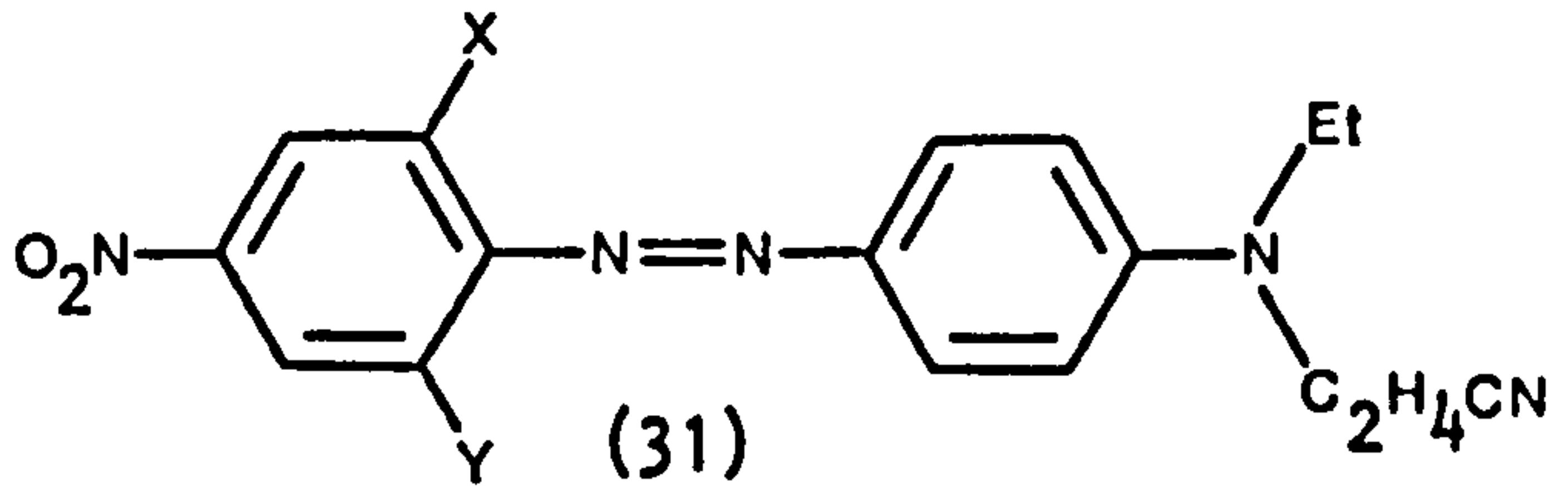


Substituent	Type	R^1	R^2	λ_{max}/nm	$10^{-4}\varepsilon_{max}$
2'-OMe	Spherical	Me[a]	Me[a]	413	—
4'-OMe		Me	Me	407	—
2'-Me	Spherical	Me	Me	410	—
4'-Me		Me	Me	407	—
2'-Br	Spherical	EtCN[b]	EtoH[b]	415	2.55
4'-Br		EtCN	EtoH	410	2.96
2'-CF_3	Spherical	EtCN	EtoH	416	2.77
4'-CF_3		EtCN	EtoH	418	2.95
2'-CO_2Et	Planar	EtCN	EtoH	405	2.72
4'-CO_2Et		EtCN	EtoH	422	2.90
2'-Ac	Planar	EtCN	EtoH	415	2.56
4'-Ac		EtCN	EtoH	429	2.91
2'-CN	Rod-like	EtCN	EtoH	433	3.09
4'-CN		EtCN	EtoH	433	3.16
2'-SO_2Me	Spherical	EtCN	EtoH	433	2.86
4'-SO_2Me		EtCN	EtoH	435	3.00
2'-NO_2	Planar	EtCN	EtoH	424	2.76
4'-NO_2		EtCN	EtoH	451	3.16

[a] Where $R^1=R^2=Me$; ref. 55

[b] Where $R^1=EtCN$, $R^2=EtOH$; ref. 67

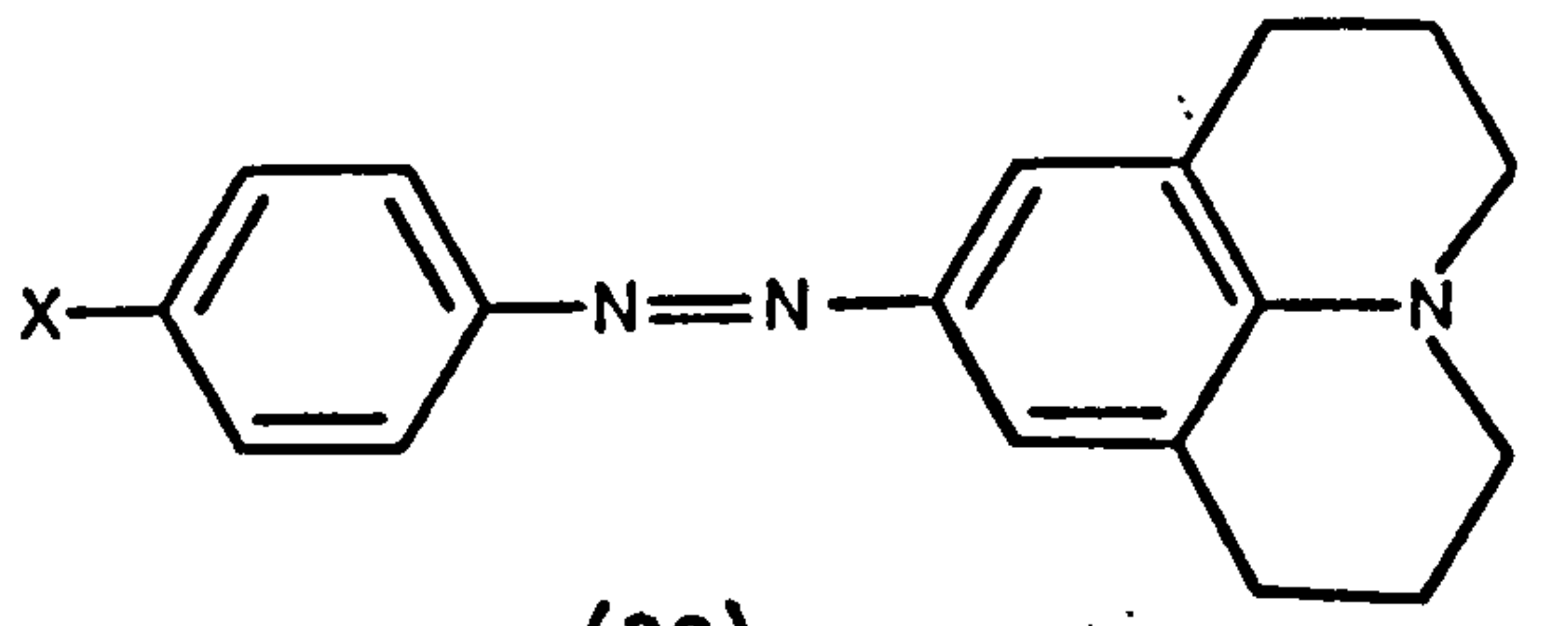
Table 1.7. Visible Absorption Spectra of some ortho-Substituted Azo Dyes (31) (in Ethanol) to Illustrate the Effect of Two ortho-Substituents.


(31)

X	Y	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm
H	H	453	4.40[b]	-
CH_3	H	454	4.20	+1
CH_3	CH_3	383	2.40	-70
CN	H	504	4.50	+51
CN	CN	549	3.80	+96
NO_2	H	491	3.80	+38
NO_2	NO_2	520	4.80	+67

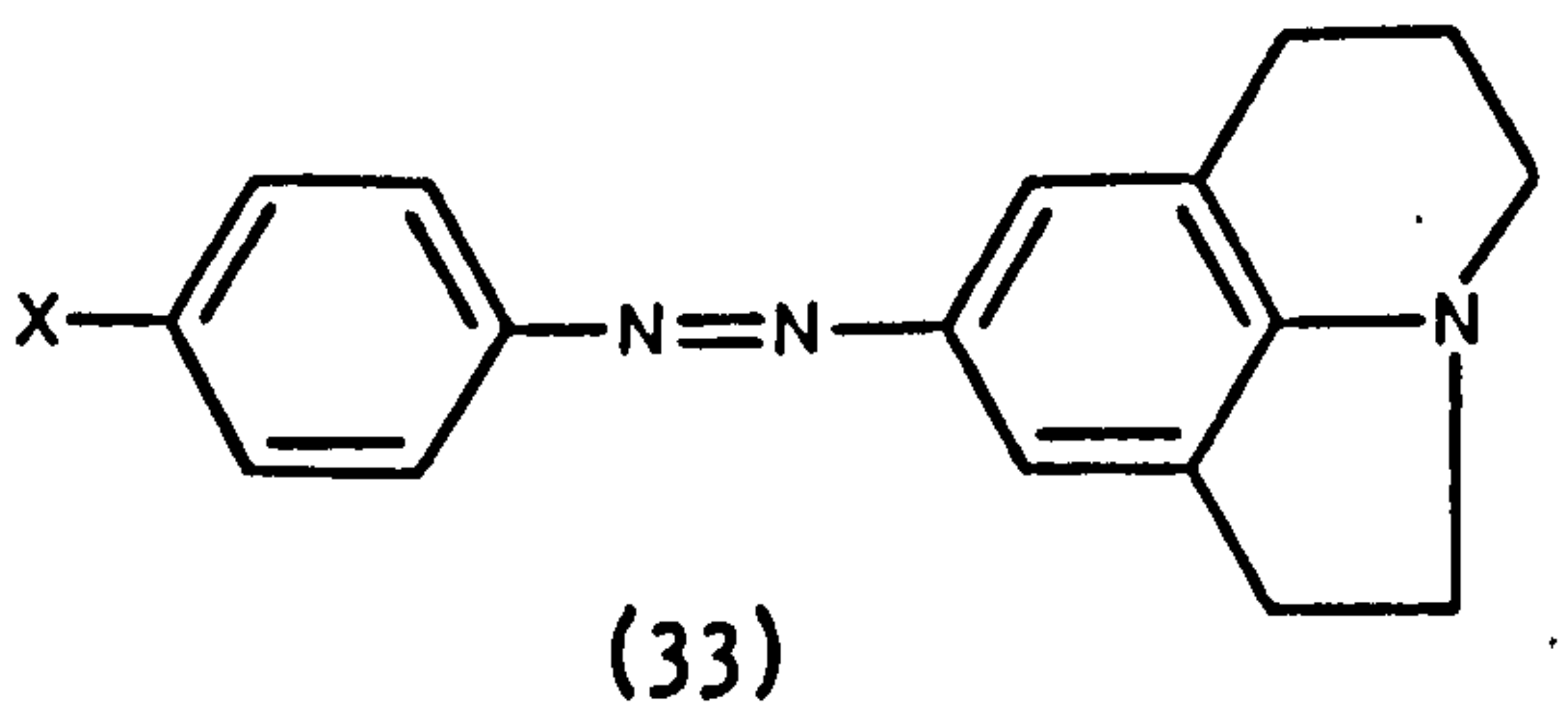
[a] Relative to X=Y=H

[b] Bridgeman and Peters[18] obtained $10^{-4}\varepsilon_{max} = 3.09$


(32)

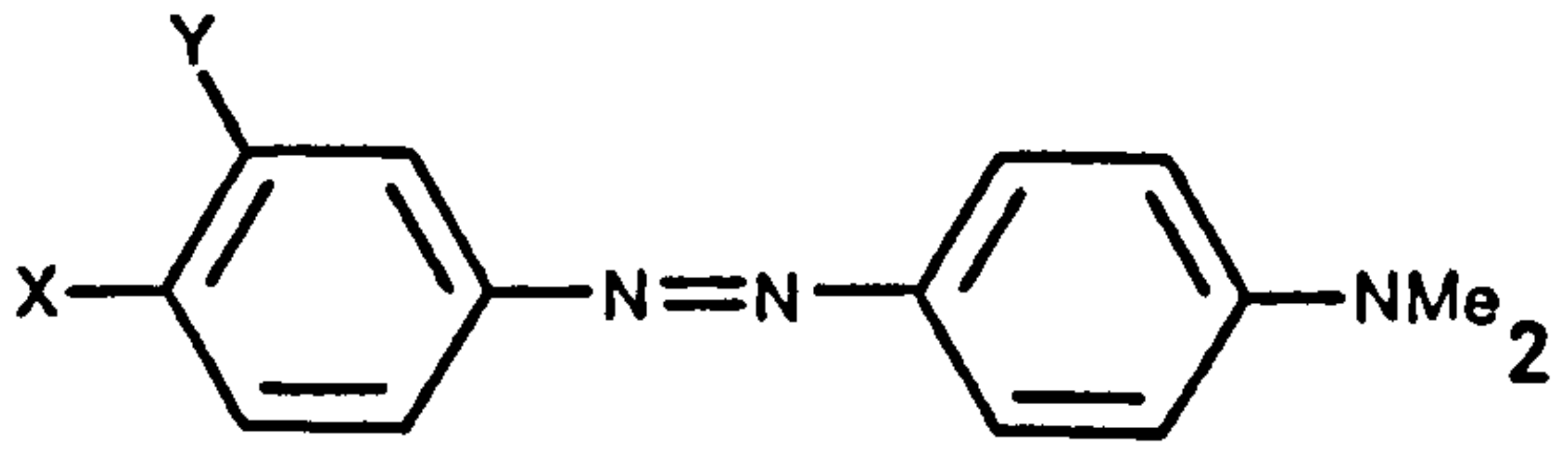
X=H; λ_{max} = 442 nm

X=OMe; λ_{max} = 452 nm


(33)

X=H; λ_{max} = 425 nm

X=OMe; λ_{max} = 417 nm



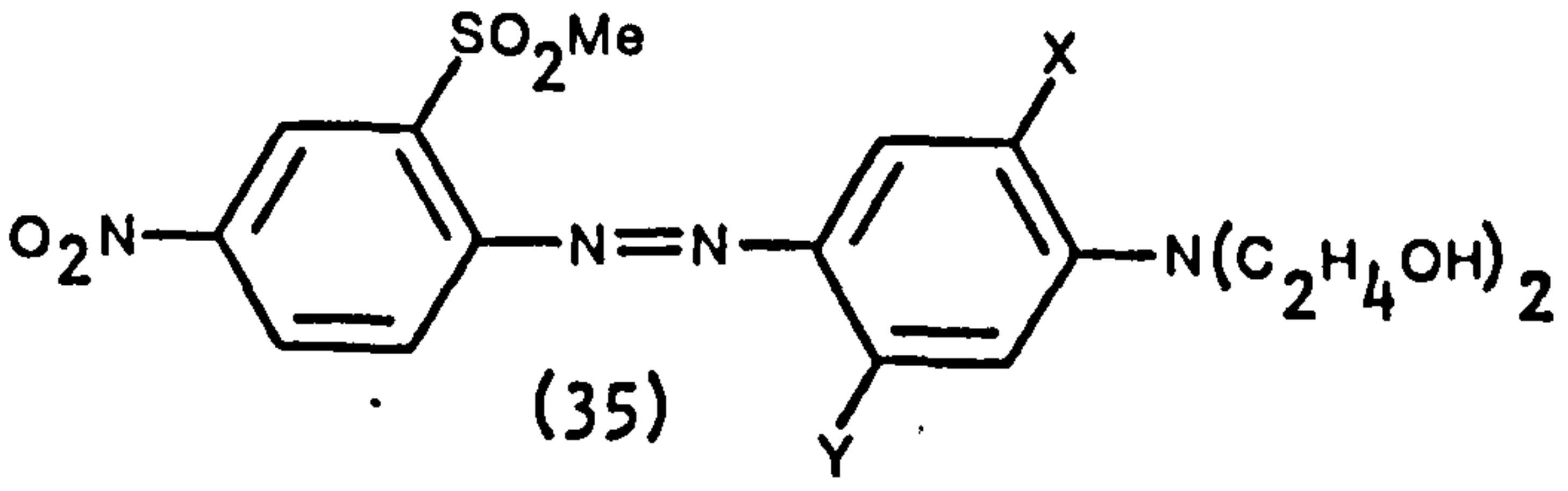
(34)

(a) X=Y=H;[55] λ_{max} = 408 nm
(b) X=OMe, Y=H;[55] λ_{max} = 407 nm
(c) X=NMe$_2$, Y=H;[55] λ_{max} = 451 nm
(d) X=H, Y=OEt;[55] λ_{max} = 412 nm

electronic distribution. On the other hand, a donor in the non-conjugating meta position, as with (34d), brings about a bathochromic movement of λ_{max} , presumably by a -I inductive effect. The PPP method of molecular orbital calculation is capable of accommodating these variations (cf. Section 1.9).[70]

A simple resonance approach to the effects of substituents in the donor ring suggests that donor groups placed in conjugating positions to the azo linkage will give rise to bathochromic shifts, whereas in the meta position inductive withdrawal should bring about a hypsochromic shift. However, experimetal data do not uphold this view. Of the three aminoazobenzenes (Table 1.4), all absorb at longer wavelengths than azobenzene but the 4-substituted isomer is the least bathochromic, contrary to resonance theory but in accordance with PPP calculations.[71] It can also be seen from the spectra of the ionised dihydroxyazobenzenes that the 2,4-derivative is the least bathochromic, again contrasting with resonance ideas. Donor groups in a 2,5-arrangement are seen to be particularly advantageous and display a synergistic effect (Table 1.8).[72]

Table 1.8. Cumulative Effect of Electron Donors in 2- and 5-Positions.



(35)

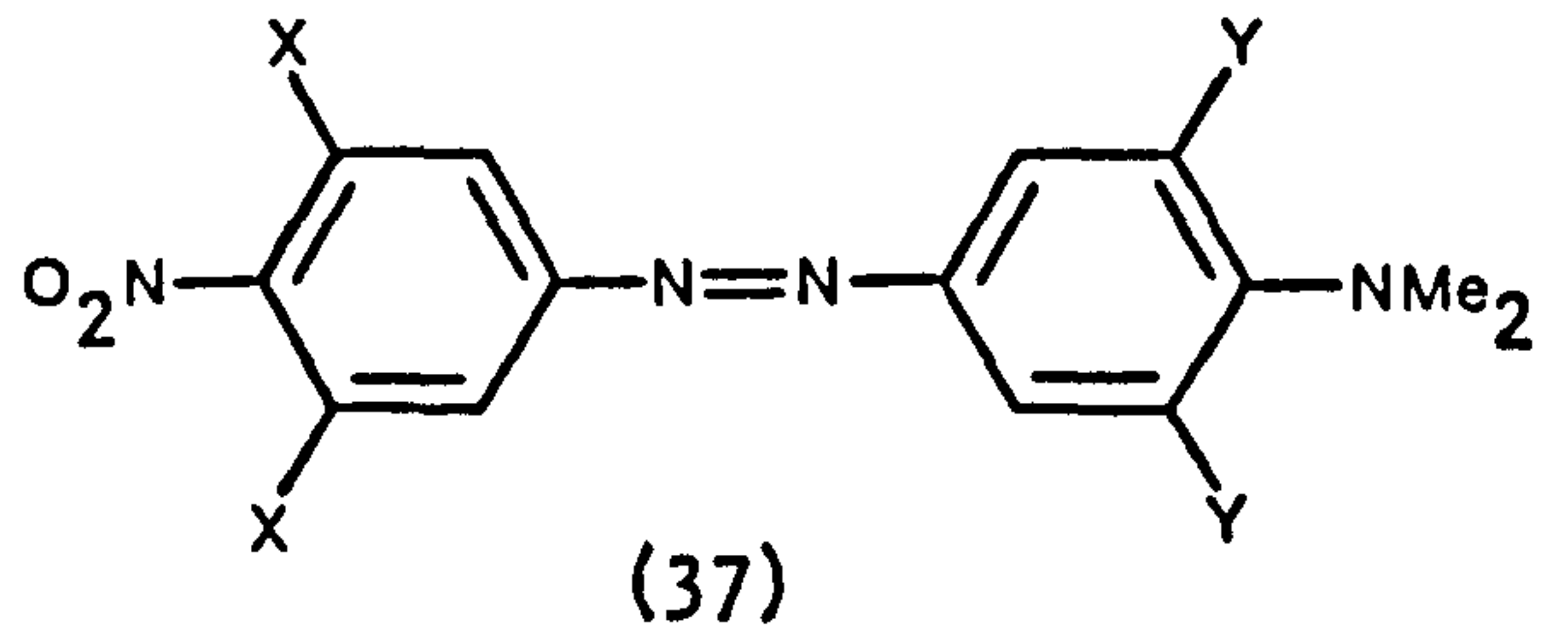
X	Y	λ_{max}/nm^{72}	$\Delta\lambda/nm^{a}$
H	H	527	-
OMe	H	545	+18
H	NHAc	547	+20
OMe	NHAc	580	+53

[a] Relative to X=Y=H

In derivatives of 4-aminoazobenzene, and in the absence of steric effects, electron donor groups in the donor ring always cause a bathochromic shift of the first absorption band, whereas acceptor groups have the opposite effect (Table 1.9). It must be stressed that for true electronic substituent effects to be observed, steric effects must not be present.

An extreme example of steric crowding is shown in the chromogen (37)[75] in which both the donor and acceptor groups are deconjugated, producing a hypsochromic shift of 97 nm and an intensity drop of 22,800 when measured in ethanol.

Azo dyes analogous to (27) in which the carbocyclic acceptor ring is replaced by an aromatic heterocyclic system give rise to

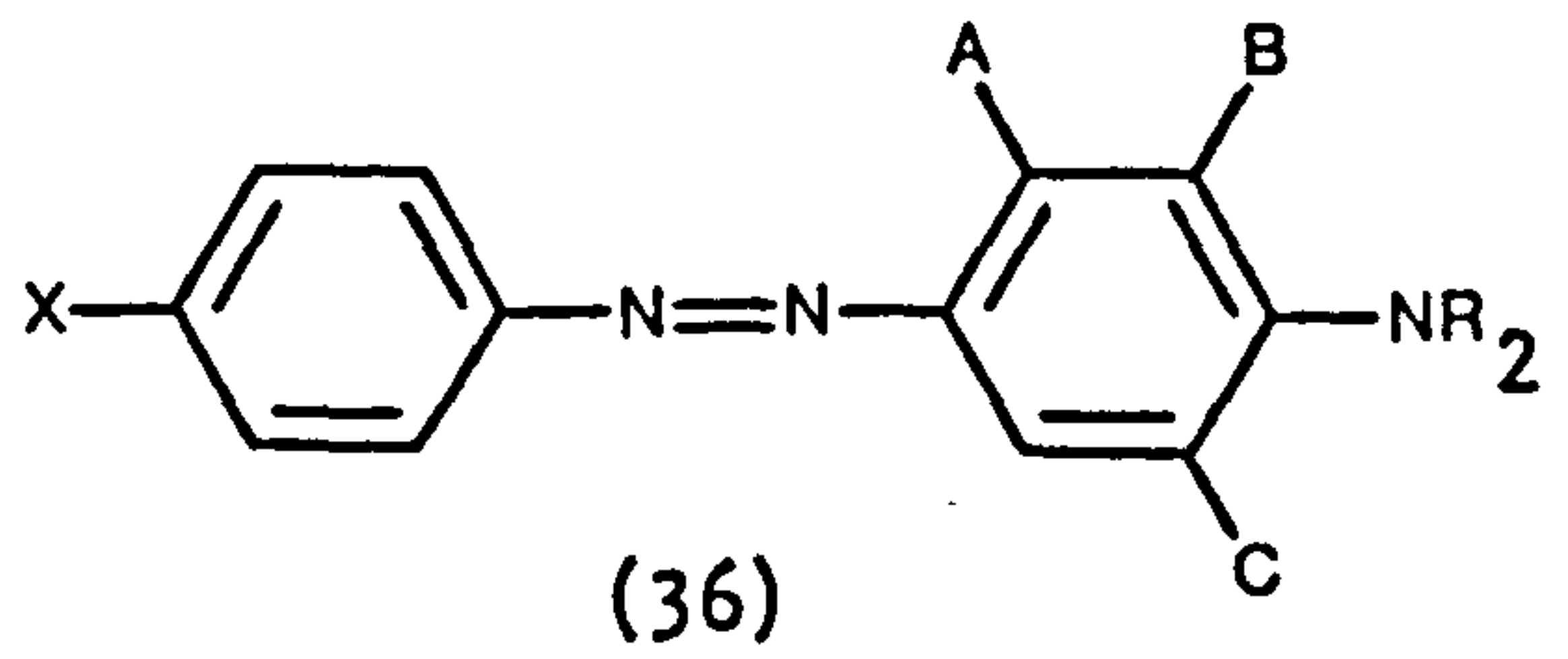


(37)

X = Y = H; λ_{max} = 479 nm, ε_{max} = 31,300

X = Y = Me; λ_{max} = 382 nm, ε_{max} = 8,500

Table 1.9. Electronic Effects of Substituents in the Donor Ring of Dye (36).[a]



(36)

X	A	B	C	R	λ_{max}/nm	$10^{-3}\varepsilon_{max}$
NO_2	H	H	H	Et	486[b]	34.0
NO_2	CH_3	H	H	Et	497[b]	33.2
NO_2	F	H	H	Et	469[b]	28.8
NO_2	H	H	H	H	445[c]	—
NO_2	H	CH_3	H	H	450[c]	—
NO_2	H	CH_3	CH_3	H	454[c]	—
H	H	H	H	H	385[d]	24.5
H	H	F	F	H	377[e]	28.8

[a] Solvent ethanol

[b] Ref.73

[c] Ref.70

[d] Ref.59

[e] Ref.74

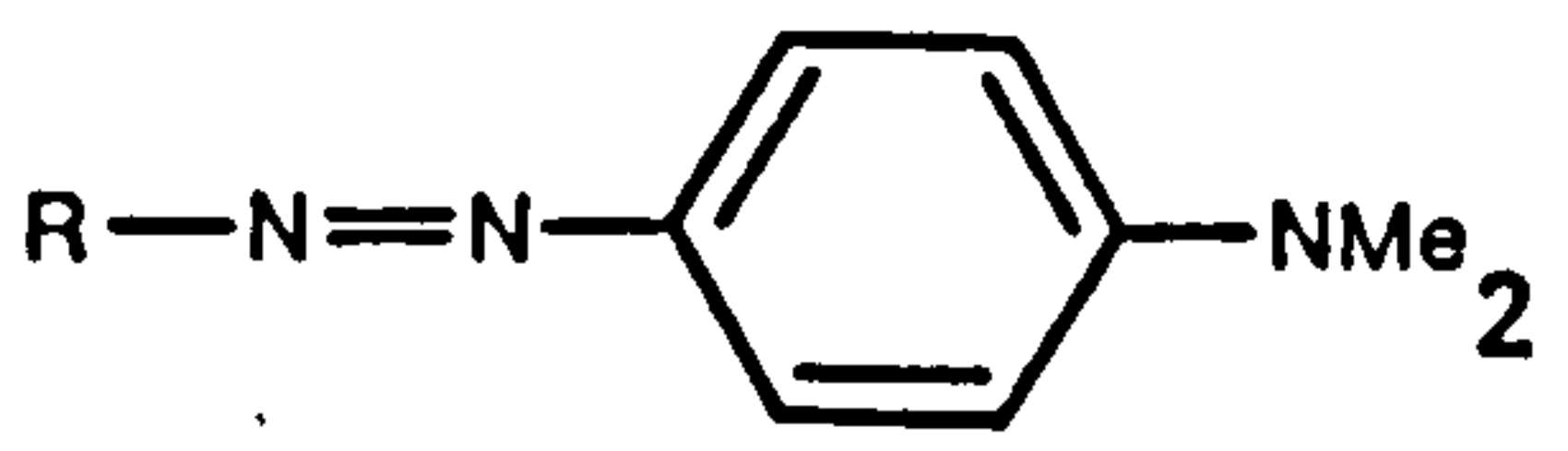
marked bathochromic shifts and increases in intensity relative to their benzene counterparts. A measure of the colour changes involved is given by the list of azo dyes (38) in Scheme 1.1, arranged in order of increasing λ_{max} (given where known); the colour is that observed on polyester.

It is difficult to obtain blues with fully benzenoid azo dyes without increasing the number of substituents in the acceptor and donor rings, whereas many heterocyclic derivatives, notably those of thiazole, isobenzthiazole and thiophene, give blues with relatively simple substitution patterns.

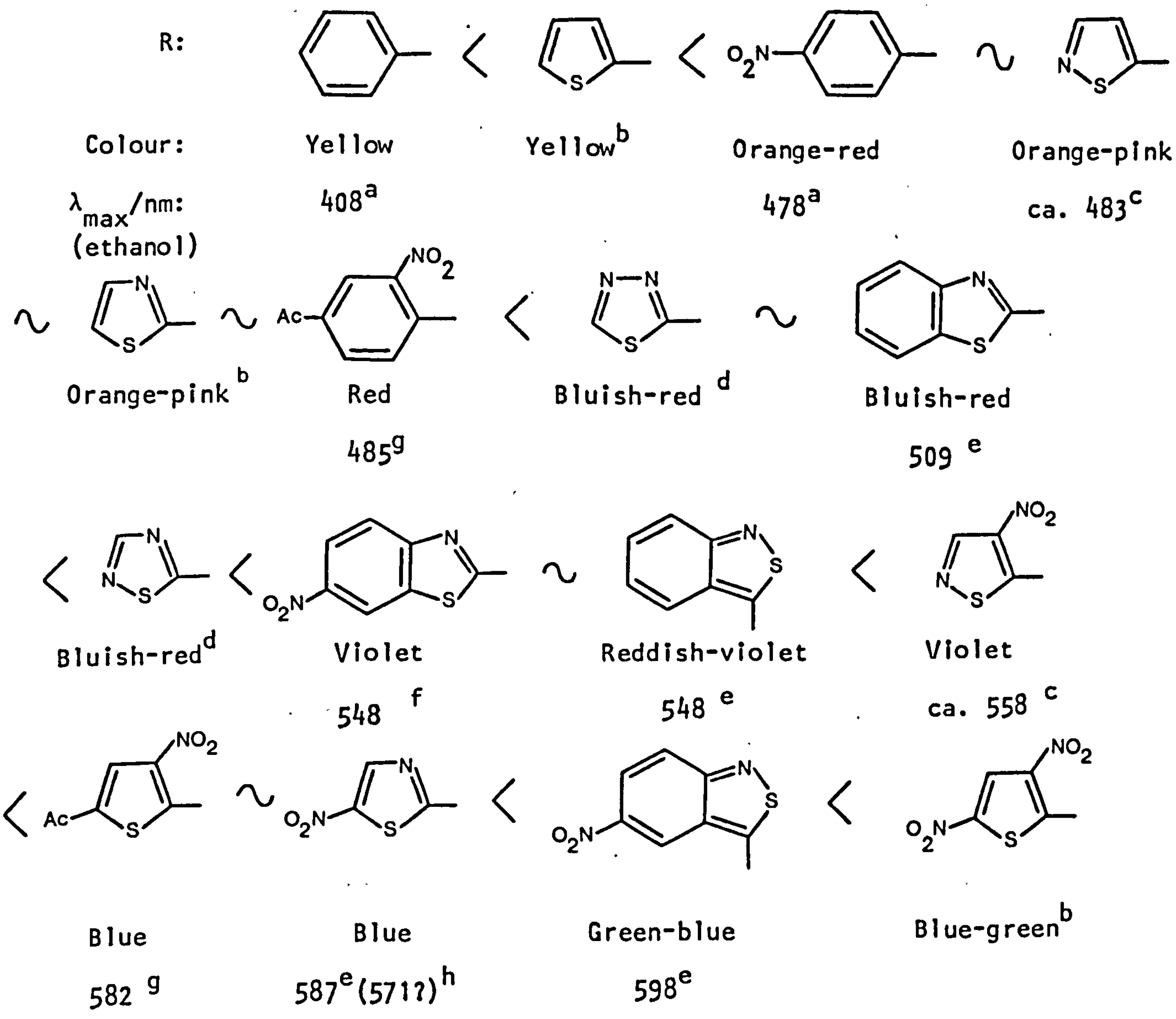
It is of interest that the difference between parent and nitro-substituted forms of the thiazole, and presumably the thiophene, types is much greater (~90nm)[21] than the corresponding benzthiazoles (~40nm),[20] probably because in the latter compounds the rest of the chromophore is somewhat insulated from the electron withdrawing power of the nitro group by the benzene ring; PPP calculations suggest that the increased diene character of the thiophene ring, and presumably of other related heterocycles, is responsible for the inherent colour shift of this system.[79]

Extinction coefficients for the simple heterocyclic azo dyes are of the order of 30,000-70,000 compared with 20,000-35,000 for the corresponding benzene analogues.

Although numerous examples of heterocyclic azo disperse dyes appear in the patent literature, relatively few investigations have been reported elsewhere.



(38)



[a] Ref. 59 [b] Likely position

[c] Value quoted is that of the 3-Me derivative - see ref. 76

[d] Suggested position - see ref. 76 [e] Ref. 76

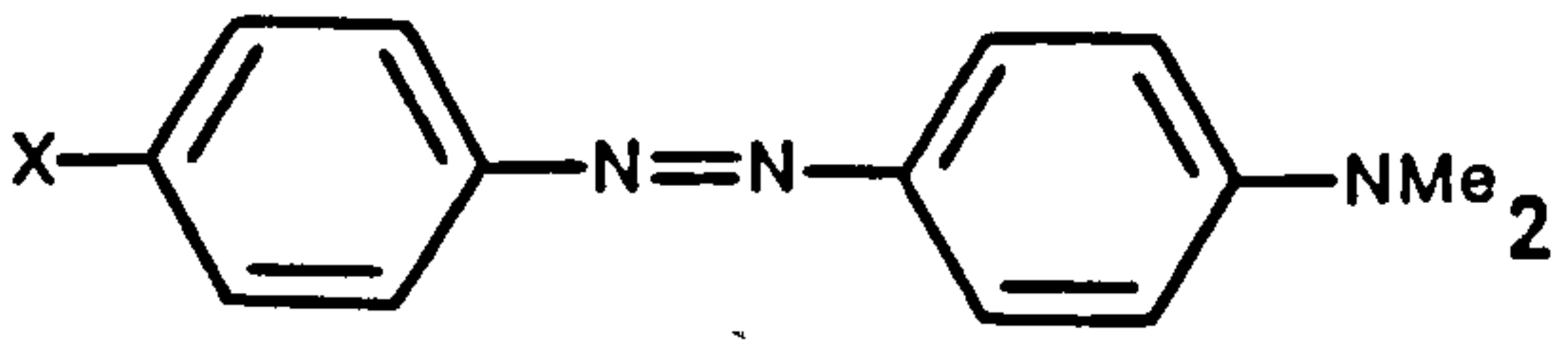
[f] Ref. 55(ref. 76 quotes 575 nm) [g] Ref. 77 [h] Ref. 78

Scheme 1.1. Order of bathochromicity of some acceptor residues.

1.6. Dipole Moment Studies

The dipole moments of derivatives of 4-aminoazobenzene give an indication of the conjugative effects between the terminal nitrogen lone pair and substituents located elsewhere in the molecule. Measurements on p-substituted 4-NN-dimethylaminoazobenzenes (Table 1.10)[80] show that the dipole moment increases with the acceptor strength of X. The large differences (Δμ) between observed and calculated values for the nitro and thiocyanate groups have been explained by the so-called enhancement of resonance effect, due to the contribution of structures

Table 1.10. Dipole Moments[a] of p-Substituted Derivatives of NN-Dimethylaminoazobenzene (39).[80]

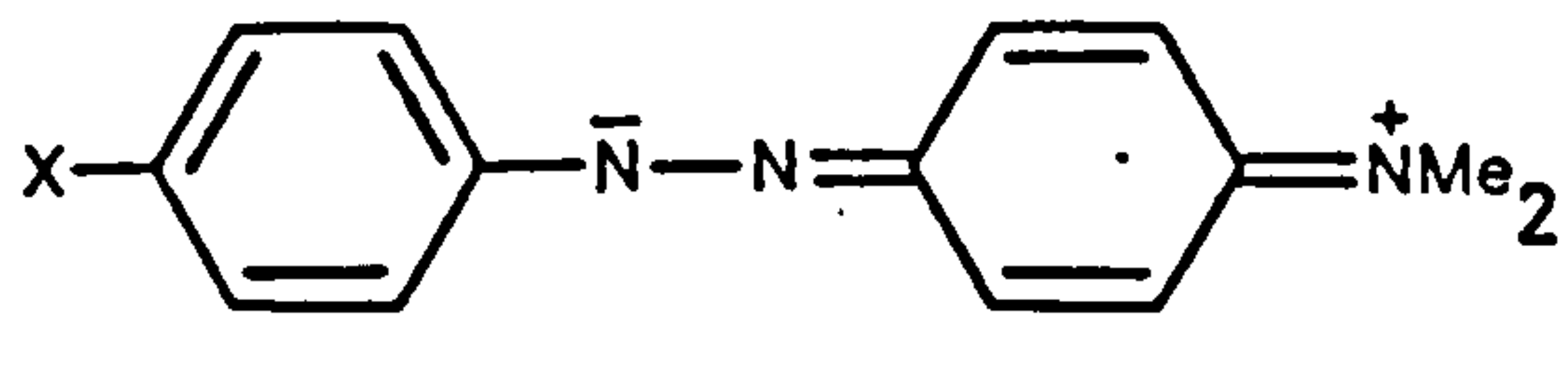


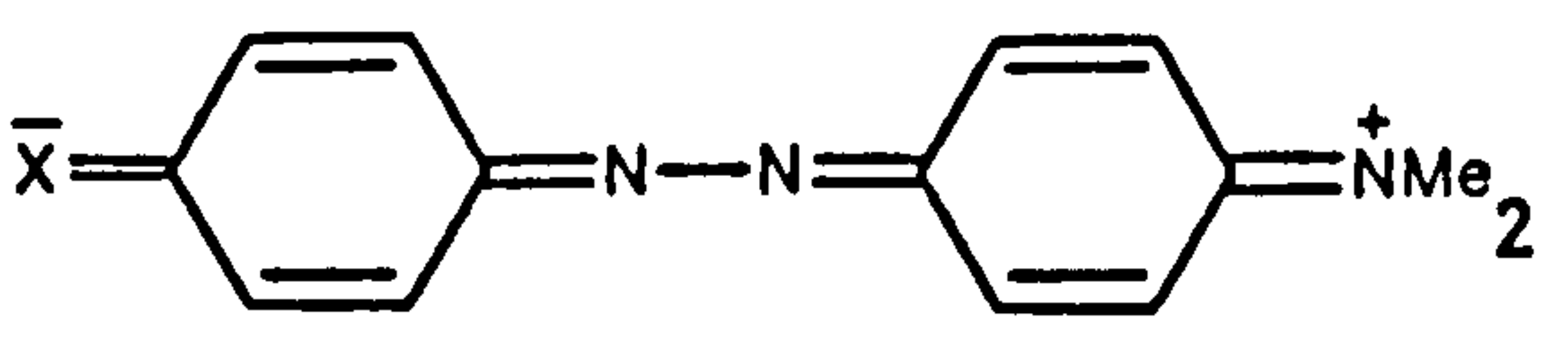
(39)

X	$\mu_{(obs.)}$	$\mu_{(calc.)}$	$\Delta\mu$
OCH_3	2.77	3.15	-0.38
CH_3	2.75	2.89	-0.14
H	3.22	—	—
Cl	4.89	4.68	+0.21
I	4.76	4.40	+0.36
SCN	6.65	5.98	+0.67
NO_2	8.16	7.01	+1.15

[a] Solvent benzene

such as (41) to the ground state, in addition to (40). The halogens are also capable of this effect to a smaller extent.


(40)


(41)

Apparent dipole moments of a series of p-substituted 9-phenylazojulolidines and their NN-diethylaminoazobenzene analogues have recently been determined (Table 1.11).[81] Vector interaction moments, $\mu_{(int)}$, in the direction of the major axis of the molecules (Fig. 1.4) were calculated in order to explain these moments. The values of $\mu_{(int)}$, for the 9-phenylazojulolidines are all greater than those for the corresponding NN-diethylaminoazobenzenes. It is suggested that ring closure leads to improved conjugation between the lone pair of electrons on the terminal nitrogen atom and the π-electron system of the aromatic ring to which it is attached. This delocalisation increases the π-electron density at the phenylazo group so that $\mu_{(int)}$ reflects the extent to which this electronic distribution is perturbed by the para-substituent. In explanation, it is proposed that the terminal nitrogen atom in the

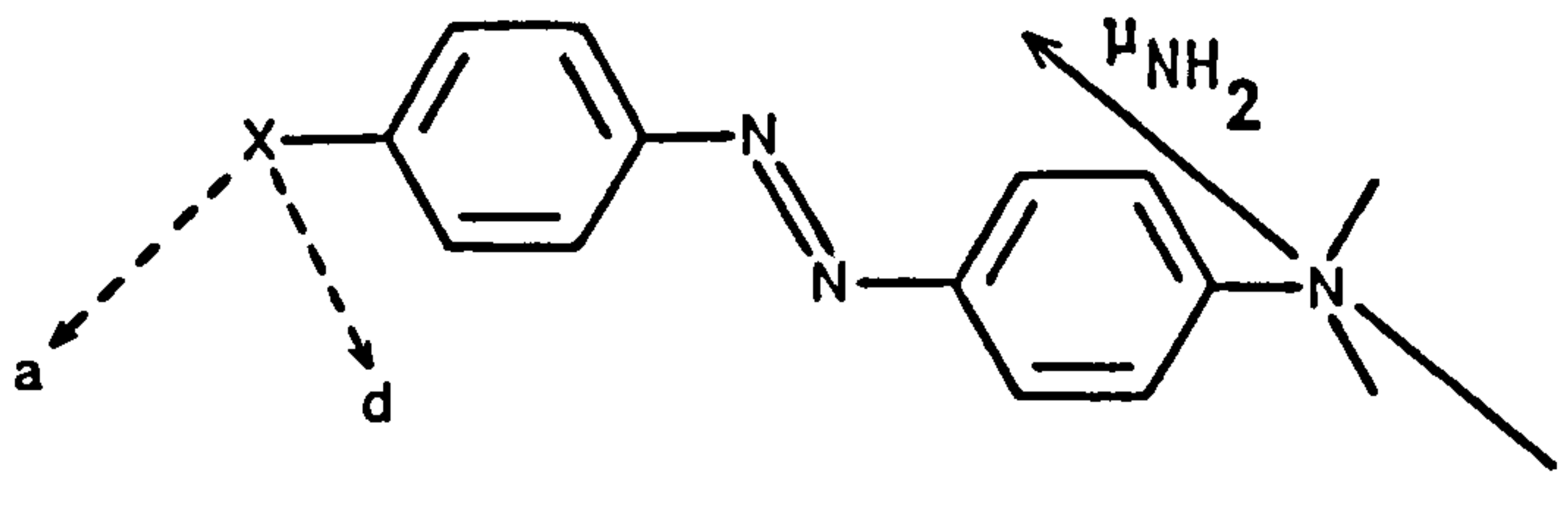
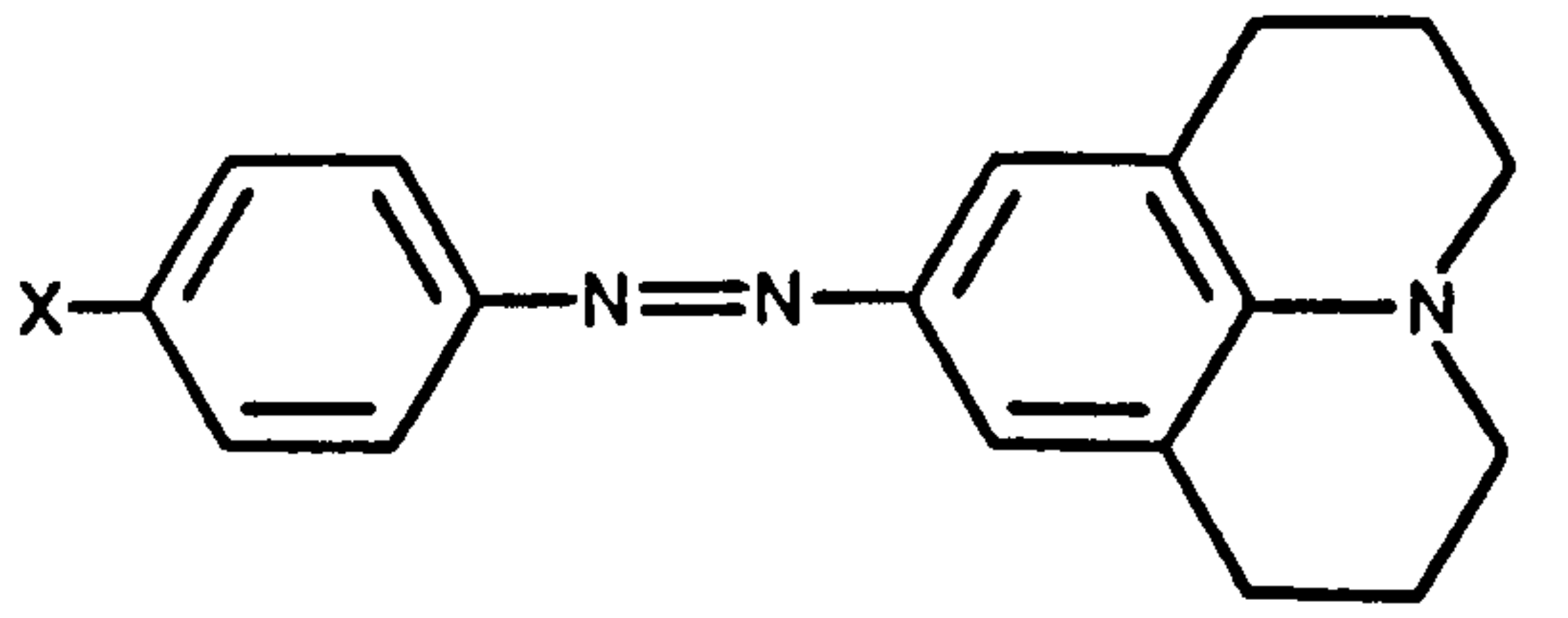


Fig. 1.4. Significance of $\mu_{(int)}$.[82]

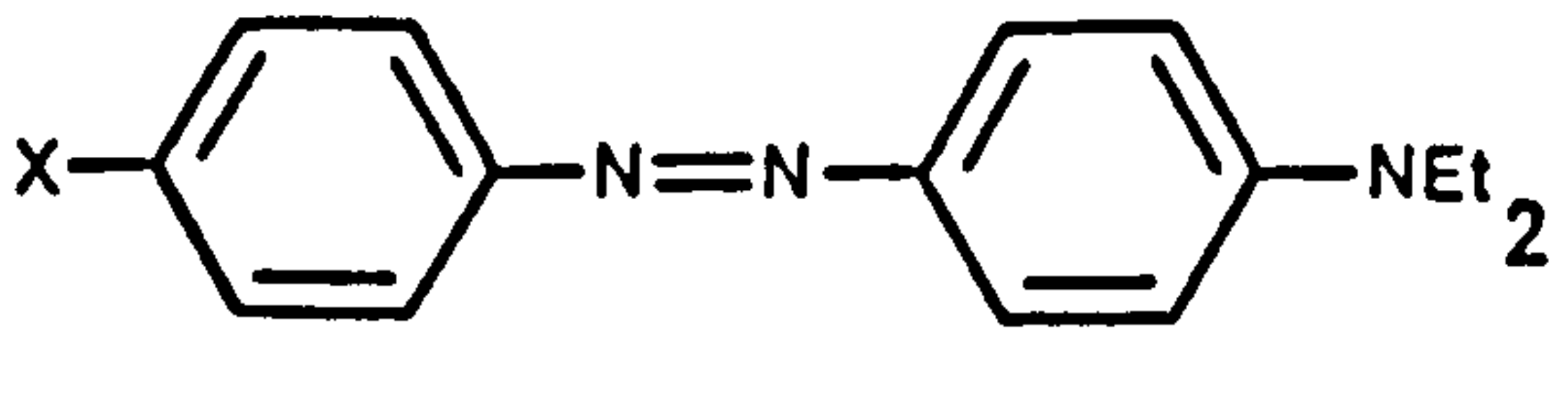
a = $\mu_{(int)}$ for electron withdrawing substituent X

d = $\mu_{(int)}$ for electron donor substituent X

Table 1.11. Comparison of Dipole Moments[a] of 9-Phenylazojulolidine (J) and NN-Diethylaminoazobenzene (D) Derivatives.[81]



(J)



(D)

X	μ/D		μ(Int)/D		Δμ (Int)	σ_p
	J	D	J	D		
OMe	3.00	—	—	—	—	—
Me	2.99	2.88	1.70	1.55	0.15	-0.17
H	3.57	3.40	1.93	1.72	0.21	0.00
F	5.08	4.82	1.99	1.69	0.30	0.06
Cl	5.14	5.01	1.95	1.79	0.16	0.24
Br	5.27	5.15	2.10	1.95	0.15	0.27
I	5.23	5.01	2.22	1.97	0.25	0.28
CF_3	6.82	6.44	2.66	2.25	0.41	0.54
CN	8.41	8.17	2.79	2.53	0.26	1.00[b]
NO_2	8.68	8.43	3.08	2.81	0.27	1.27[b]

[a] Solvent benzene

[b] Enhanced σ values

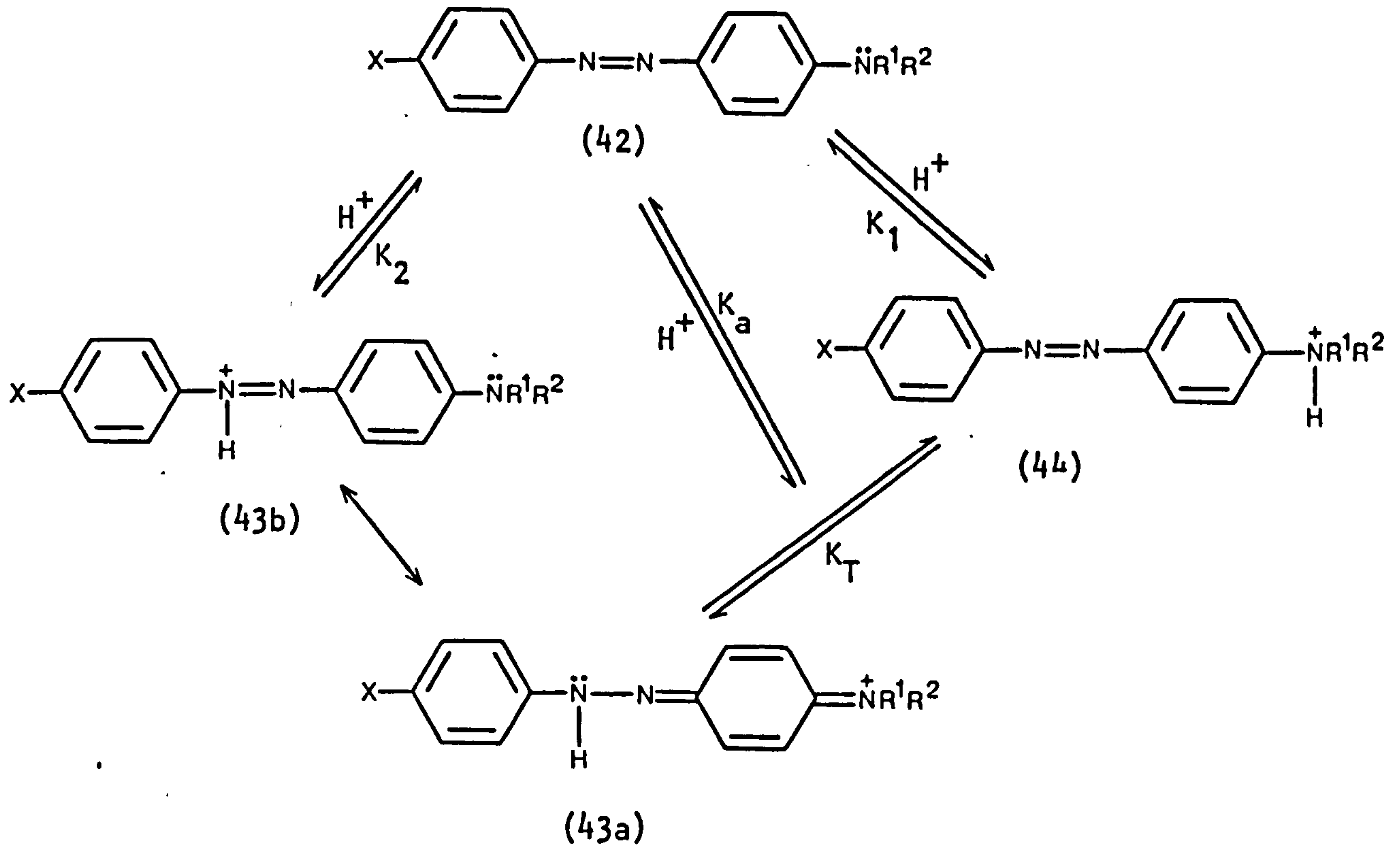
9-phenylazojulolidines is more nearly sp^2-hybridised than that in the NN-diethylaminoazobenzenes and suggested that the hybridisation may be influenced by strongly electron withdrawing substituents.

In both series of dyes, $\mu_{(int)}$ increases with increase in the Hammett σ_p constant, although there is no consistent trend in the differences between $\mu_{(int)}$ for the two series; $\mu_{(int)}$ may arise by interaction of the para-substituent only with the π-electron distribution of its adjacent aromatic ring.

1.7. Protonation Equilibria of Aminoazo Dyes

Many p-aminoazo dyes (42) undergo a pronounced change in colour on addition of acid (halochromism). This phenomenon is well documented in the literature and a useful review has appeared.[83] Solutions of the mono-acid salts of derivatives of 4-aminoazobenzene generally show two absorption bands, corresponding to an equilibrium mixture of two tautomeric forms,[84] the azonium cation (43) in which the proton is attached to the β-azo nitrogen atom[85] (absorbing at 500-550 nm) and the ammonium cation (44) where protonation at the terminal nitrogen atom[86] prevents conjugation of its lone pair, thus shifting the absorption band to shorter wavelengths (about 320 nm) near to that of azobenzene itself.

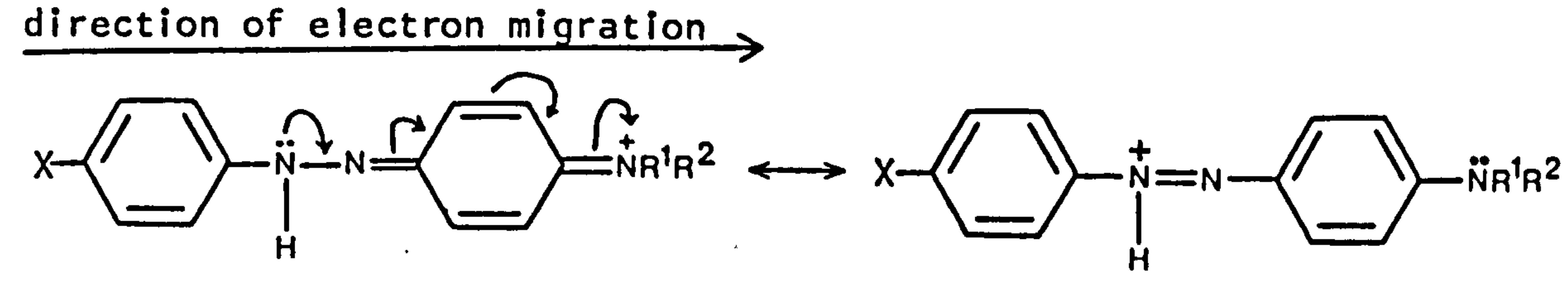
The tautomeric equilibrium constant, K_T, is defined as $K_T = [\text{azonium}] / [\text{ammonium}]$; [86-88] it should be noted, however, that some workers have used $K_T = [\text{ammonium}] / [\text{azonium}]$.[89-92] It would seem preferable to use the former equation, since addition of acid to the equilibrium mixture causes an increase in the amount of azonium cation present (i.e. the azonium cation is effectively the product of the reaction); also, the $C_\varepsilon/A_\varepsilon$ ratios as used by Sawicki are more directly applicable (see eqn. 1.3, section 1.8).



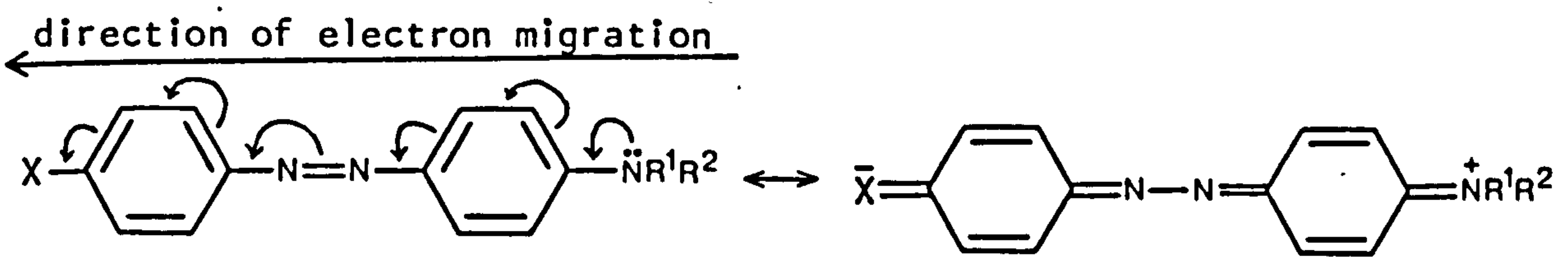
K_T is dependent upon the solvent and usually shows a gradual increase with increasing acid concentration.[86] The relative amounts of each tautomer can be estimated spectroscopically or from pK_a values.[83] It should be noted that halochromism only occurs when the amino group is *para* to the azo linkage, but that such protonation characteristics are also shown by *p*-hydroxy- and *p*-alkoxyazo compounds, although more strongly acidic conditions are required.

The tautomeric equilibrium is dependent on steric effects, especially those which deconjugate the donor group. Thus, dye (37; X=H, Y=CH_3) gives virtually no azonium tautomer,[93] whereas the protonated azojulolidine dyes (32), with optimal conjugation of the terminal nitrogen lone pair, exist almost entirely in the azonium form.[56] These observations confirm the established view that the basicities of the β-nitrogen and the terminal nitrogen atoms (and consequently the equilibrium) are mainly governed by the degree of conjugation between the amino group and the rest of the molecule.[89,90]

Applying resonance theory to the azonium cation, the ground state of the molecule is best represented by (43a) and the excited state by (43b).



(43a) (43b)



(42a) (42b)

Comparison with the neutral dye (42) shows that, in the azonium species, the ground and excited states are much closer together in energy terms so that a bathochromic shift of the first absorption band is observed on protonation (positive halochromism). It can also be seen that the direction of charge migration accompanying electronic excitation in the azonium form is opposite to that found in the neutral dye. This difference suggests that substituents X should have the opposite effect in neutral and in protonated dyes and, indeed, electron donors, by stabilising the azonium excited state relative to the ground state, produce increased bathochromic shifts (Table 1.3). Electron acceptor groups behave in a less obvious manner (cf. electron donor groups in the acceptor ring of neutral dyes); powerful acceptors produce modest hypsochromic shifts, whilst some weaker acceptors can give rise to slight bathochromic shifts (Table 1.3).

The displacement of the absorption band is again roughly proportional to the Hammett σ constant of the substituent X. However, excellent linear correlations are found between the wavelength shift, $\lambda_{azonium} - \lambda_{neutral}$ $(\Delta\lambda)$, or, more precisely, the frequency difference ($\Delta\nu$), and the appropriate Hammett σ constant[55-57] (Table 1.3 and Fig. 1.5) in accordance with theoretical expectations.[94]

As the electron withdrawing capacity of X increases, $\Delta\lambda$ decreases and can in fact become zero or even negative; the azonium cation absorbs at a shorter wavelength than the neutral dye. By extrapolation of the plot in Fig 1.5, it is possible to estimate the value of σ, and hence the type substituent, needed to produce such negative halochromism;[95] thus, $\sigma_{\Delta\lambda=o}=1.24$. From Table 1.12, it can be seen that dye (I), with $\sigma_{\Sigma(p+m')}$ somewhat less than 1.24, shows positive halochromism. Dye (II), having $\sigma_{\Sigma(p+m')}$ slightly above 1.24, exhibits a small negative halochromism whereas dye (III) shows the relatively large negative halochromic effect expected for $\sigma_{\Sigma(p+m')}$ moderately larger than 1.24.

Examples of negative halochromism are quite rare when only one electron withdrawing group is present; examples include dyes (42; $R^1=R^2=Et$, $X=C(CN)=C(CN)_2$; $\Delta\lambda = -6$ nm)[96] and (42; $R^1=R^2=Me$, $X=N_2^+$; $\Delta\lambda = -90$ nm).[95] The julolidine derivative (32; $X=NO_2$), with its optimal conjugation of the nitrogen lone pair, shows a hypsochromic shift of 4 nm on protonation.[68] Introduction of a heterocyclic residue can also promote this effect.

Thus, by using appropriate substituents, it is possible to design dyes which show no colour change in acid ($\Delta\lambda \sim 0$) and which in theory should make good textile dyes, where pH sensitivity is undesirable.[97] Alternatively, dyes which show a marked colour change in acid can be made for use as indicators, exemplified by Methyl Orange (42; $R^1=R^2=Me$, $X=SO_3H$).

As the acid concentration increases, there is a gradual shift in the equilibrium between the azonium and ammonium cations towards the former species. This behaviour has been attributed in the 4-aminoazobenzenes to

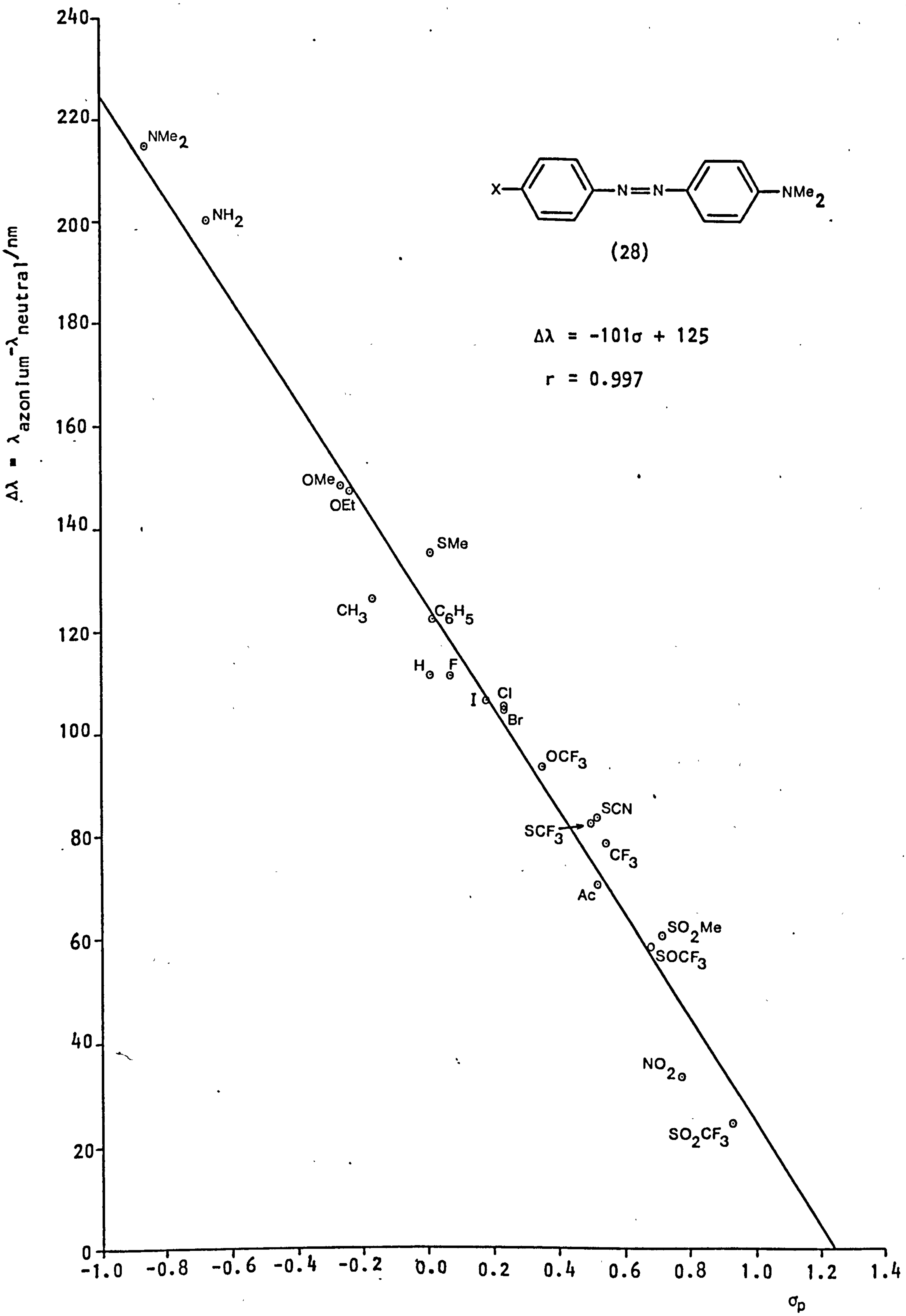
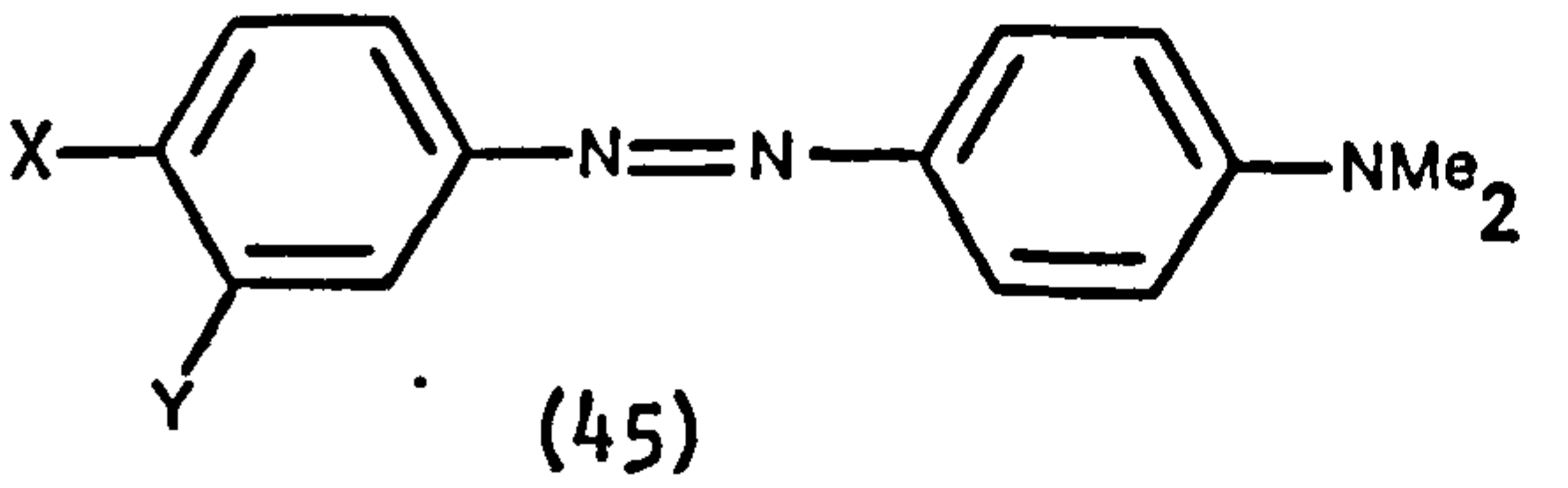


Fig. 1.5. Relation of $\lambda_{azonium} - \lambda_{neutral}$ to σ_p for some azo dyes (28).

Table 1.12. Effect of Substituents on the Halochromism of Dyes (45)[a].



(45)

No.	X	Y	$\lambda_{neutral}$/nm[b]	$\lambda_{azonium}$/nm[c]		$\sigma_{\Sigma(p+m')}$[d]
I	NO_2	CF_3	487	503	16	1.10
II	SO_2CH_3	SO_2CF_3	497	494	-3	1.29
III	SO_2CF_3	NO_2	522	490	-32	1.46

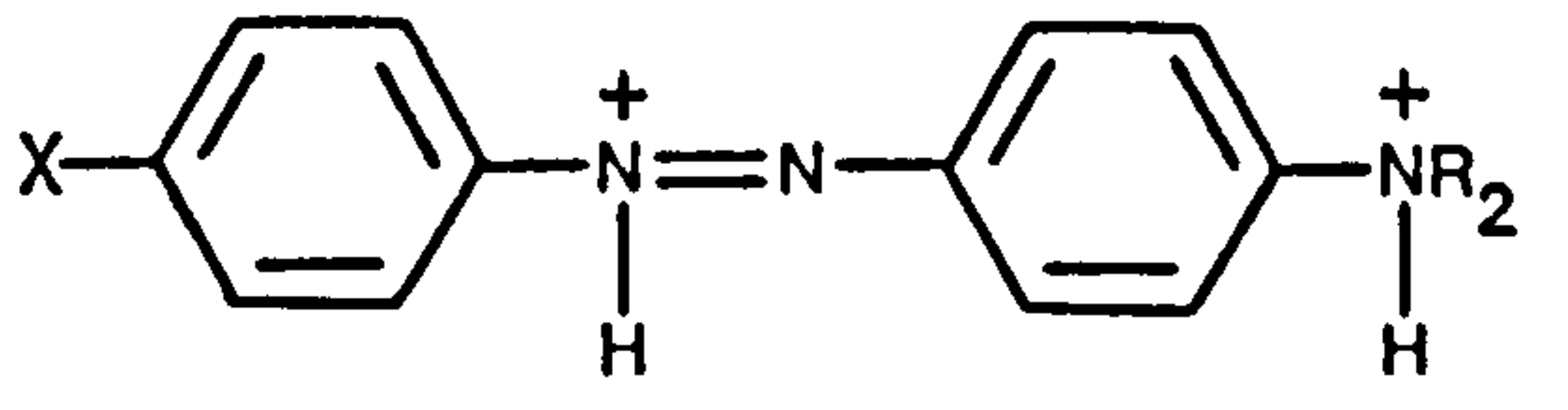
[a] Ref. 95 [b] In ethanol [c] In ethanolic hydrogen chloride

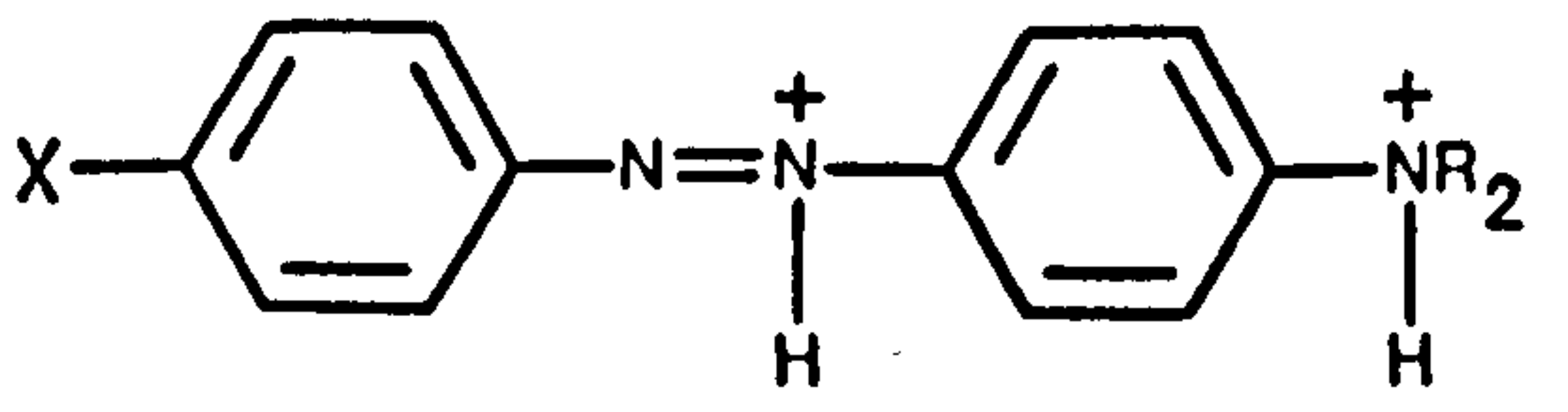
[d] Effective σ due to para and meta (converted) substituents.

differences in solvation of the cation concerned through hydrogen bonding.[91] In NN-disubstituted aminoazobenzenes this type of solvation will be appreciably less in the case of the ammonium ion and non-existent for the azonium form. A more important consideration may be the hybridisation of the terminal nitrogen atom; the tetrahedral configuration of this atom, due to sp^3 hybridisation, in the ammonium species makes the access of the counter-ions difficult, whereas the same atom in the azonium form is sp^2 hybridised and has a planar arrangement which allows the approach of counter-ions from above and below the plane of the molecule, with a resultant drop in free energy and stabilisation of the azonium form. As the acid concentration increases this stabilisation will increase, compared with the ammonium cation, as counter-ions cluster around the positive centre, causing an increase in the amount of azonium form present.

Once the saturation concentration of counter-ions at the terminal nitrogen atom is reached, the maximum amount of azonium species will be present.

In very strong acid conditions addition of a second proton may occur to give a species which absorbs in the 410-440 nm region. This latter band has been attributed to structures of type (46)[98,99] although


(46a)


(46b)

there is some doubt as to the exact nature of the equilibrium set up.[83] Recent ^{15}N and ^{13}C n.m.r. experiments involving ^{15}N-enriched 4-aminoazobenzene have suggested that protonation takes place at the α-azo and terminal nitrogen atoms (46b).[100]

1.8 Relationships Between pK_a Values, $C_\varepsilon/A_\varepsilon$ Ratio and Protonation Equilibria in Monoazo Dyes

In the various derivatives of 4-aminoazobenzene there are two main basic centres, namely the β-azo and the terminal nitrogen atoms. Since in acid solution an equilibrium exists in most cases, it is impossible to measure the individual basicity of each nitrogen atom. However, a value for the overall basicity of the molecule (pK_a) can be easily obtained.[101]

A rough idea of the tautomeric equilibrium can be obtained by measurement of ε_{max} values at the wavelength maxima of the azonium (C band) and ammonium (A band) forms. This procedure gives the ratio $C_\varepsilon/A_\varepsilon$ which is roughly proportional to K_T (eqn. 1.3) if it is assumed that the absorption of the azonium ion at the λ_{max} of the ammonium ion is zero, and vice-versa.

$$K_T = \frac{[\text{azonium}]}{[\text{ammonium}]} = k\frac{C_\varepsilon}{A_\varepsilon} \alpha \frac{pK_2}{pK_1} \alpha \frac{\text{Basicity at } \beta\text{-N}}{\text{Basicity at t-N}} \qquad (1.3)$$

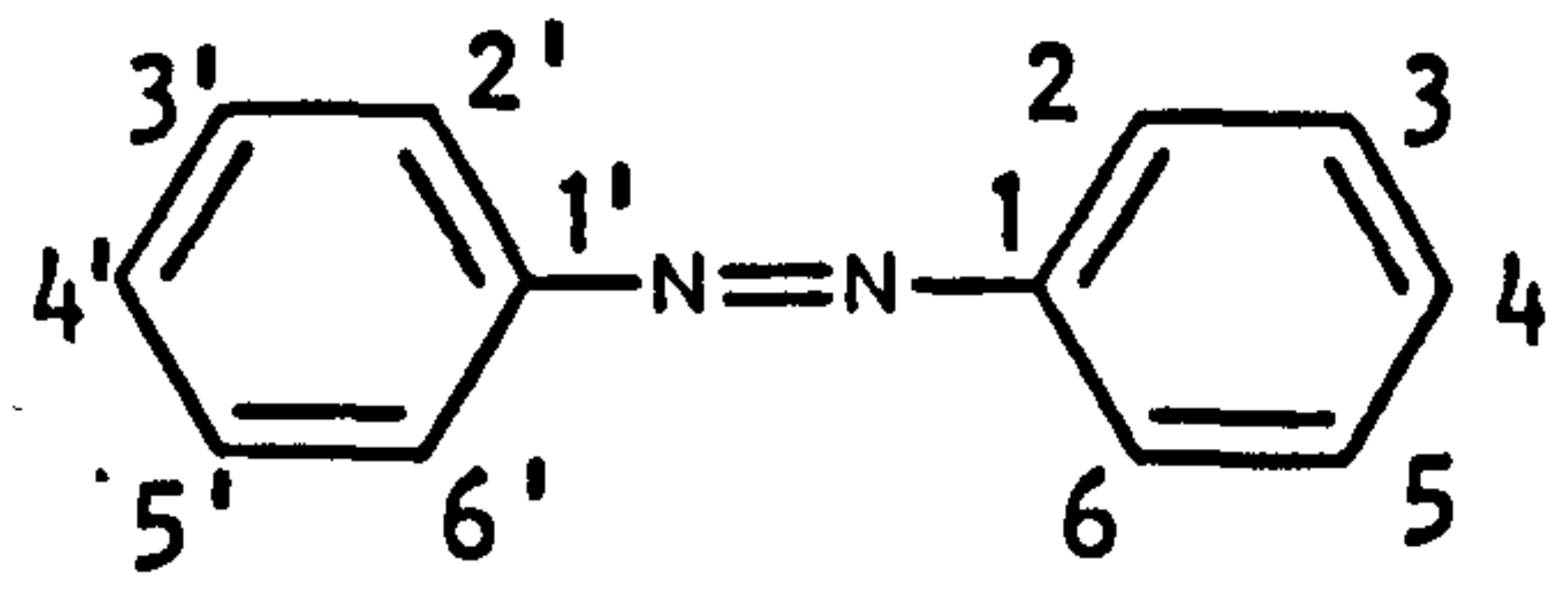
The value of k takes into account the fact that the absolute ε_{max} value for the ammonium tautomer does not equal that of the azonium tautomer. Although such values have not been measured directly, data from Yamamoto et al.[89] and Hallas[56] suggest absolute ε_{max} values (ε^o) of 20,000-25,000 for the ammonium tautomer (which agrees well with the value for azobenzene of 22,400) and 55,000-65,000 for the azonium tautomer. The value of k can then be obtained (eqn. 1.4) and thus $C_\varepsilon/A_\varepsilon$ ratios can be used quantitatively to determine K_T. The constant k has also been obtained graphically, leading to similar values.[89]

$$k = \frac{A_{\varepsilon^\circ}}{C_{\varepsilon^\circ}} = 0.38 \pm 0.07 \qquad (1.4)$$

Recently, doubt has been cast on the validity of the assumption that the azonium cation does not absorb at the λ_{max} of the ammonium cation.[102] Absolute values of K_T have been determined graphically, by a method not based on this assumption, by utilising the fact that the tautomeric equilibrium changes as the acid concentration changes.

The $C_\varepsilon/A_\varepsilon$ and pK_a values for a particular molecule give information on the effect of a substituent within that molecule.[103] This situation can be illustrated using data from Table 1.13. Other things being equal, increasing the basicity of the β-nitrogen atom or decreasing the basicity of the terminal nitrogen atom increases the value of $C_\varepsilon/A_\varepsilon$. For example, 4-diethylaminoazobenzene has pK_a 3.08 and $C_\varepsilon/A_\varepsilon$ 0.5. Successive replacement of ethyl by methyl lowers pK_a to 2.58, then to 2.28, since the inductive effect of methyl is less than that of ethyl, so that the two basic centres as a whole show a drop in electron density. However, the

Table 1.13 Values of pK_a and $C_\varepsilon/A_\varepsilon$ Ratios for Aminoazobenzene Derivatives in 50% Ethanol at 26°C.[103]



Substituents	pK_a	$[HCl]$ /M	$C_\varepsilon/A_\varepsilon$
2-NH_2	1.8	1.0	0.00
3-NH_2	3.0	1.2	0.00
4-NH_2	2.35	1.0	0.73
4-NMe_2	2.28	1.2	3.62
4-NMeEt	2.58	1.0	1.4
4-NEt_2	3.08	1.0	0.5
4-NMe_2-4'-OMe	2.4	1.2	1.0
4-NMe_2-4'-Et	2.3	1.2	2.6
4-NMe_2-4'-Me	2.36	1.2	2.6
4-NMe_2-4'-H	2.28	1.2	3.62
4-NMe_2-4'-F	2.00	-	—
4-NMe_2-4'-Cl	2.00	-	—
4-NMe_2-4'-SCN	—	1.2	4.5
4-NMe_2-4'-Ac	2.16	1.2	7.5
4-NMe_2-4'-NO_2	1.81	1.0	8.7
4-NMe_2-2-Me	3.08	1.2	10.0
4-NMe_2-3-Me	3.46	1.0	0.025
4-NMe_2-2'-Me	2.04	1.2	0.29
4-NMe_2-3'-Me	2.33	-	—
4-NMe_2-2'-Et	1.85	1.0	0.14

alkyl groups affect the terminal nitrogen atom much more than the remote β-azo nitrogen atom, lowering the electron density at the former and consequently increasing the $C_\varepsilon/A_\varepsilon$ ratio to 1.4, then to 3.62. Replacement of the methyl groups by hydrogen atoms might be expected to give a further drop in pK_a. However, there is a small increase in this parameter, indicating that the loss of the +I alkyl effect is more than compensated for by hydrogen bonding of the amino hydrogen atoms with solvent molecules. This process results in an increase of electron density, and therefore of basicity, at the terminal nitrogen atom. The low pK_a value (1.8) of 2-aminoazobenzene[104] is due to intramolecular hydrogen bonding which effectively involves the β-nitrogen atom and makes protonation at this site very difficult. Indeed, the $C_\varepsilon/A_\varepsilon$ ratio shows almost exclusive protonation at the terminal nitrogen atom. Mesomeric donation is impossible in the case of 3-aminoazobenzene so that the amino nitrogen atom has a high basicity and, again, the azonium species is not favoured.

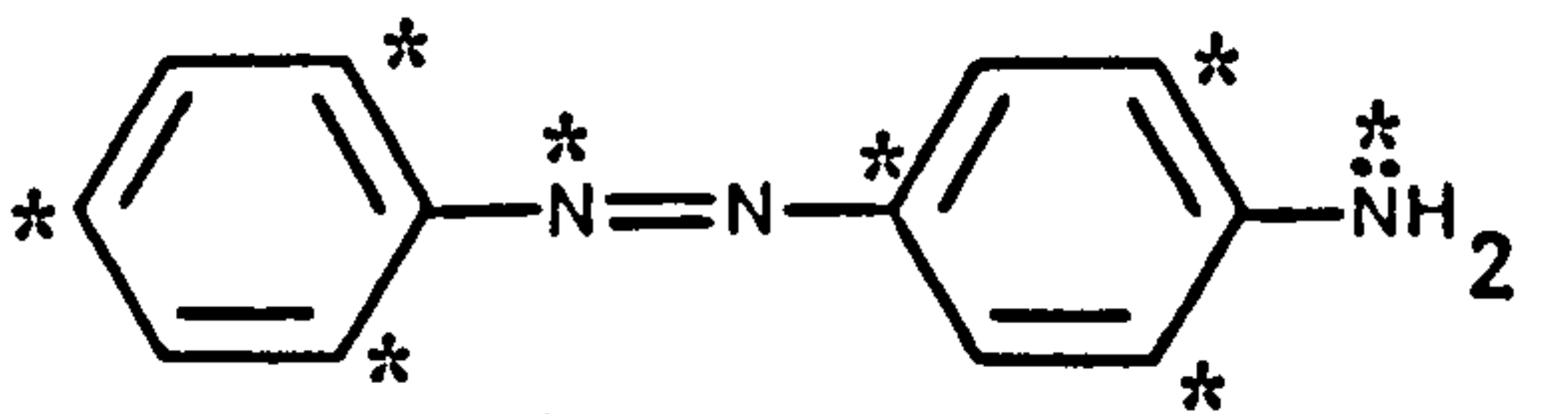
A methyl group in the 2-position increases the basicity at the β-nitrogen atom,[101,105] presumably by the +I effect; thus 4-dimethylamino-2-methylazobenzene has a value for pK_a of 3.08 and a $C_\varepsilon/A_\varepsilon$ ratio of 10.0, both values being significantly greater than those of the parent 4-dimethylaminoazobenzene (Table 1.13). The methyl group in the corresponding 3-methyl isomer also increases the pK_a (to 3.46) due to steric crowding of the terminal dimethylamino group which is partially deconjugated and therefore more basic; $C_\varepsilon/A_\varepsilon$ drops to 0.025. A methyl group at the 2'-position causes a drop in basicity at the β-nitrogen by hindering the access of a proton. The terminal nitrogen atom remains unaffected so that a drop in pK_a (to 2.04 from 2.28) and a decrease in $C_\varepsilon/A_\varepsilon$ (to 0.29 from 3.62) is observed. The larger ethyl group exaggerates this effect thereby causing further reductions in the two values.

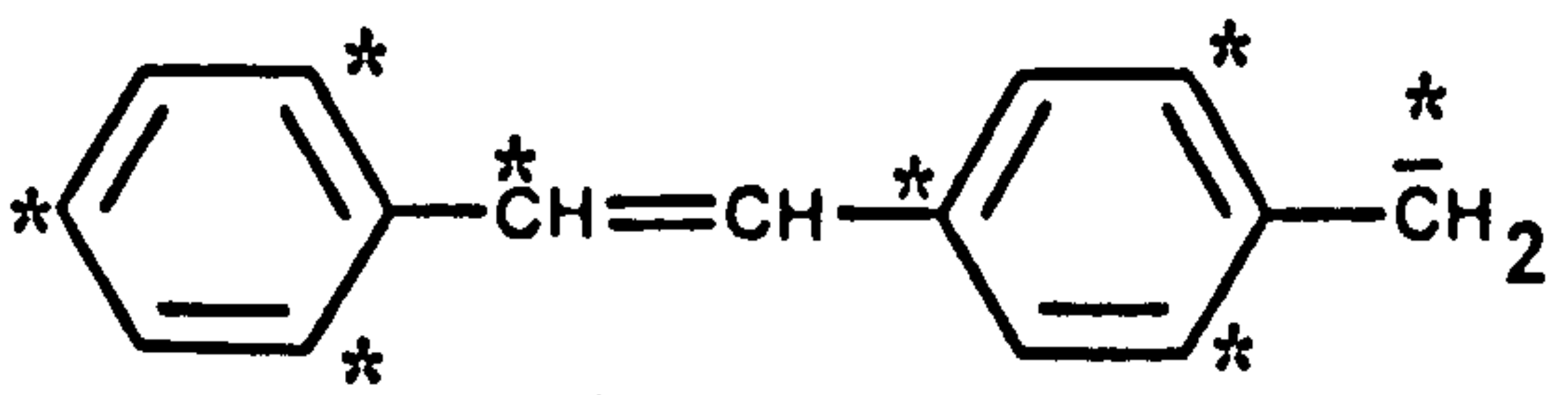
An electron donor substituent (methoxy) at the 4'-position causes only a small increase in pK_a, although the $C_\varepsilon/A_\varepsilon$ ratio drops to 1.0. These effects have been attributed to a +M effect (or +I for methyl) which is said to increase the basicity of the α-nitrogen atom at the expense of the β-nitrogen atom. On the other hand, an electron acceptor, such as nitro, at the 4'-position decreases pK_a by lowering the overall electron density at the two protonation sites. However, the increased conjugation of the terminal nitrogen atom decreases the basicity of the terminal group and at the same time increases the basicity of the β-nitrogen atom, so that $C_\varepsilon/A_\varepsilon$ increases (to 8.7 in the case of nitro). In these 4'-acceptor-substituted dyes, a linear correlation has been found to exist between the pK_a values and the appropriate Hammett σ constant.[106]

Only a limited amount of work has been published on diprotonated equilibria. As expected for a doubly charged ion, the equilibrium is on the side of the monoprotonated species,[107] and very strongly acidic conditions are required to permit the addition of a second proton.

1.9: Application of Perturbational Molecular Orbital (PMO) Theory to Aminoazo Dyes

As Dewar has pointed out,[50] it is significant that the large majority of coloured organic molecules are isoconjugate with odd alternant hydrocarbons, or are derivatives of such substances, or contain pairs of cross conjugated - and therefore independent - odd alternant systems. Even systems, such as the polyenes, show strong colour only when they contain many conjugated double bonds, as with the carotenes. It is helpful to consider azobenzene and its derivatives. The parent trans-azobenzene molecule has a high intensity $\pi \rightarrow \pi^*$ absorption band in the near ultraviolet at 320 nm ($\varepsilon \sim 22{,}000$)[108] and a low intensity $n \rightarrow \pi^*$ band in the visible region at 443 nm (ε∿400).[108] Introduction of a mesomeric electron donor group effectively converts an even alternant π-system into an odd alternant system. Thus, 4-aminoazobenzene (47) is iso-π-electronic with the odd alternant carbanion (48) and PMO theory[109] predicts that

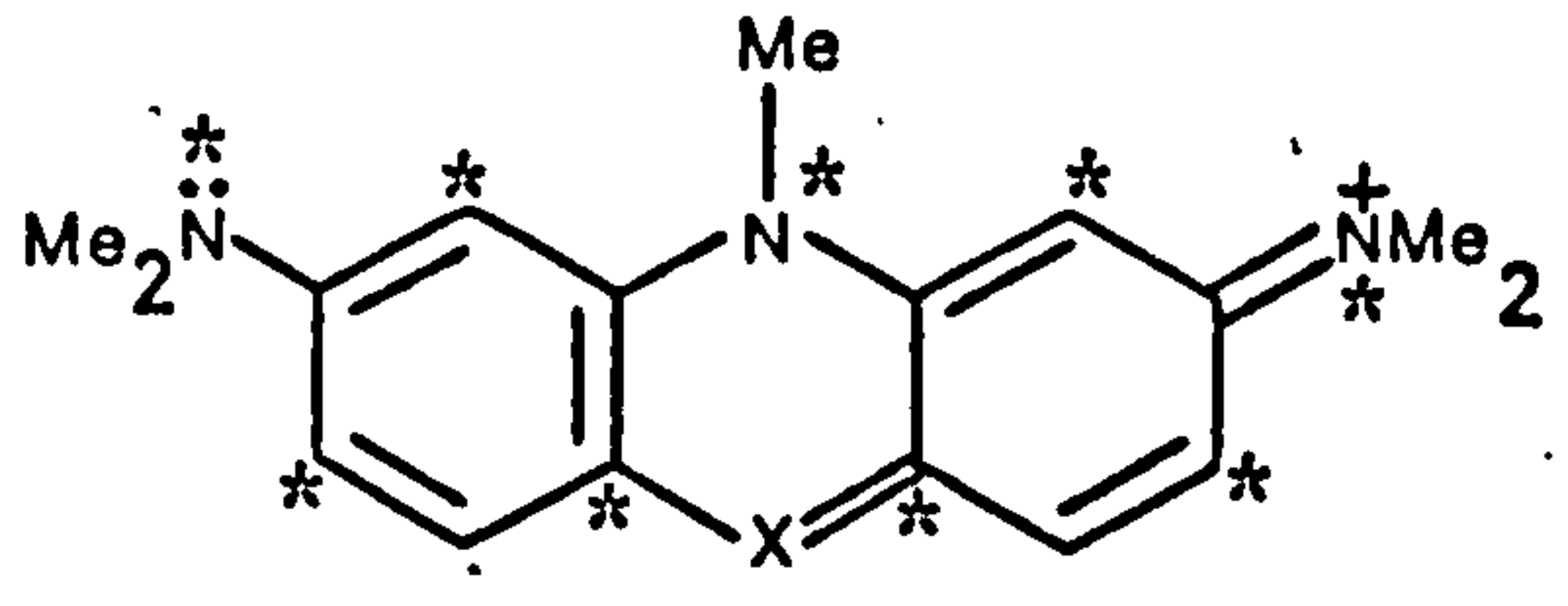

(47)


(48)

a new delocalised π orbital is introduced into the azo molecule, classed as a non-bonding molecular orbital (NBMO) because of its proximity to the zero energy level.[110] This new NBMO contains two electrons, and excitation of one of these to the lowest unoccupied molecular orbital (LUMO) gives rise to a low energy (long wavelength) absorption band.[111] The transition is allowed and intense (ε∿25,000) and is responsible for the colour of the dye. The electronic excitation process causes a general migration of electron density from the donor atom to the rest of the chromogen so that such absorptions are often described as intramolecular charge transfer transitions. The NBMO→π^* band of azo dyes often completely obscures the n→π^* band even though the latter is of moderate intensity (ε∿500; cf. azoalkanes where ε∿10) due to intensity 'borrowing' from the energetically close NBMO→π^* band.[112]

The special properties of a NBMO enable predictions to be made about substituent effects in odd alternant systems, which were originally formulated into a set of rules by Dewar in 1950.[109,110] Dewar's rules can be summarised (with examples)as follows:

(a) An increase in electronegativity at an unstarred position gives a bathochromic shift.

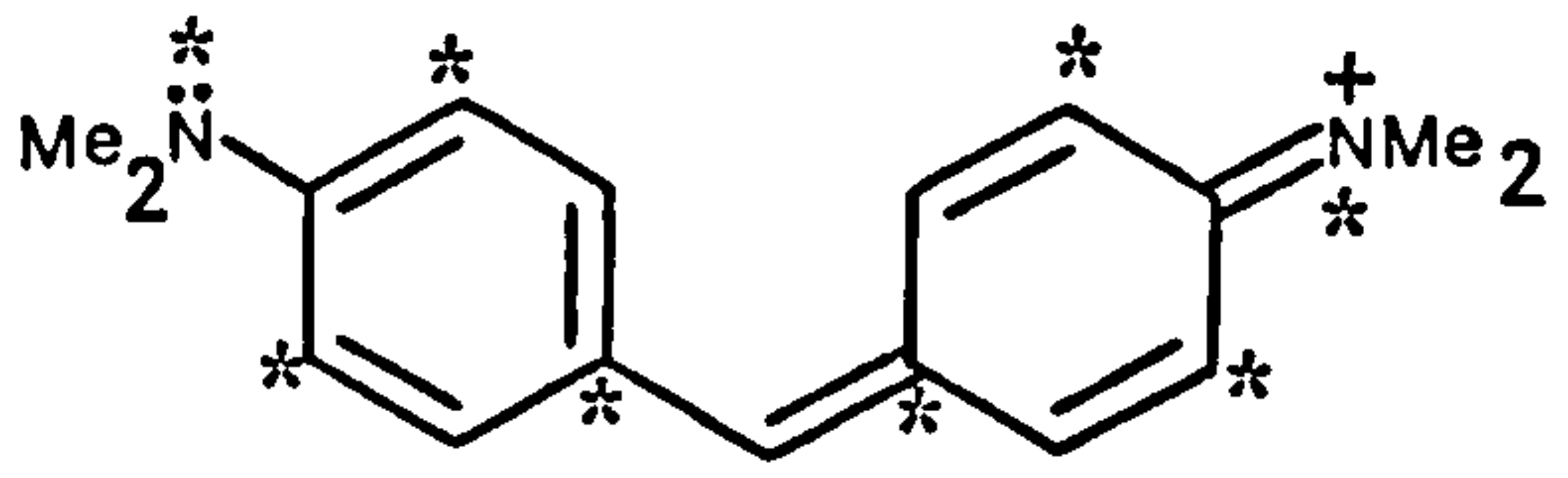


(49)

X = CH; λ_{max} = 491 nm

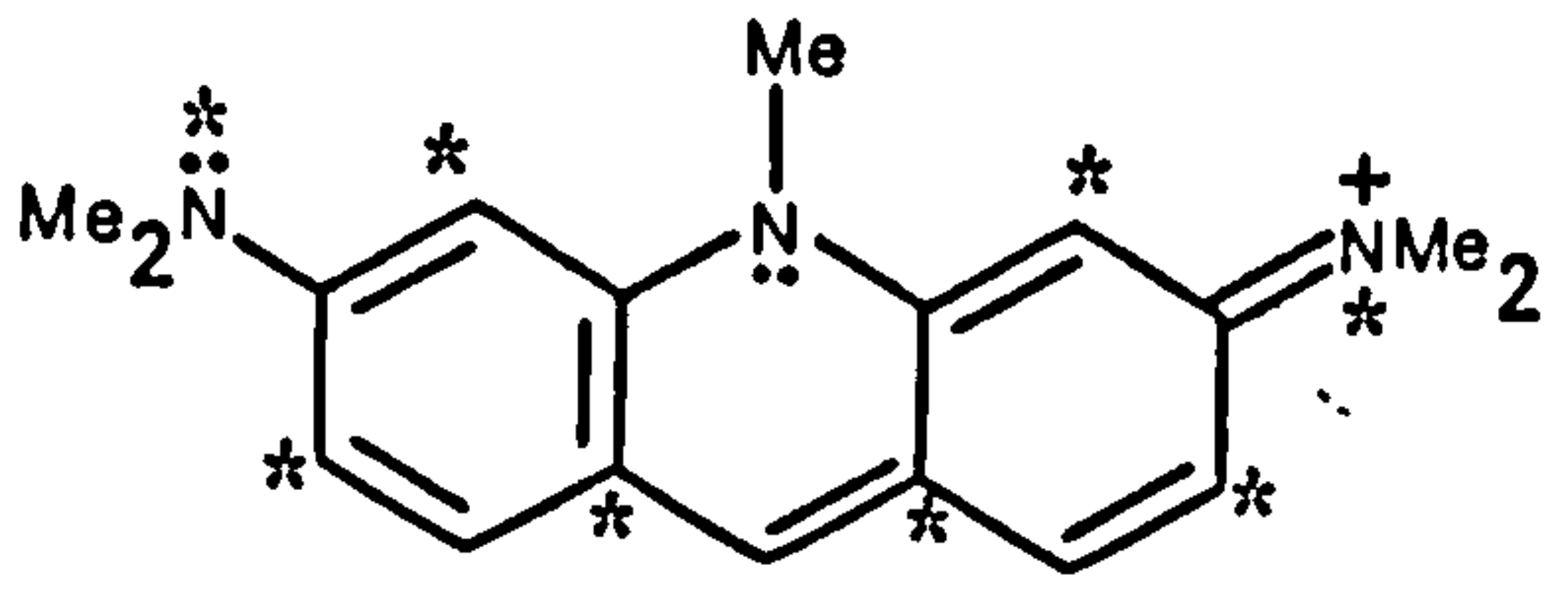
X = N; λ_{max} = 564 nm

(b) A decrease in electronegativity at an unstarred position gives a hypsochromic shift.



(50)

λ_{max} = 610 nm

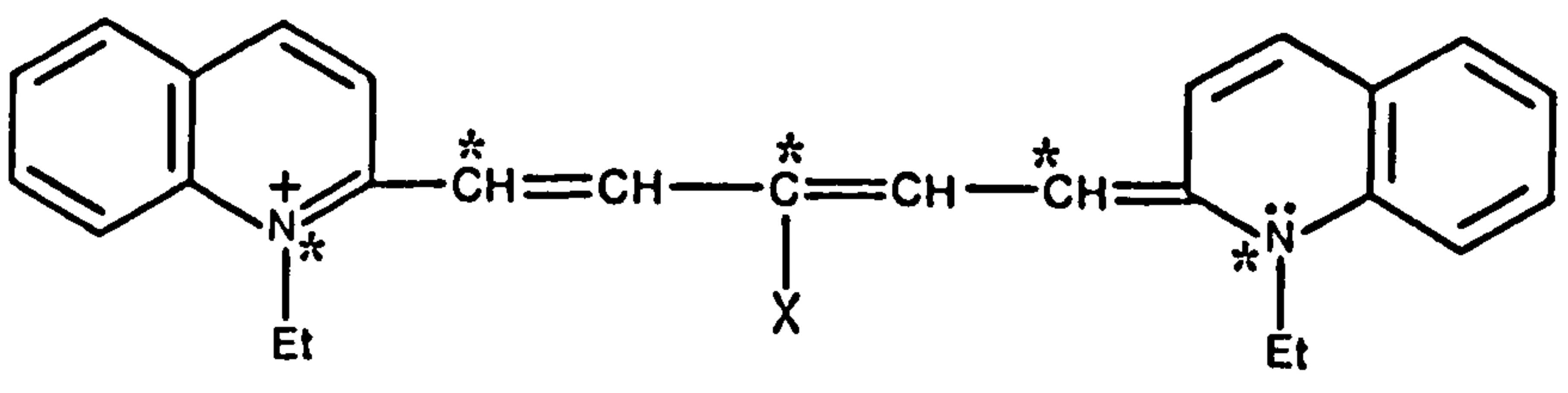


(51)

λ_{max} = 491 nm

Attachment of the mesomeric donor group ($\ddot{N}$Me) across two unstarred positions effectively lowers the electronegativity at these positions.

(c) Increasing the electronegativity at a starred position gives a hypsochromic shift.

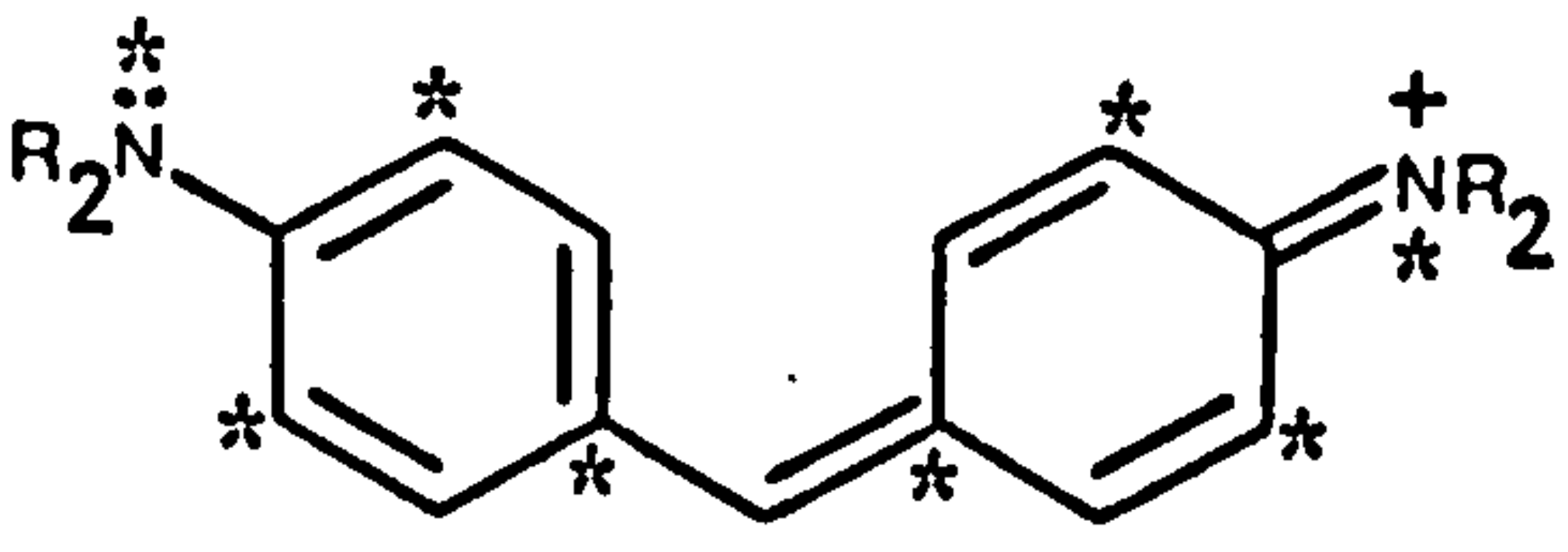


(52)

X = H; λ_{max} = 708 nm

X = NO_2; λ_{max} = 580 nm

(d) Decreasing the electronegativity at a starred position produces a bathochromic shift.

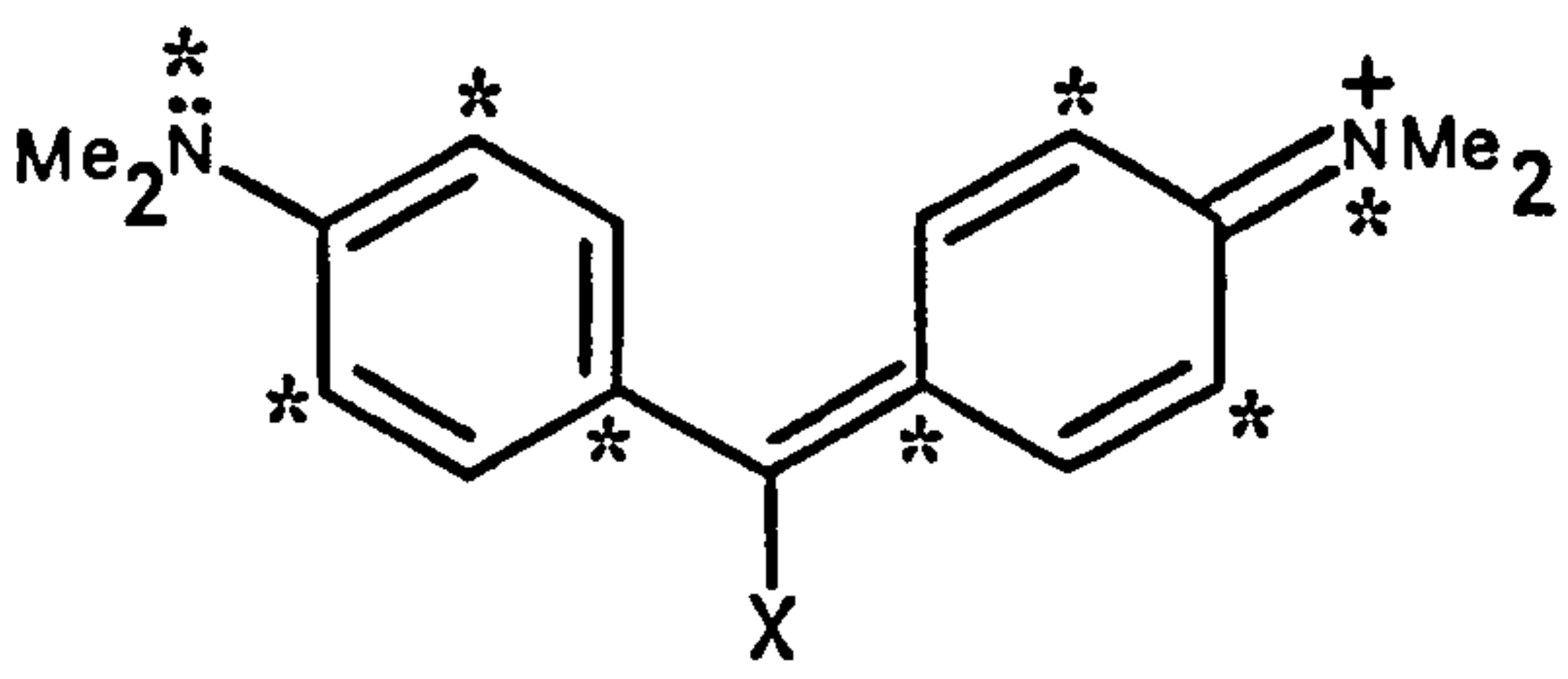


(53)

R = H; λ_{max} = 558 nm

R = Me; λ_{max} = 610 nm

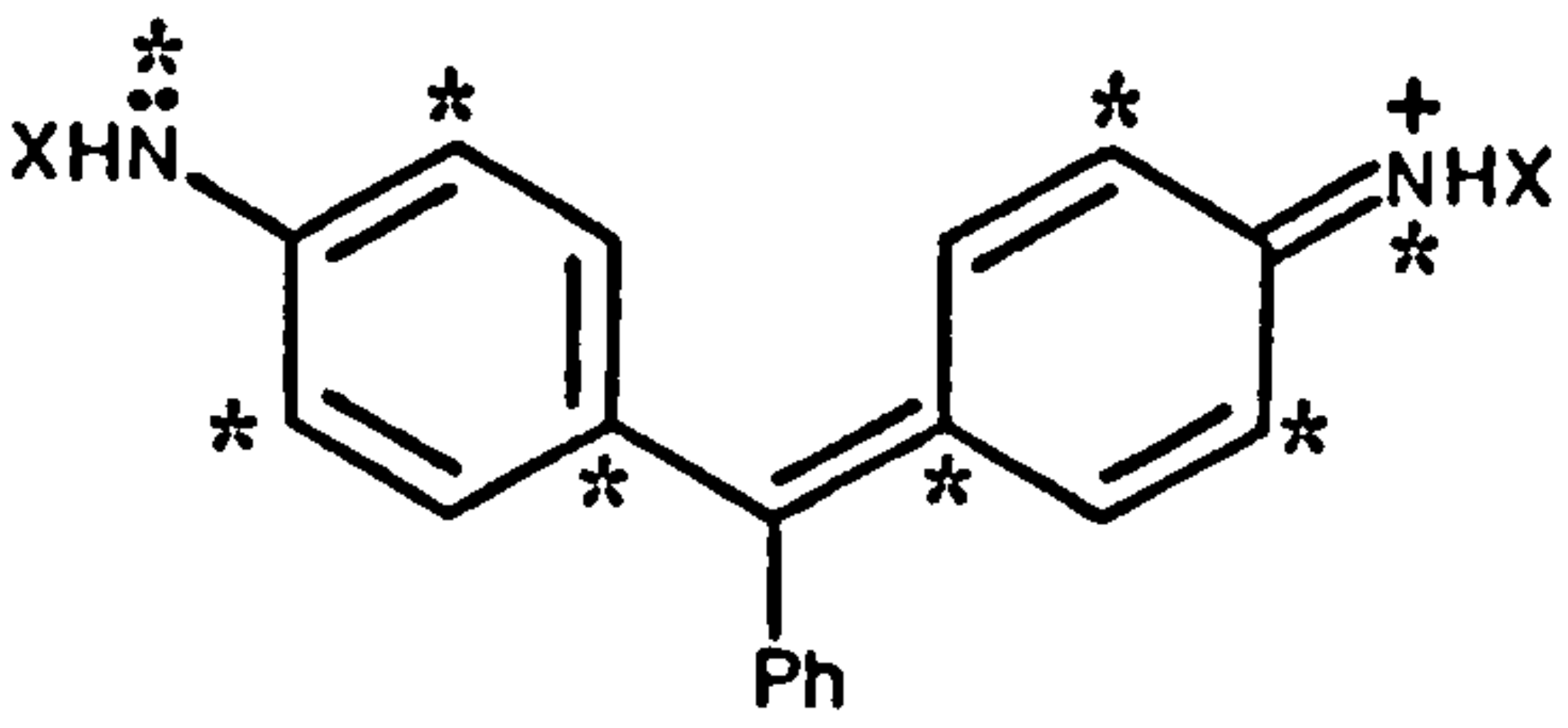
(e) Extending the conjugation with a neutral unsaturated group always gives a bathochromic shift, irrespective of the point of attachment.



(54)

X = H; λ_{max} = 610 nm

X = Ph; λ_{max} = 621 nm

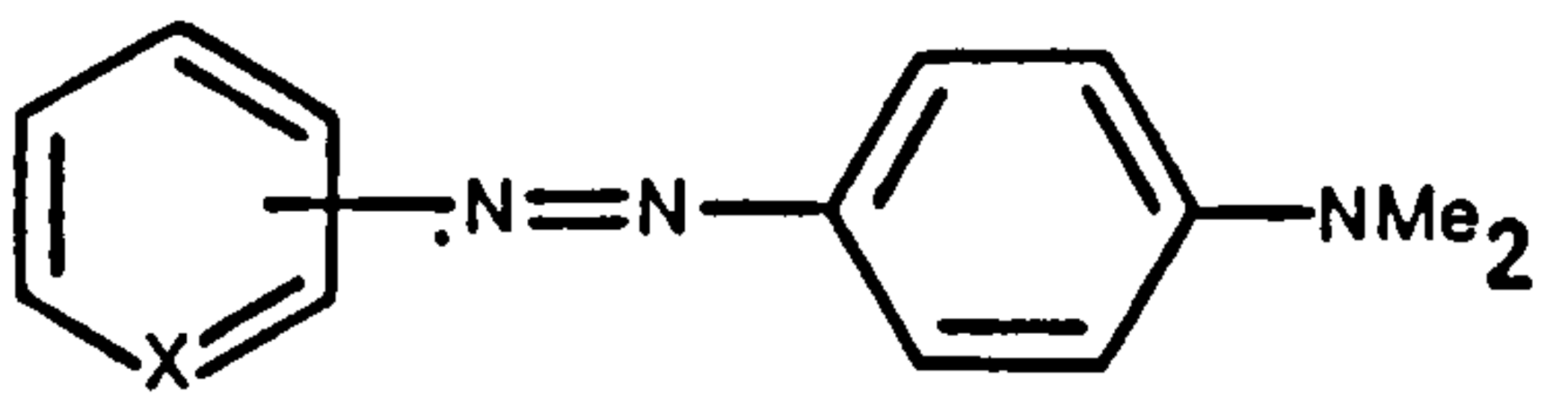


(55)

X = H; λ_{max} = 562 nm

X = Ph; λ_{max} = 637 nm

Dewar's rules are similar in many respects to Knott's rules[113] although the former have the advantage of being based on sound theoretical principles. The main limitations of Dewar's rules arise from the doubtful assumption that all 'odd alternant' chromogens are strictly comparable with a true alternant hydrocarbon. Theory suggests the latter species have a uniform bond order of about 1.6-1.7 rather than alternate single and double bands. This condition holds in cyanine-type dyes which are therefore particularly well-suited to application of the rules. However, donor-acceptor chromogens, such as the aminoazo dyes, show a high degree of bond alternation in the ground state and it is less justifiable to apply the rules to these systems. A neat illustration of these limitations is given by dyes (56) in which steric factors do not apply.[114] Thus, Dewar's rules predict hypsochromic shifts for the ortho and para isomers relative

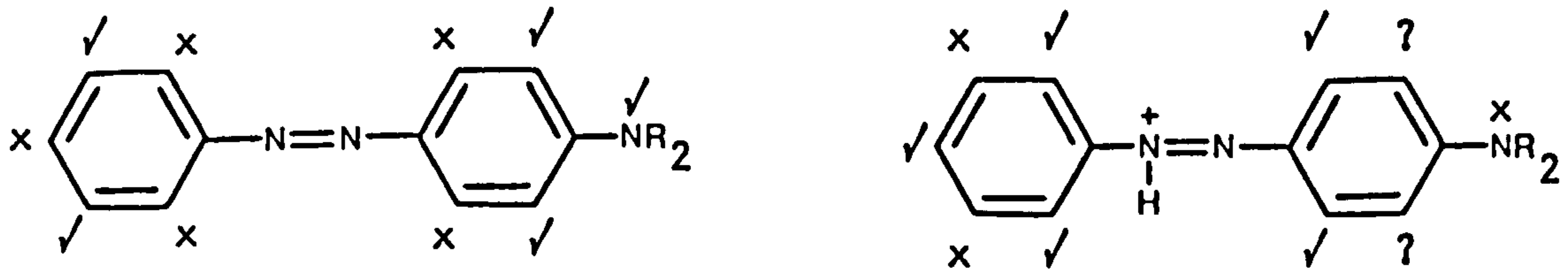


(56)

X = CH, λ_{max} = 408 nm; X = N, o: λ_{max} = 432 nm
m: λ_{max} = 428 nm
p: λ_{max} = 444 nm (solvent ethanol)

to the parent compound (X=CH); in fact, all three isomers produce bathochromic shifts.

The azonium tautomers, because of the delocalised positive charge, have somewhat greater bond uniformity compared with their neutral counterparts, so that Dewar's rules should become more applicable. Nevertheless, it is apparent that the rules fail as often as they succeed for monoazo dyes (Fig. 1.6).[73] A further drawback is that the rules cannot be applied to ring systems with odd numbers of atoms since the starring system breaks down in these cases.[115]



(a) (b)

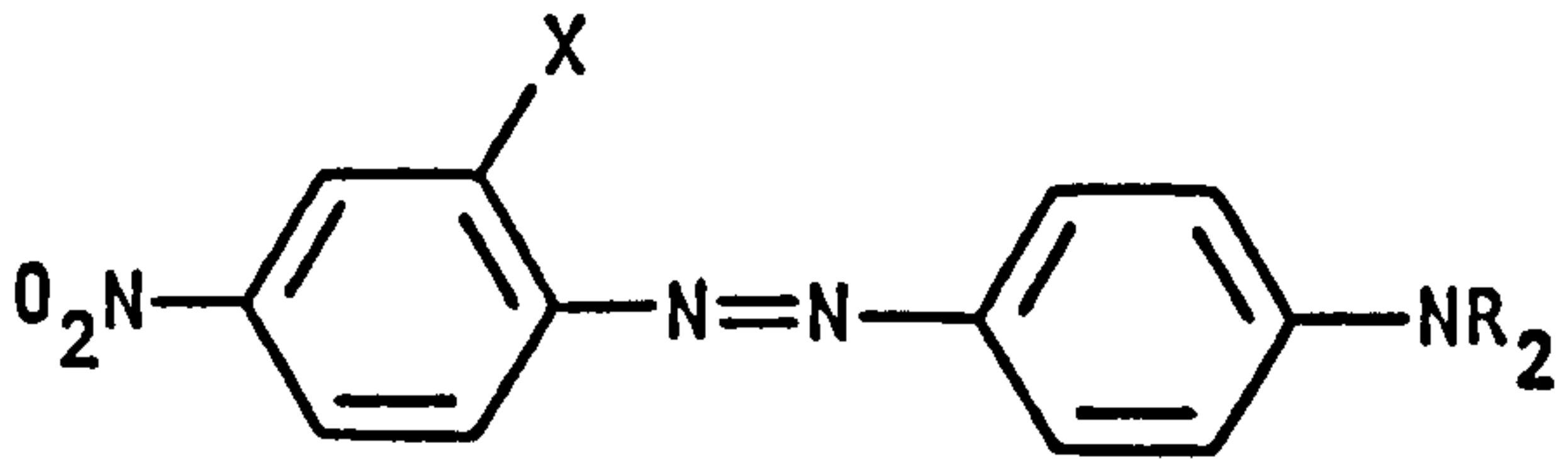
Fig. 1.6. The applicability of Dewar's rules to (a) neutral and (b) protonated 4-aminoazobenzene derivatives:

✓ indicates correct prediction of substituent effect.
x indicates incorrect prediction of substituent effect.
? indicates rigorous experimental treatment not yet attempted.

As an alternative to resonance theory and to Dewar's rules for the prediction of colour in azo dyes, and in most other systems, the PPP molecular orbital method,[116] using computers, is rapidly gaining in popularity. This approach can be used both qualitatively, to predict trends within and between series of dyes, and quantitatively, to calculate absolute absorption values, although the accuracy varies in this respect from one system to another. Notable successes using this method include the correct order of wavelengths in the three isomeric aminoazobenzenes[71] and prediction of the pronounced bathochromic shifts shown by heterocyclic azo dyes, relative to their carbocyclic analogues (see Appendix I), neither of which could be deduced from resonance theory. Table 1.14 shows recent work[117] which further illustrates the usefulness of the PPP method.

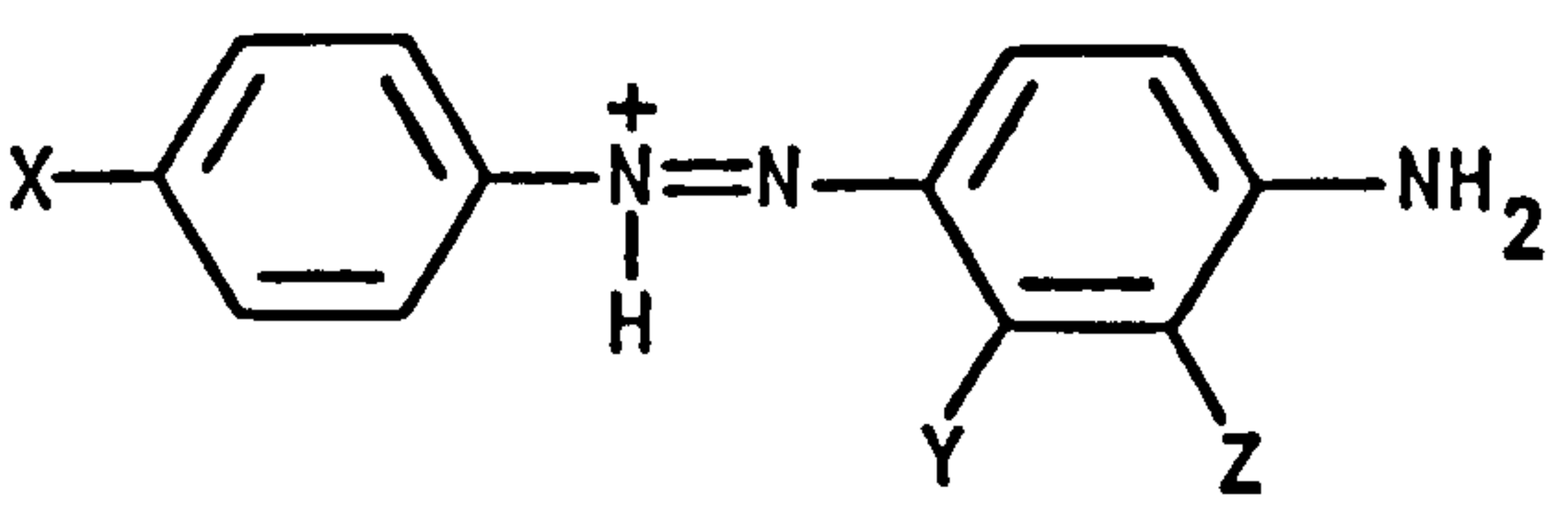
The PPP calculations are ideally suited for use with computers since they can be carried out rapidly and the required programmes are readily available. It is to be expected, therefore, that the method will be used more extensively in future routine applications to colour and constitution problems.

Table 1.14. Some Examples of Visible Absorption Spectra Calculated by the PPP Method.[117]



(57)

X	R	λ_{max}/nm (Cyclohexane)	λ_{max}/nm (Calculated)	Comments
H	H	-	410	Unexpected batho.shift predicted
OMe	H	-	423	
H	Et	456	-	Batho.shift observed
OMe	Et	463	-	



(58)

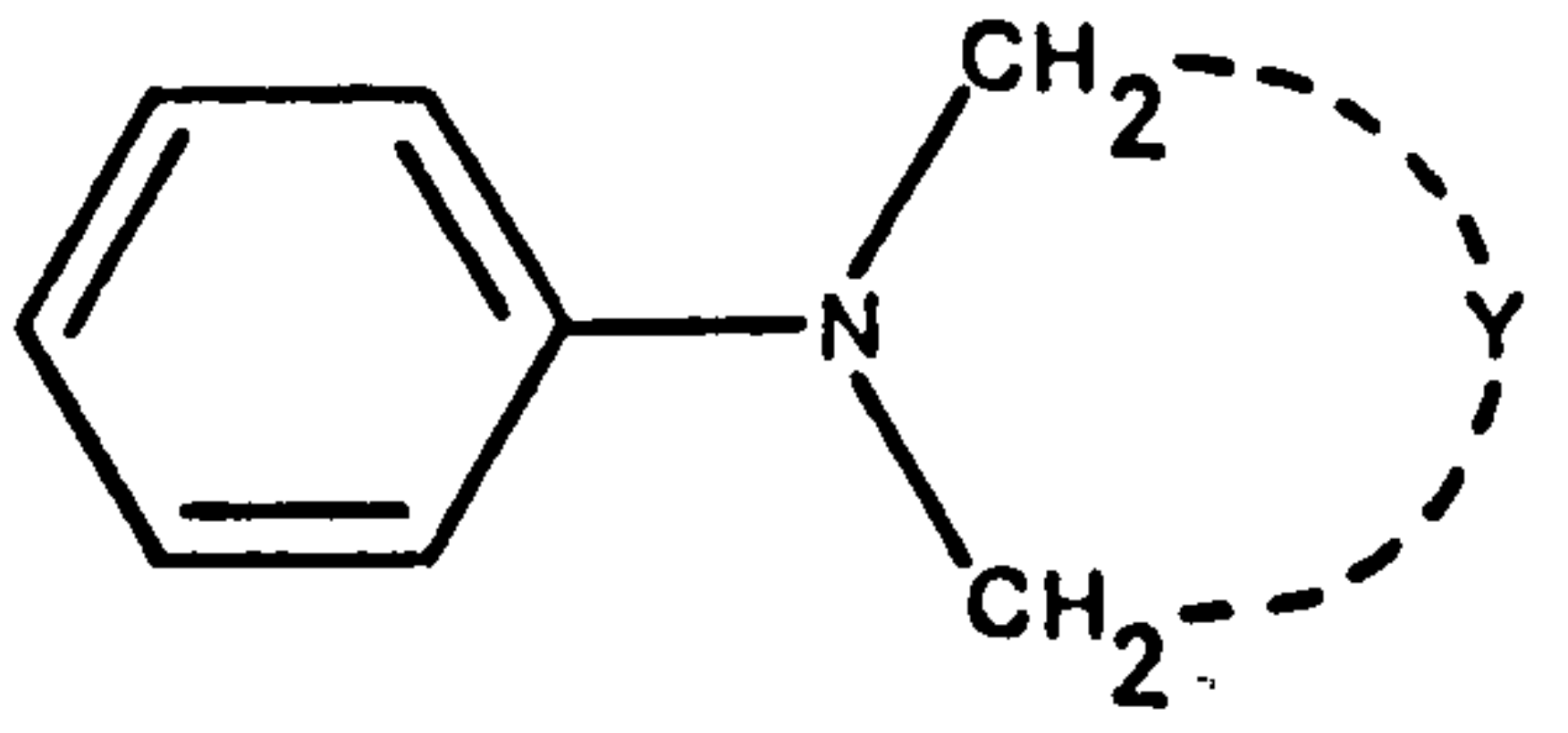
	X	Y	Z	λ_{max}/nm (EtOH/HCl)[a]	λ_{max}/nm (Calculated)	Comments
	H	H	H	497	469	Predicts the observed unexpectedly small difference
(A)	NO_2	H	H	507	468	
	NO_2	OMe	H	471	456	Predicts hypso.shift relative to (A)
	NO_2	H	OMe	509	495	Predicts batho.shift relative to (A)
	NO_2	CN	H	529	490	Predicts batho.shift relative to (A)
	NO_2	H	NO_2	510	481	Predicts batho.shift relative to (A)

[a] Should strictly be a non-polar solvent

2. DISCUSSION OF RESULTS

2.1. Coupling Components

The coupling components used in the synthesis of the azo dyes were all tertiary aromatic amines, of general structure (59), in which the nitrogen atom forms part of a saturated ring system. Details are given below:



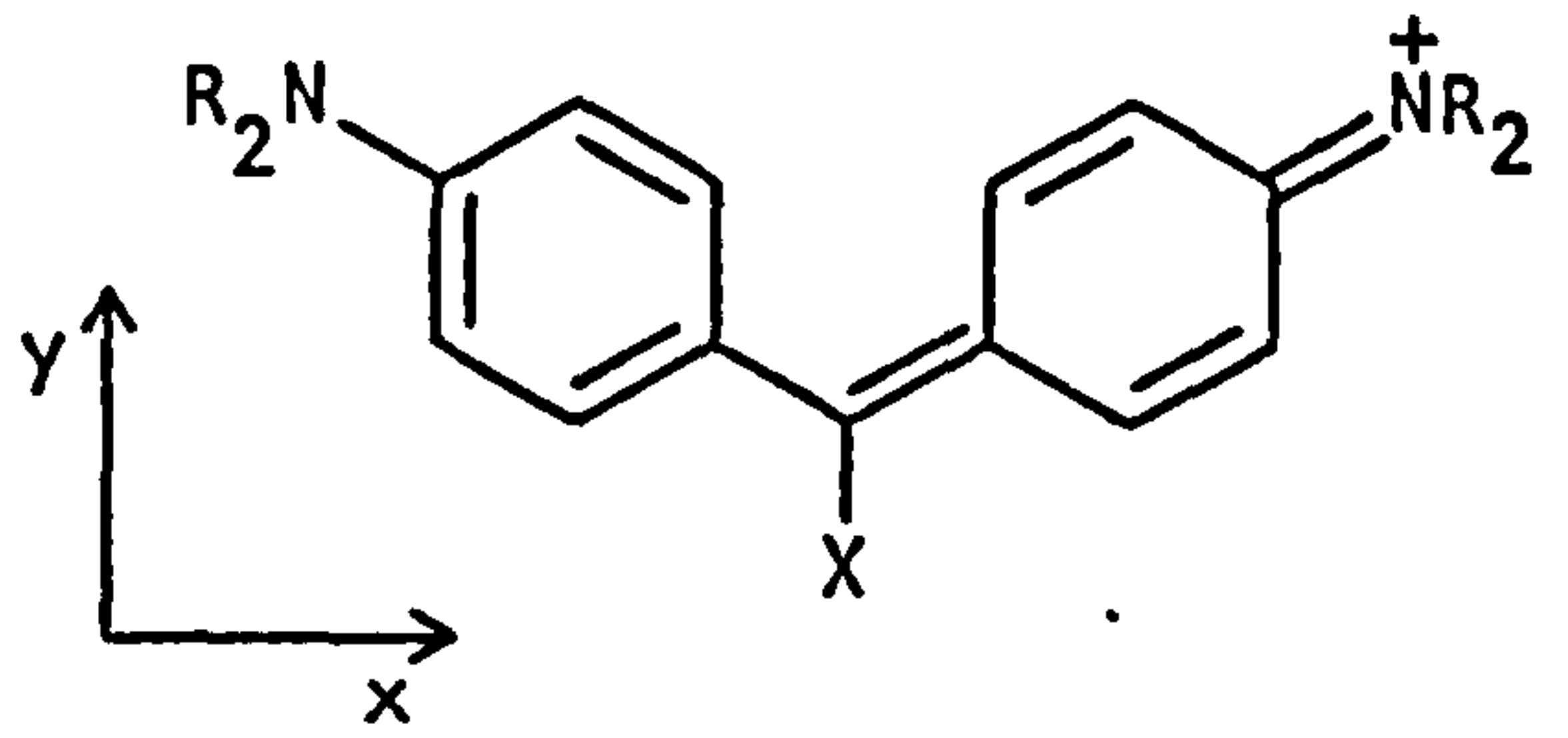
(59)

Y	Coupling Component
$-CH_2CH_2-$	N-Phenylpyrrolidine (59a)
$-CH_2CH_2CH_2-$	N-Phenylpiperidine(59b)
$-CH_2OCH_2-$	N-Phenylmorpholine(59c)
$-CH_2SCH_2-$	N-Phenylthiomorpholine(59d)
$-CH_2SO_2CH_2-$	N-Phenylthiomorpholine-1,1-dioxide(59e)
$-CH_2N(Et)CH_2-$	N-Phenyl-N'-ethylpiperazine(59f)
$-CH_2N(Me)CH_2-$	N-Phenyl-N'-methylpiperazine (59g)
$-CH_2N(Ac)CH_2-$	N-Phenyl-N'-acetylpiperazine(59h)

2.2. Electronic Absorption Spectra of Some Related Di- and Tri-Phenylmethane Dyes.

Several di- and tri-phenylmethane dyes derived from some of the coupling components used in the present work have been synthesised previously; the spectral characteristics of these dyes are shown in Table 2.1. On the basis that improved conjugation of the terminal

Table 2.1. Visible Spectra of Some Di- and Tri-phenylmethane Dyes.



60; X = Ph

61; X = $PhNR_2$

62; X = H

	98% Acetic Acid				10% Acetic Acid			
	x-band		y-band		x-band		y-band	
Type	λ_{max} /nm	$10^{-4}\varepsilon$	λ_{max} /nm	$10^{-4}\varepsilon$	λ_{max} /nm	$10^{-4}\varepsilon$	λ_{max} /nm	$10^{-4}\varepsilon$
60;Malachite Green[a]	621	10.4	427.5	2.0				
60;Brilliant Green[a]	629.5	11.9	430	1.8				
60;Pyrrolidine Green[b]	629	11.1	426	1.7				
60;Piperidine Green[b]	634	10.4	431	1.7				
60;Morpholine Green[c]	623	9.0	433	1.9				
61;Crystal Violet[a]	589	11.6			-	-	∿425	0.3
61;Ethyl Violet[a]	592.5	13.0			641	7.2	426	1.2
61;Pyrrolidine Violet[b]	591	12.1			-	-	-	-
61;Piperidine Violet[b]	602	11.5			643	5.1	426	1.6
61;Morpholine Violet[c]	596	10.6			-	-	-	-
62;Michler's Hydrol Blue[a]	607.5	14.75						
62;Diethyl Analogue[a]	613	17.6						
62;Pyrrolidine Analogue[b]	613	15.7						
62;Piperidine Analogue[b]	619	0.23						
62;Morpholine Analogue[c]	615	1.91						

[a] Ref. 118 [b] Ref. 119 [c] Ref. 120

nitrogen lone pair of electrons leads to bathochromic shifts of the longest wavelength absorption band (x-band) of these types of dye,[118] and by considering only the inductive (+I) effect of the alkyl groups attached to the terminal nitrogen atom, one might expect similar λ_{max} values (x-band) for the diethyl and pyrrolidine types; the piperidine analogues should absorb at slightly longer wavelengths. This order is indeed shown experimentally and suggests that the electron donor character of the piperidine ring is greater than that of the pyrrolidine ring. However, the piperidine analogue of Michler's Hydrol Blue, unlike the corresponding pyrrolidine compound, exhibits an extremely low extinction coefficient, thereby indicating that the solution equilibrium between hydrol and dye cation is heavily in favour of the former species, presumably because the conjugation of the nitrogen lone pair in this system is insufficient to stabilise the initially formed cation. Additionally, the ease of protonation of the piperidino- group is apparent from the readiness with which Piperidine Violet reverts to a Piperidine Green type in 10% acetic acid; Pyrrolidine Violet shows no such tendency.

In view of this conflicting evidence, it is therefore of interest to examine the spectral characteristics of some corresponding azo dyes.

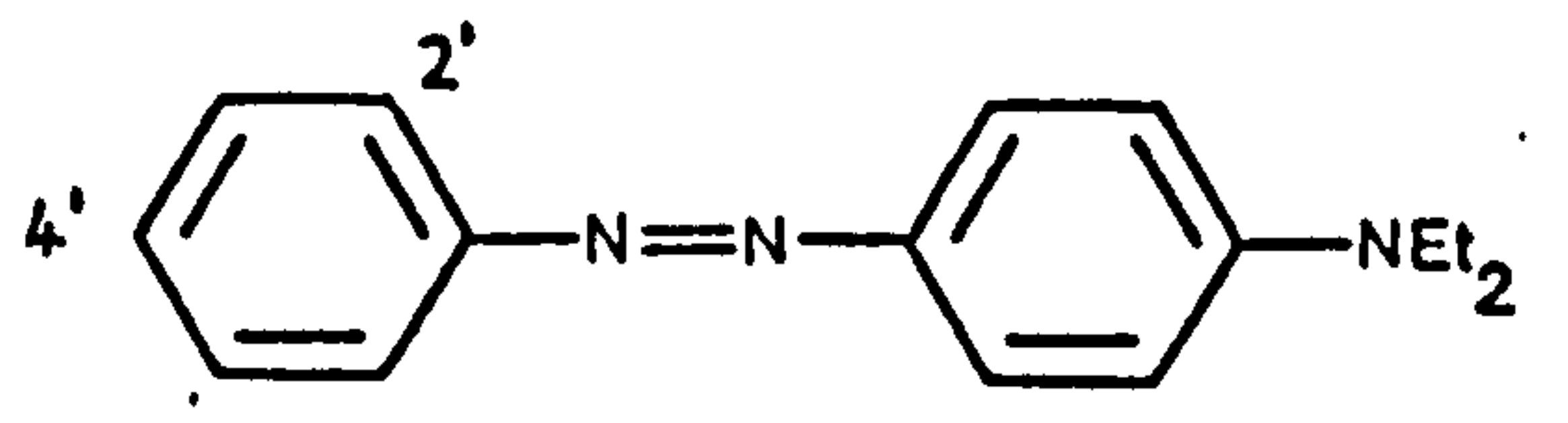
2.3. Electronic Absorption Spectra of the Various Azo Dyes

Spectral data for each series of dyes are given in Tables 2.5-2.12, obtained from solutions of the dyes in cyclohexane, ethanol and ethanolic hydrogen chloride.

2.3.1. Neutral Solution

It is clear from Tables 2.5 and 2.6 that dyes derived from N-phenylpyrrolidine are more bathochromic than their counterparts obtained from N-phenylpiperidine, in contrast to the behaviour of the corresponding di- and tri-phenylmethane dyes. Comparison with the λ_{max} values of some 4-NN-dimethylamino- and 4-NN-diethylaminoazobenzenes (Tables 1.3 and 2.2, respectively) indicate that the electron donor power decreases in the order pyrrolidino $\sim$ NN-diethylamino > NN-dimethylamino > piperidino; this overall trend is supported by other experimental data (Table 2.3). Thus, the ^{13}C-n.m.r. spectra of N-phenylpyrrolidine and NN-diethylaniline are very similar, whereas the ortho- and para-carbon shieldings reflect the decreased phenyl ring-nitrogen resonance interaction in the case of N-phenylpiperidine.[122] The exaltation of molar refraction (ΔR_D) is the difference between calculated and experimental values and can be used as a qualitative measure of resonance energy.[123] The ΔR_D values for a series of aromatic amines have been observed to increase with increasing phenyl ring-nitrogen interaction,[124] and in fact do so for the series under discussion. It is interesting to note that this parameter suggests rather more effective conjugation by the pyrrolidino group than the NN-diethylamino group, and is supported by the results of ^{1}H-n.m.r. studies in the present work and elsewhere[125-8] (see Section 2.5) and also by the dipole moment values of a series of 4-pyrrolidino- and 4-NN-diethylaminoazobenzenes.[89] Curiously, this situation is not clearly reflected in the λ_{max} value of the dyes, which are very similar in both non-polar and polar solvents; the pyrrolidinoazo dyes absorb almost identically to their NN-diethylamino counterparts in cyclohexane, but are slightly hypsochromic in ethanol. It may be that the ground state of the pyrrolidine dyes is more stable than that of the NN-diethylamino types due to hybridisation differences at the terminal nitrogen atom; this would help to explain the aforementioned

Table 2.2. Visible Spectra of Some Derivatives of 4-NN-Diethylaminoazobenzene.[a]



(30)

Substituent	λ_{max}/nm	$10^{-4}\varepsilon$	λ_{max}/nm	$10^{-4}\varepsilon$	λ_{max}/nm	$10^{-4}\varepsilon$
	(Methanol)		(Cyclohexane)		(Hexane)	
4'-OMe	414	3.24	407[c]	—	404	3.63
4'-Me	416	3.16	407[d]	33.4[d]	403	3.39
4'-H	416	2.88	408[d]	32.3[d]	404	3.39
4'-Cl	425	3.16	416[d]	34.0[d]	413	3.55
4'-Br	427	3.31	418[c]	—	415	3.98
4'-CF_3	434[c]	—	425[c]	—	421[c]	—
4'-Ac	462[b]	2.82[c]	435[c]	—	431[c]	—
4'-CN	466[b]	3.24[c]	438[c]	—	436[c]	—
4'-NO_2	489	3.98	458[c]	—	453	3.80
2'-CN,4'-NO_2	536[c]	—	502[c]	—	-	—

[a] Ref. 121 unless otherwise stated

[b] Ref. 54

[c] Authors data

[d] Ref. 89

Table 2.3. Physical Data of Some Coupling Components.

Compound	^{13}C Chemical Shift (p.p.m. w.r.t. benzene)[a] C_1	C_{ortho}	C_{meta}	C_{para}	ΔR_D[b]	pK_a[c,d]
N-Phenylpyrrolidine	-20.3	15.5	-1.6	12.3	1.64	3.71
NN-Diethylaniline	-19.9	15.3	-1.4	12.2	1.58	5.71
NN-Dimethylaniline	-22.6	15.6	-1.0	11.5	1.49	4.22
N-Phenylpiperidine	-24.7	10.9	-1.6	8.7	0.96	4.60

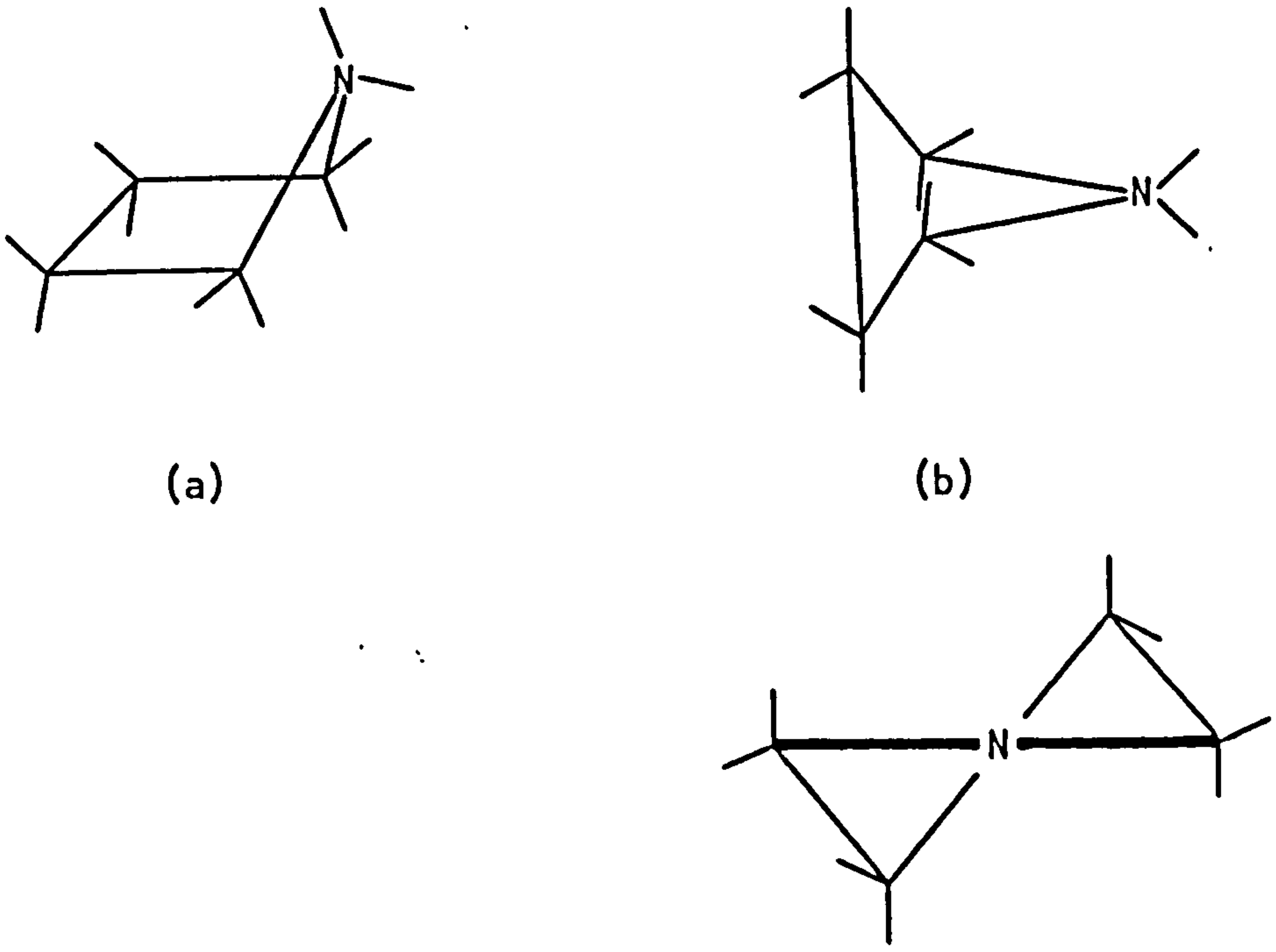
[a] Ref. 122 [b] Ref. 123 [c] 50% Aqueous ethanol at 20°C, ref. 129

[d] Other workers [123-5,129] have observed similar trends.

ground state data. Additionally, any stabilisation of the pyrrolidinoazo excited state due to increased conjugation of the lone pair may be offset by the increase in energy associated with the eclipsed protons of the five membered ring (see below).

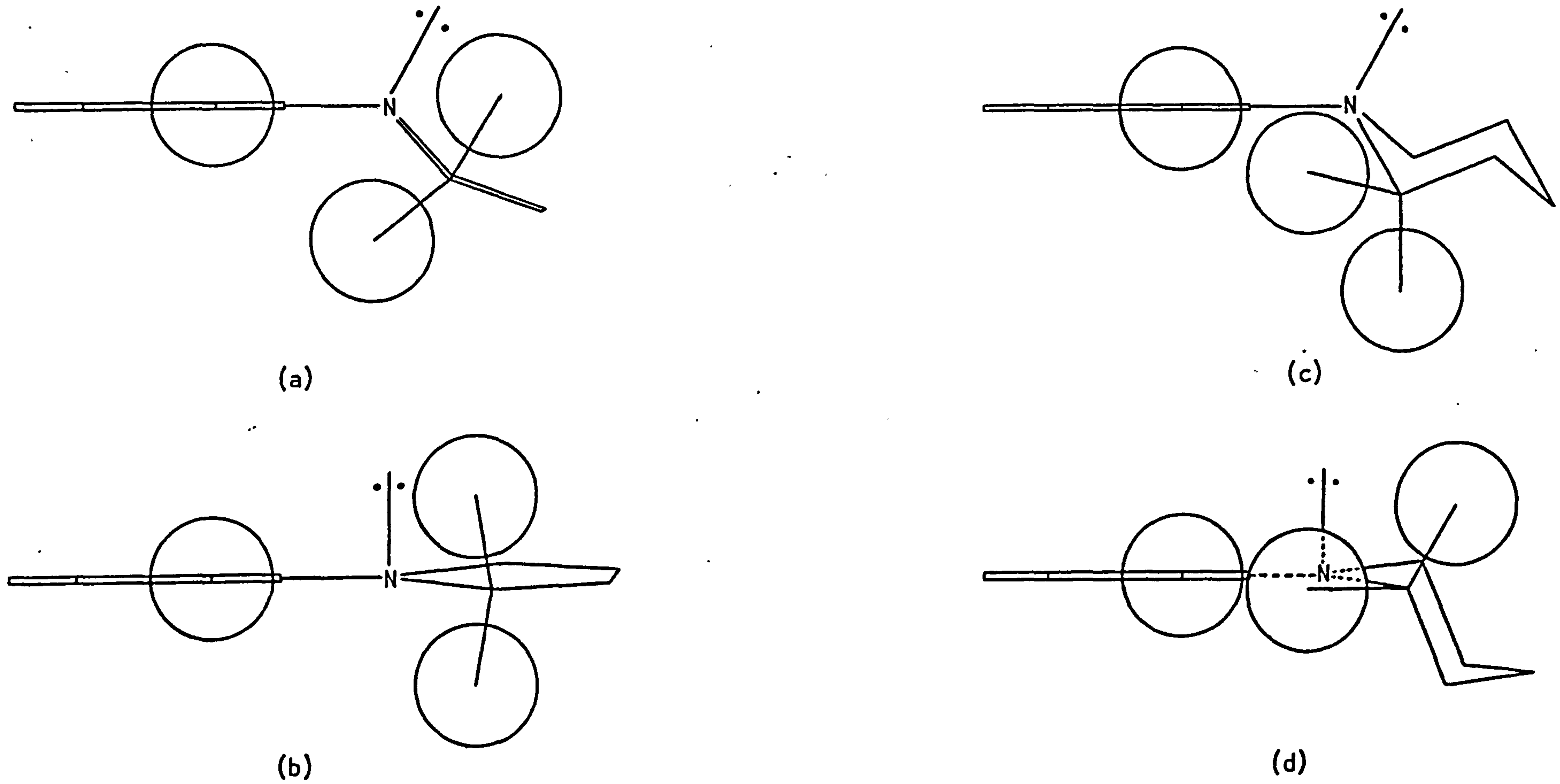
Measurements of pK_a also confirm the order of conjugation, with the exception of NN-diethylaniline, the anomalous high value of which has been attributed to the loss of solvation owing to the congested situation obtaining in the vicinity of the nitrogen atom, which destabilises the base relative to the ammonium ion.[122]

The relative donating capacity of the pyrrolidino group compared with that of the piperidino group can be accounted for in terms of steric effects.[129,130] By analogy with cyclopentane,[131-3] the pyrrolidine ring can be regarded as a pentagon which is somewhat distorted from planarity by puckering of the ring in order to reduce the torsional strain experienced by the eclipsed protons. Such distortion leads to the envelope (C_S) conformation[133] [Fig. 2.0(a)], in which a single atom is out of the plane containing the other four, and the half-chair (C_2) conformation[133,134] [Fig. 2.0(b)], where three adjacent atoms are in one plane, with the other two twisted such that one is as much above the plane as the other is below. Pseudorotation[131] causes these departures from planarity to be averaged around the ring, as the molecule passes through its various possible forms, giving internal bond angles approaching 109.5°; thus, the terminal nitrogen atom can be accommodated in an sp^3 arrangement with negligible angle strain. Mesomeric interaction with the phenyl ring will, however, increase the sp^2 character of the atom (and consequently the p character of the orbital containing the lone pair of electrons) and will also obviate any steric crowding between the *ortho* protons of the phenyl ring and the α-methylene protons of the five-membered ring [Fig. 2.1(a)], particularly in the excited state



(a) (b)

Fig. 2.0. Typical envelope (a) and half-chair (b) forms for a five membered ring.



(a)

(b)

(c)

(d)

Fig. 2.1. The relative spatial arrangement of ortho-phenyl and α-methylene protons in N-phenylpyrrolidine (envelope form): (a) ground state, (b) excited state, and in N-phenylpiperidine: (c) ground state, (d) excited state.

[Fig. 2.1.(b)]. Unfortunately, this interaction also causes the pyrrolidine ring protons to become more eclipsed. Thus, a balance must be achieved between steric and mesomeric interactions.

The piperidine ring will adopt a chair conformation in order to reduce angle strain, resulting in bond angles of 109.5°, ideal for an sp^3-hybridised nitrogen atom; conjugation with the phenyl ring will again confer sp^2 character. However, molecular models (Dreiding) show that the equatorial protons of the α-methylene groups in the six-membered ring are directed towards the ortho-protons of the phenyl ring [Fig. 2.1(c)] giving rise to a steric clash much greater than that caused by the pyrrolidine ring protons, and which is even more accentuated in the excited state [Fig. 2.1.(d)] when the protons in question are actually in the same plane. Rotation about the C_{ar}-N bond to reduce this crowding will remove the nitrogen lone pair electrons from the optimum position of overlap with the aromatic π-electron cloud (Fig. 2.2; $\theta=0^o$) to a position of reduced overlap (Fig. 2.2; $\theta>0^o$). This rotation will increase the sp^3 character of the nitrogen atom, causing a hypsochromic shift of λ_{max}. The angle of twist (θ) can be estimated by using the simple empirical relationship[135,136]

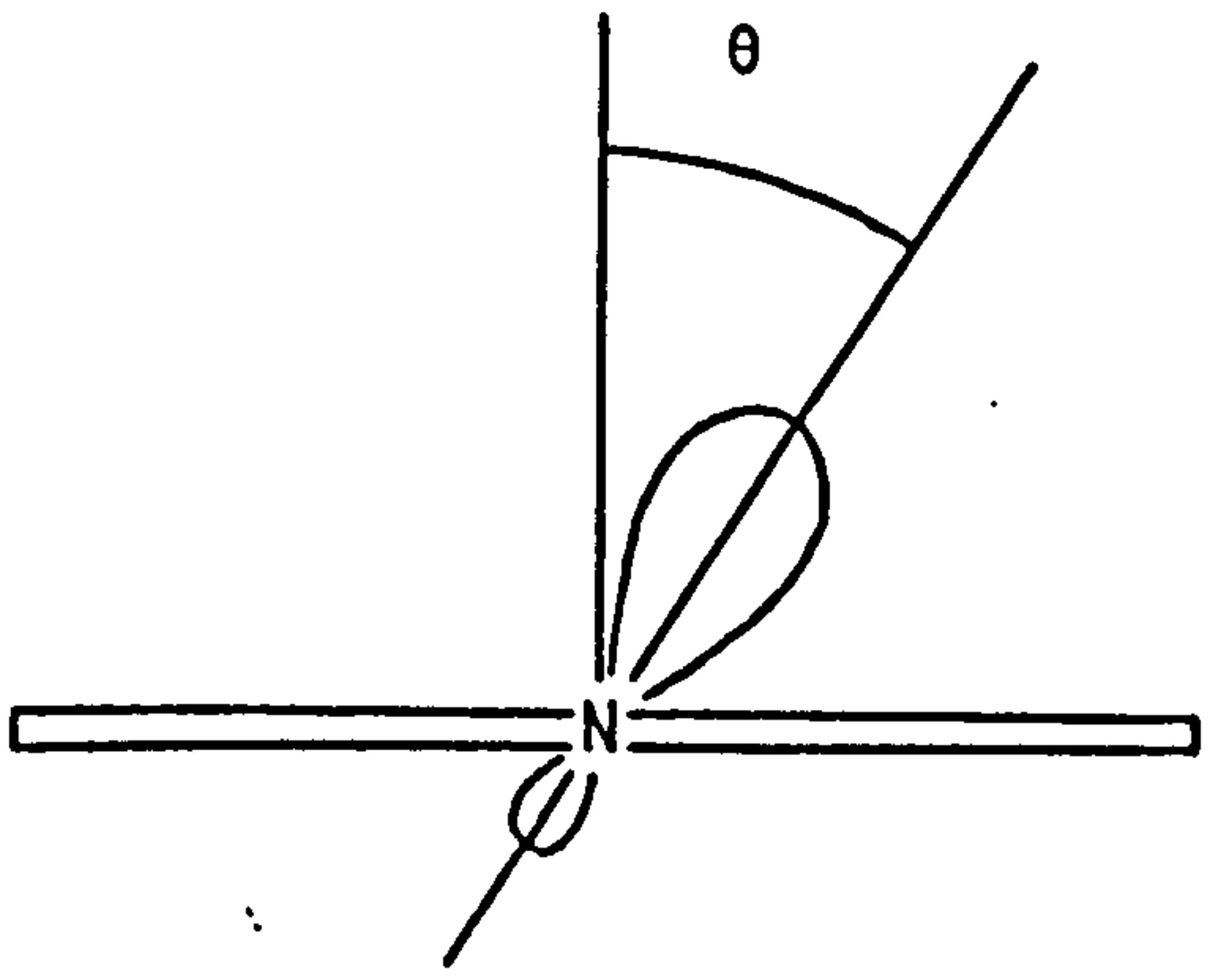
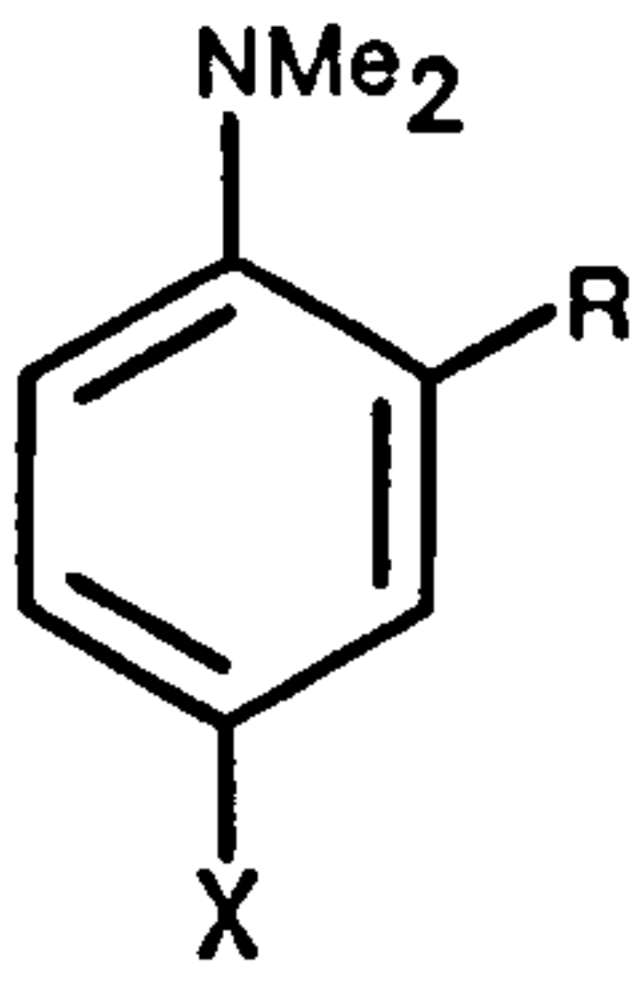


Fig. 2.2. Angle of Twist of the Nitrogen Lone Pair Orbital.

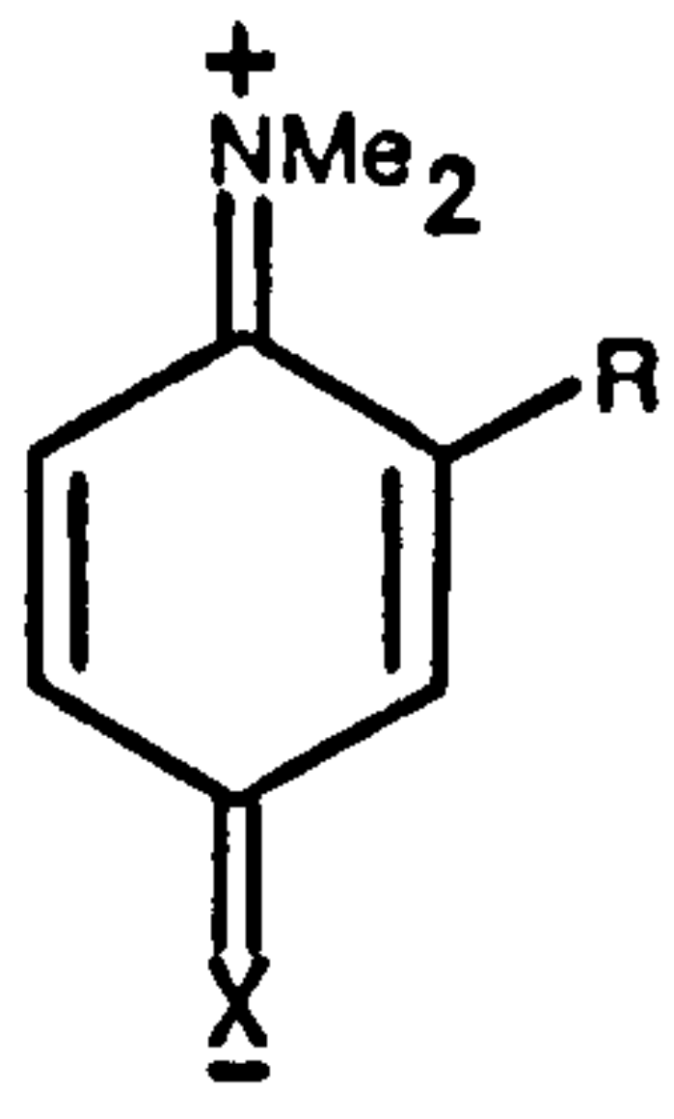
$$\varepsilon/\varepsilon_o = \cos^2\theta$$

where ε and ε_o are the molecular extinction coefficients of the non-planar molecule and the appropriate planar molecule, respectively.

Values of θ can be used as a test for the presence of electronic buttressing[137] in 4-aminoazobenzene-type systems.[138] This phenomenon arises from the conjugative interaction between a mesomeric donor group (e.g. amino) and an electron withdrawing group attached to the same aromatic ring. Thus, for example, the para-substituted aniline derivative (63) may be regarded as a resonance hybrid of the extreme canonicals (63a) and (63b), with the C_{ar}-N bond thus gaining partial double bond character.



(63a)



(63b)

Bulky substituents (R) tend to enforce rotation of the amino group, but this occurs less readily as the double bond character of the C_{ar}-N bond increases, i.e. as the electron withdrawing strength of the substituent X increases, and consequently values of θ should decrease. This resistance to sterically induced rotation by electron withdrawing groups is termed electronic buttressing.

Calculated θ values for some representative piperidinoazo derivatives are given in Table 2.4 (the ε_o values used are those of the pyrrolidino analogues). In this case, the steric interaction is between the ortho-phenyl and the α-methylene protons, rather than with a bulky group R, but similar arguments apply. In accordance with earlier findings,[138] θ does not decrease as the electron withdrawing strength of X in the azobenzene types (64) increases, indicating that the substituent is too far removed from the amino group to exert any significant buttressing effect. The phenylazo group itself does exert an appreciable buttressing effect, however,

Table 2.4. Comparison of the Estimated Angles of Twist, θ,[a] of Some Piperidinoazo Dyes (64-67; Y = $-CH_2CH_2CH_2-$).[b]

Substituent	θ/°	Δλ/nm[c]
64;4'-Me	25	14
64;4'-H	21	13
64;4'-CF_3	22	11
64;4'-NO_2	26	18
64;2'-CN,4'-NO_2	22	7
65;6'-OEt	20	5
65;6'-H	15	4
65;6'-SO_2Me	11	2
65;6'-NO_2	9.5	2
66;5'-H	22	6
66;5'-NO_2	10.5	2
67;3'-NO_2,5'-Ac	9.5	3

[a] See Fig. 2.2

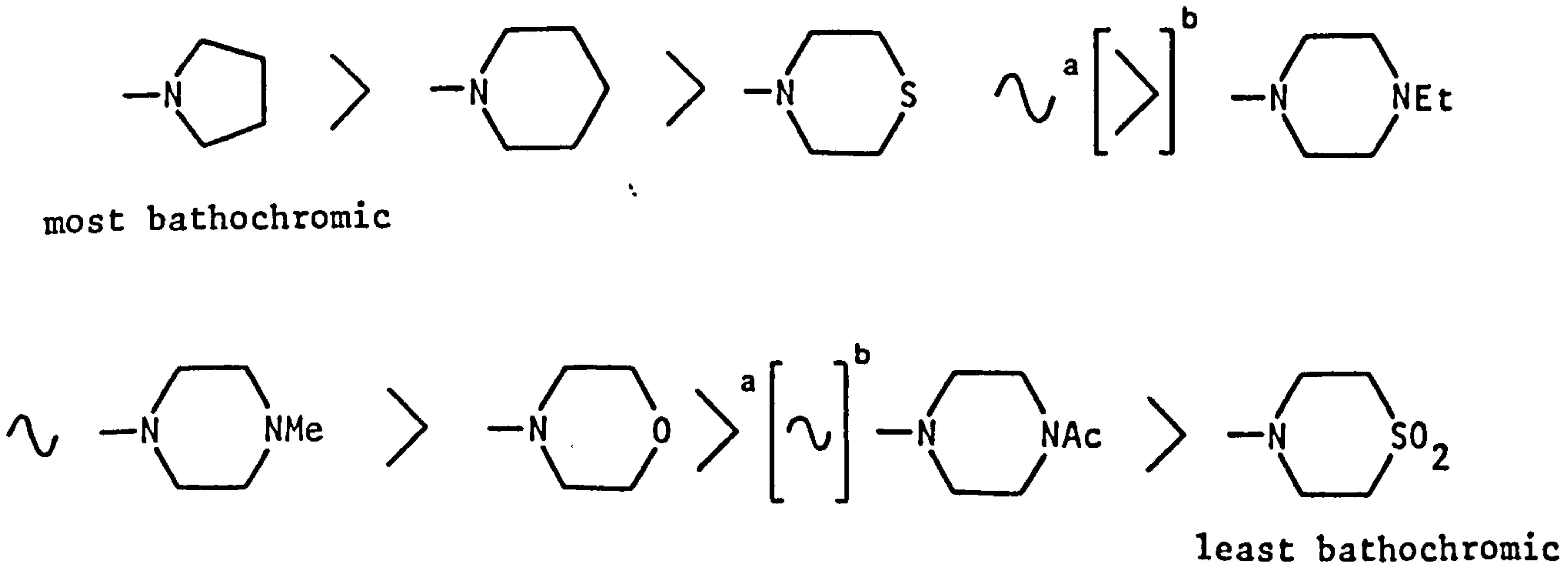
[b] Solvent ethanol

[c] λ_{max}(pyrrolidino)-λ_{max}(piperidino)

since ultraviolet spectroscopic data for the parent amine, N-phenylpiperidine, give a value of $\theta \sim 45^\circ$ (in methanol)[125] whereas in the case of the phenylazo analogues, θ falls within the range 15-25° (in ethanol). In the 4'-phenylazo types, Δλ increases as the electron withdrawing power of X increases, in accordance with simple perturbation theory.[139]

In contrast to their benzene analogues, the values of the heterocyclic piperidinoazo dyes (65)-(67) suggest that the electronic buttressing effect is present in these compounds. Strongly electron withdrawing groups in the latter systems give rise to θ values of about 8-10°, significantly less than in the corresponding azobenzenes. The improved conjugation in these types is reflected not only in their intensity values, but also in their wavelength maxima, which are almost as bathochromic as their pyrrolidino counterparts. However, the hypsochromic effects caused by partial deconjugation of the lone pair are not completely overcome; if this were indeed the case, the increased +I effect of the five methylene groups in the piperidine ring would result in these dyes absorbing at somewhat longer wavelengths than their pyrrolidino analogues.

In the remaining six-membered ring systems, the -I effect of the heteroatom in the γ-position reduces lone-pair conjugation still further, resulting in hypsochromic shifts of the visible absorption band, the magnitude of which increases as the strength of the inductive effect increases. The following overall order of electron donor strength is observed:

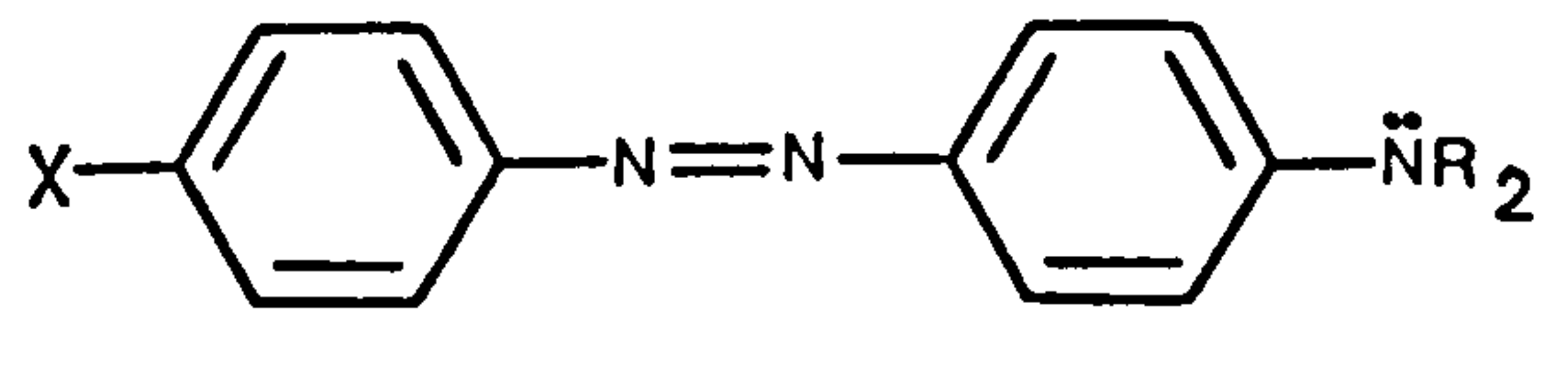


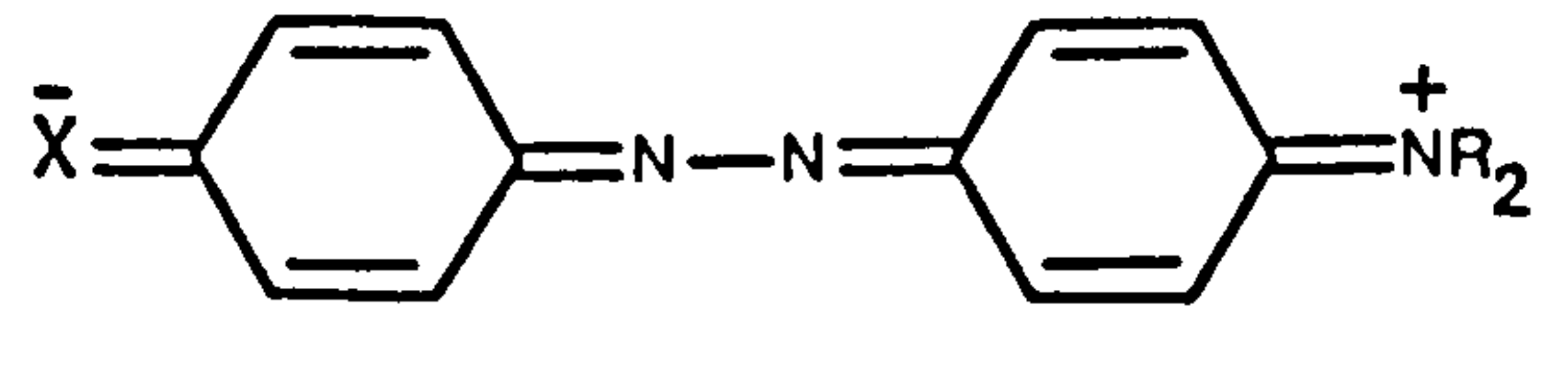
[a] in cyclohexane

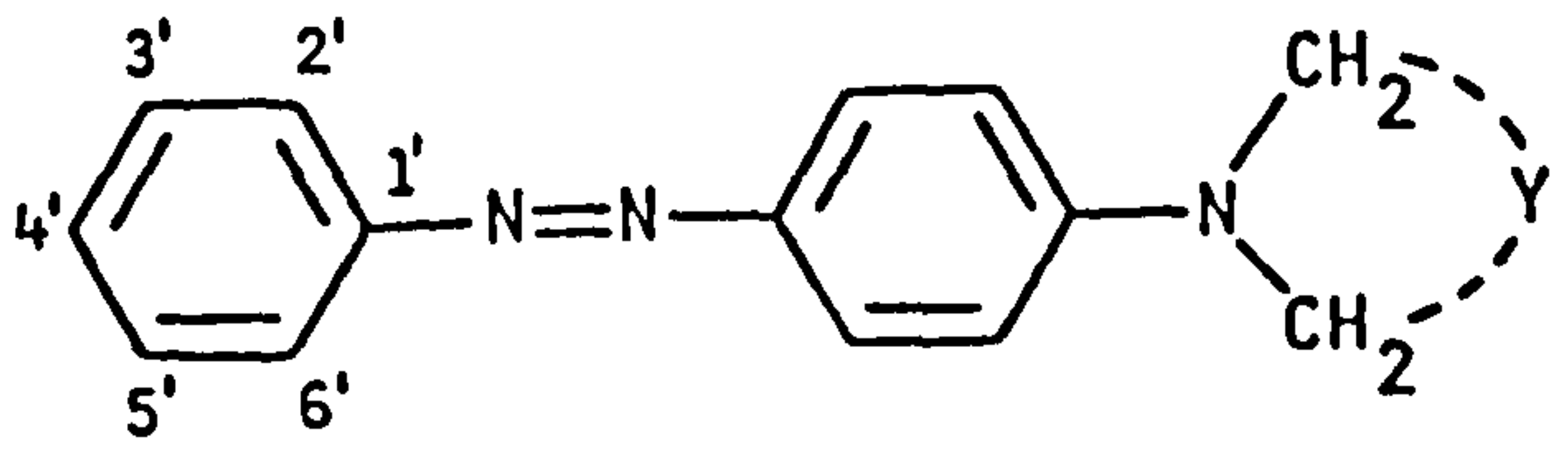
[b] in ethanol

The wavelength range (in ethanol) along this sequence varies from 37 nm for the parent azo dyes to 66 nm for the 4'-nitro derivatives, thereby illustrating the combined effect of steric and inductive forces. These factors are emphasised by comparison with other systems. In particular, it is found that the hypsochromic effect of the morpholino group is considerably greater than that of the *NN*-bis-β-hydroxyethyl group and virtually as great as that of the *NN*-bis-β-cyanoethyl group (*cf*. Table 1.4). The hypsochromic shifts observed along the series are accompanied by gradual decreases in the intensity of absorption.

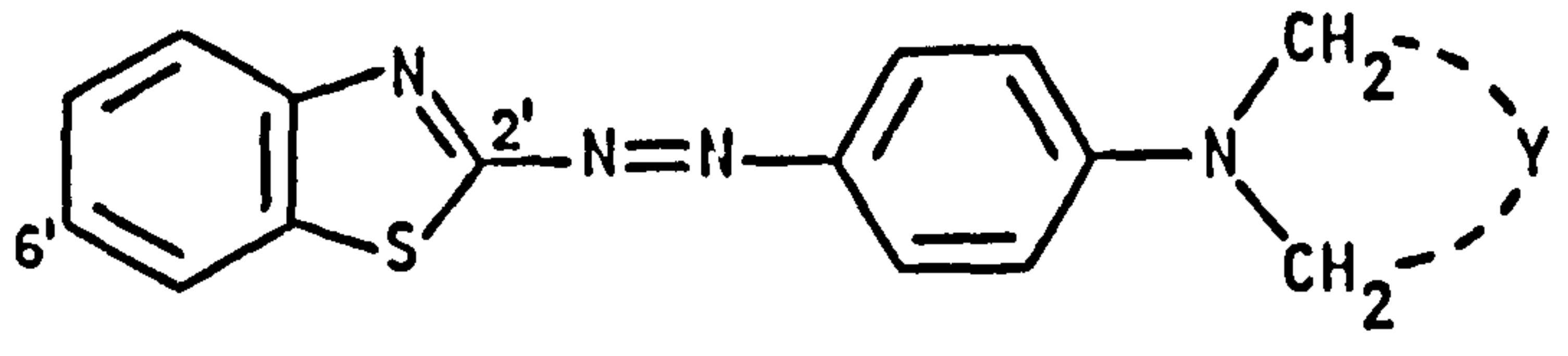
The terminal amino substituents have a somewhat variable effect on the positive solvatochromism of the azo dyes. The piperidinoazo derivatives are less sensitive to the change of solvent than are the more polar pyrrolidinoazo compounds, which is to be expected since in the latter case stabilisation of the excited state (71b) of the molecule, on changing from a non-polar to a polar solvent, will be greater. However, the anticipated relationship between solvatochromic sensitivity and wavelength shift across the series does not entirely hold when a heteroatom is present. This finding may be linked to the hydrogen bonding capacity of the atom or group; for instance, the *N*'-acetyl-*N*-phenylpiperazine dyes (64; Y = $-CH_2-N(Ac)CH_2-$) show greater solvatochromism than the more bathochromic *N*'-ethyl-*N*-phenylpiperazine dyes (64; Y = $-CH_2N(Et)CH_2-$), possibly due to the extra stabilisation of the excited state by solvation at the polar acetyl group.


(71a)

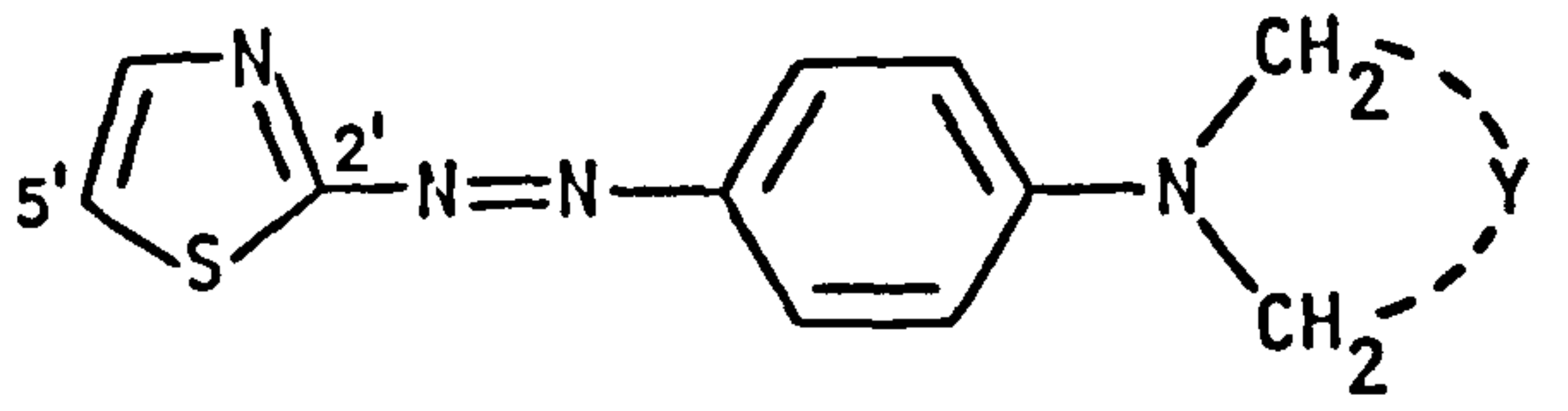

(71b)



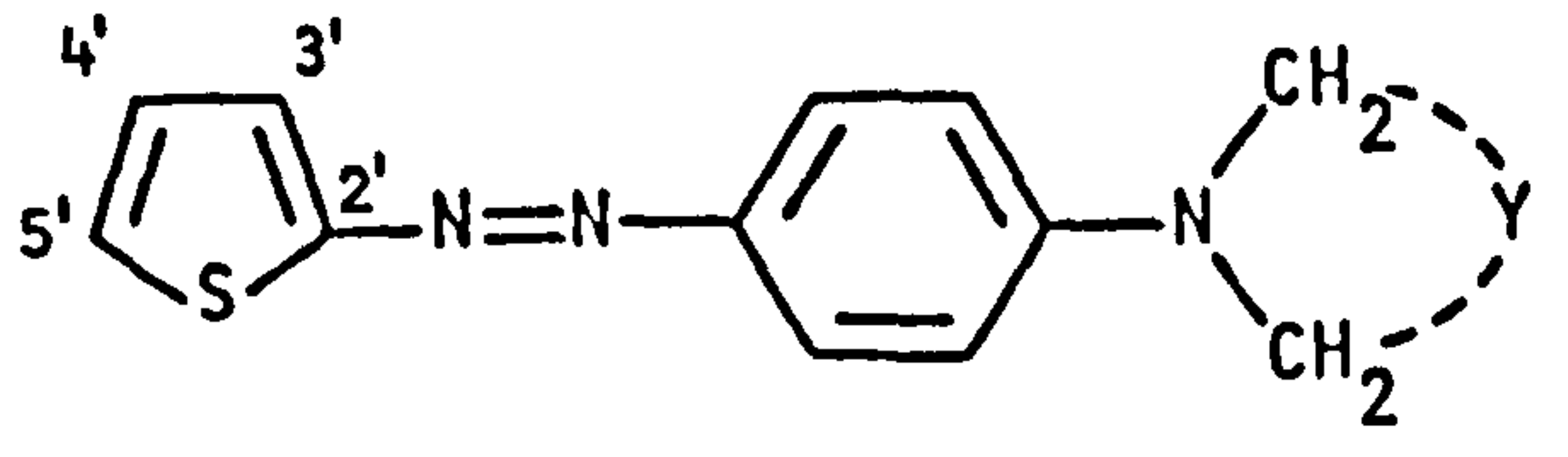
(64)



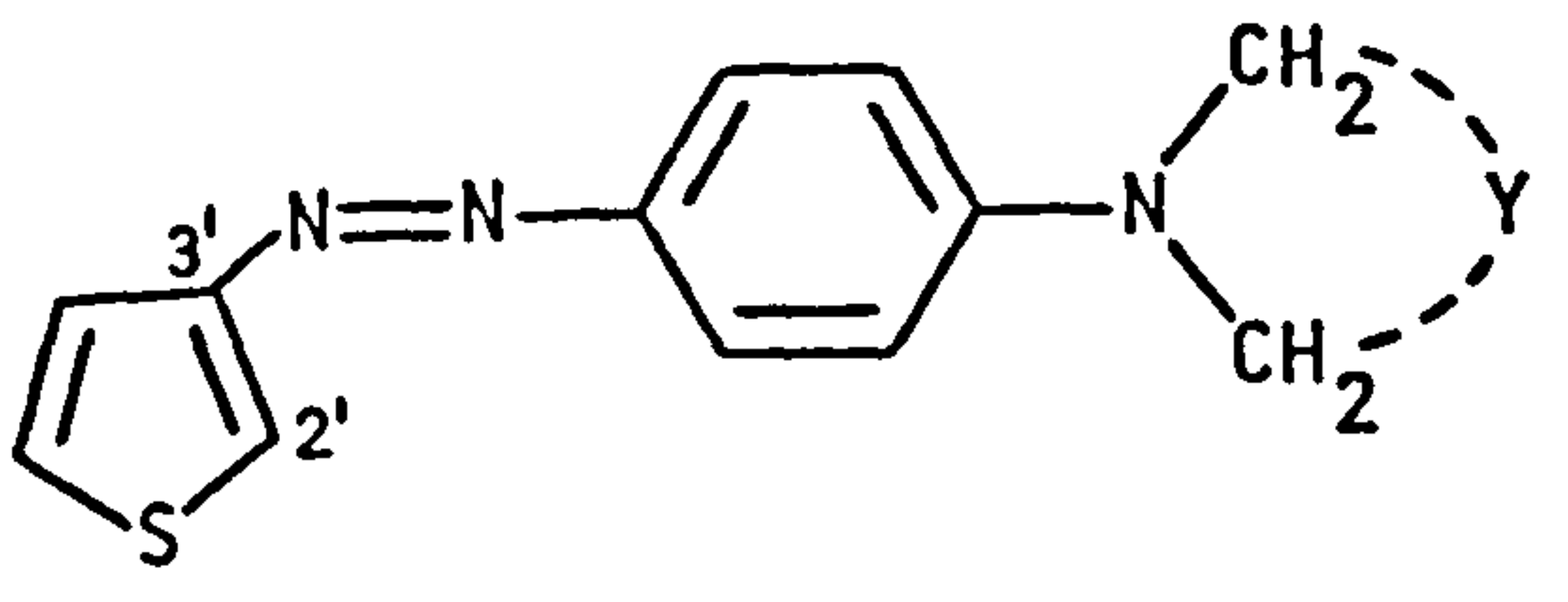
(65)



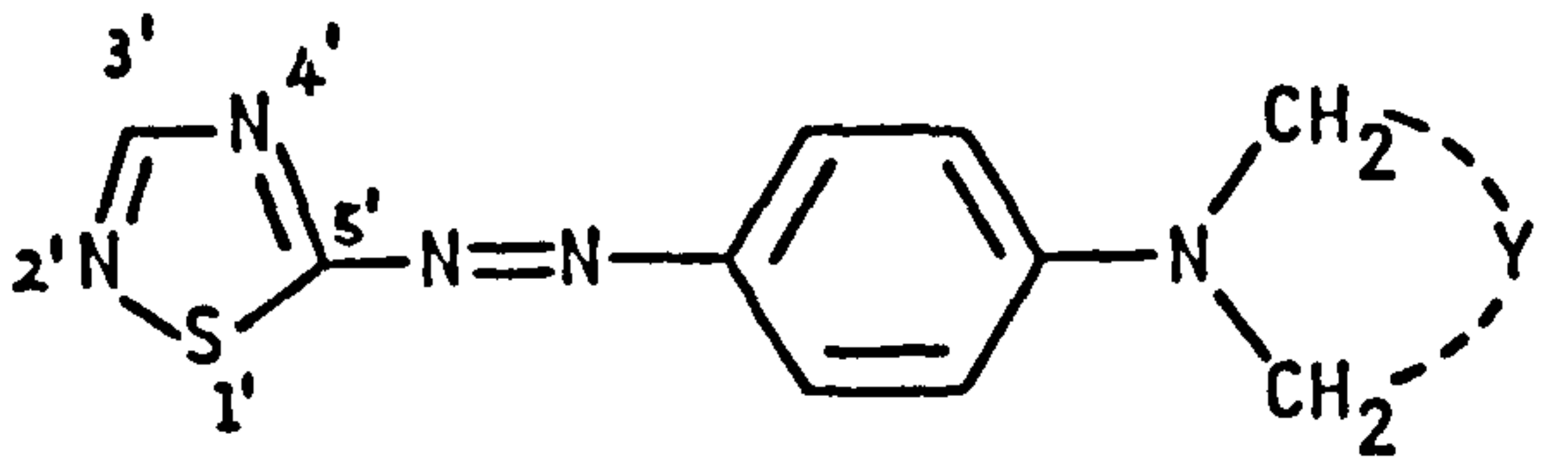
(66)



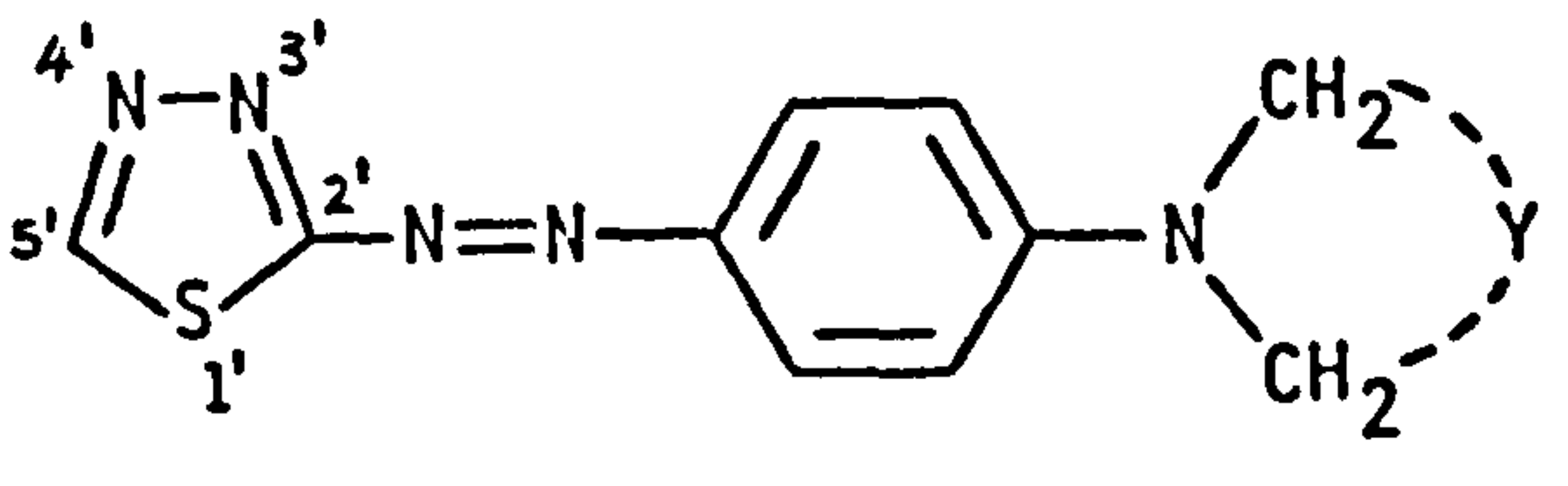
(67)



(68)



(69)



(70)

Scheme 2.1. Types of dye prepared.

Table 2.5. Visible Spectra of Some Dyes Derived from N-Phenylpyrrolidine (59; Y = $-CH_2CH_2-$).

										Modified Values^d	
Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm^a	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm^b	$10^{-3}E^c$	λ_{max}/nm	$\Delta\lambda$/nm^b
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	407	3.44	4	411	2.98	559	5.90	148	7	-	-
4'-Me	407	3.45	5	412	3.02	532	5.98	120	7	540	128
4'-H	407	3.48	6	413	2.86	519	5.77	106	7	530	117
4'-Cl	416	3.40	7	423	3.08	524	5.88	101	7	534	111
4'-Br	418	3.86	7	425	3.32	524	6.23	99	7	535	110
4'-CF_3	424	3.45	10	434	3.14	507	5.82	73	7	514	80
4'-Ac	434	3.75	20	454	3.25	520	6.34	66	7	531	77
4'-CN	438	3.70	22	460	3.52	512	6.19	52	7	518	58
4'-NO_2	459	3.50	29	488	3.43	512	6.82	24	7	518	30
2'-CN	438	3.32	20	458	3.08	505	3.40	47	300	-	-
2'-CN,4'-NO_2	503	4.03	33	536	4.44	498	6.47	-38	400	-	-
3',5'-$(CF_3)_2$	435	3.51	18	453	3.32	497	5.35	44	7	-	-
F_5	424	3.15	19	443	2.94	468	4.32	25	370	-	-

continued/ ....

Table 2.5., continued/ ....

Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	Modified Values[d] λ_{max}/nm	Modified Values[d] $\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(ii) Heterocyclic Dyes (65-70)											
65;6'-OEt	478	-	38	516	5.51	618	8.90	102	30	615	99
65;6'-H	471	-	43	514	5.48	600	10.45	86	26	598	84
65;6'-SO_2Me	495	-	42	537	5.66	586	7.58	49	120	580	43
65;6'-NO_2	505	-	46	551	6.48	585	7.50	34	120	580	29
66;5'-H	452	-	42	494	3.93	589	7.65	95	13	586	92
66;5'-NO_2	529	-	55	584	5.17	572	5.12	-12	1000	-	-
67;3',5'-$(CN)_2$, 4'-Me	538	-	30	568	5.79	522	3.61	-46	2000	-	-
67;3'-NO_2,5'-Ac	547	-	42	589	4.28	528	4.00	-61	2000	-	-
67;3',5'-$(NO_2)_2$	589	-	50	639	5.94	519	5.18	-120	670	-	-
68;2'-CO_2Me	430	-	20	450	2.83	525	5.17	75	10	-	-
68;2'-COMe	440	-	37	477	2.73	534	4.30	57	12	-	-
69;3'-Ph	472	-	52	524	4.86	*ca.*570?	-	*ca.*46?	-	-	-
69;3'-SMe	474	-	52	526	4.60	*ca.*560?	-	*ca.*34?	-	-	-
70;5'-SEt	467	-	47	514	5.24	582	6.36	68	240	-	-

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol
[b] Difference between wavelengths of neutral dye and azonium cation
[c] No. of equivalents of acid required to produce optimum amount of azonium ion
[d] See footnote to tables, p.78

Table 2.6. Visible Spectra of Some Dyes Derived from N-Phenylpiperidine (59;$Y{=}{-}CH_2CH_2CH_2{-}$).

										Modified Values[d]	
Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	392	2.69	6	398	2.80	558	0.12	160	1.0	-	-
4'-Me	391	2.82	7	398	2.47	534	0.28	136	1.0	541	143
4'-H	392	2.63	8	400	2.49	521	0.35	121	1.0	528	128
4'-Cl	403	2.80	9	412	2.85	524	0.26	112	1.0	534	122
4'-Br	404	3.01	9	413	2.60	525	0.29	112	1.0	534	121
4'-CF_3	411	2.71	12	423	2.69	509	0.64	86	1.2	515	92
4'-Ac	420	2.76	16	436	3.08	522	0.96	86	1.3	530	94
4'-CN	427	3.11	15	442	2.89	515	0.99	73	1.0	521	79
4'-NO_2	444	2.95	26	470	2.76	516	1.33	46	1.5	522	52
2'-CN	428	2.77	14	442	2.83	498	-	56	c.HCl	-	-
2'-CN,4'-NO_2	499	3.27	30	529	3.83	498	0.39	-31	200	-	-
3',5'-$(CF_3)_2$	425	2.44	18	443	2.82	498	0.51	55	1.3	499	56
F_5	414	2.21	19	433	2.48	462	0.35	29	300	-	-

Continued/ ....

Table 2.6., Continued/ ....

Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	Modified Values[d] λ_{max}/nm	Modified Values[d] $\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(ii) Heterocyclic Dyes (65-67)											
65;6'-OEt	-	-	-	511	4.85	621	5.40	110	4.4	614	103
65;6'-H	-	-	-	510	5.10	603	8.34	93	7.6	599	89
65;6'-SO_2Me	-	-	-	535	5.46	588	6.33	53	15.0	584	49
65;6'-NO_2	-	-	-	549	6.30	587	6.88	38	17.0	583	34
66;5'-H	-	-	-	486	3.37	592	5.23	106	0.36	588	102
66;5'-NO_2	-	-	-	582	5.00	574	2.16	-8	1100	-	-
67;3'-NO_2,5'-Ac	-	-	-	586	4.16	529	3.58	-56	2400	-	-

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.7. Visible Spectra of Some Dyes Derived from N-Phenylmorpholine (59; Y = $-CH_2OCH_2-$).

Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	Modified Values[d] λ_{max}/nm	Modified Values[d] $\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	378	2.60	8	386	2.77	566	1.04	180	50	-	-
4'-Me	375	2.54	9	384	2.45	538	2.04	154	50	547	163
4'-H	377	2.33	9	386	2.39	525	2.33	139	40	535	149
4'-Cl	388	2.80	8	396	2.51	530	1.68	134	50	540	144
4'-Br	392	2.78	5	397	2.72	530	1.84	133	50	541	144
4'-CF_3	395	2.58	8	404	2.31	514	3.05	110	50	523	119
4'-Ac	402	2.83	12	415	2.94	527	3.87	112	50	536	121
4'-CN	409	2.86	11	420	2.85	520	3.80	100	50	526	106
4'-NO_2	424	2.48	13	437	2.73	520	4.78	83	100	528	91
2'-CN	412	2.51	9	421	2.44	515	0.52	94	650	516	95
2'-CN,4'-NO_2	469	2.51	27	496	2.80	516	3.94	20	860	520	24
3',5'-$(CF_3)_2$	410	2.52	10	420	2.60	505	2.45	85	50	508	88
F_5	398	2.30	14	412	2.45	476	0.46	64	370	-	-

continued/ ....

Table 2.7., continued/ ....

										Modified Values[d]	
Dye	λ_{max} /nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$ /nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\ \varepsilon_{max}$	$\Delta\lambda$ /nm[b]	$10^{-3}E$[c]	λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(ii) Heterocyclic Dyes (65-67)											
65;6'OEt	-	-	-	495	4.10	620	7.26	125	100	616	121
65;6'-H	-	-	-	490	3.77	607	9.31	117	100	604	114
65;6'-SO_2Me	-	-	-	514	4.18	595	7.58	81	1000	592	78
65;6'-NO_2	-	-	-	527	4.37	598	6.72	71	1000	591	64
66;5'-H	-	-	-	463	2.91	587	5.86	124	282	584	121
66;5'-NO_2	-	-	-	558	4.48	604	5.57	46	252	600	42
67;3'-NO_2,5'-Ac	-	-	-	555	3.41	540	4.64	-15	2000	-	-

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.8. Visible Spectra of Some Dyes Derived from N-Phenylthiomorpholine (59; Y = $-CH_2SCH_2-$).

Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$ /nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$ /nm[b]	$10^{-3}E$[c]	Modified Values[d] λ_{max}/nm	$\Delta\lambda$ /nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	385	2.56	8	393	2.49	569	1.53	176	30	-	-
4'-H	386	2.23	9	395	2.33	531	3.38	136	22	536	141
4'-Cl	394	2.52	13	407	2.52	534	3.40	127	30	541	134
4'-CF_3	400	2.53	17	417	2.54	517	4.56	100	30	525	108
4'-CN	418	2.79	16	434	2.83	522	5.65	88	35	529	95
4'-NO_2	433	2.68	23	456	2.83	526	6.74	70	40	535	79
2'-CN,4'-NO_2	485	3.30	29	514	3.59	525	1.95	11	2000	-	-
(ii) Heterocyclic Dyes (65,66)											
65; 6'-NO_2	-	-	-	537	5.68	606	8.42	69	200	602	65
66; 5'-NO_2	-	-	-	568	4.01	606	4.14	38	650	602	34

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.9. Visible Spectra of Some Dyes Derived from N-Phenylthiomorpholine-1,1-dioxide (59; Y = $-CH_2SO_2CH_2-$).

										Modified Values[d]	
Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	369	-	12	381	3.01	558	6.08	177	800	-	-
4'-H	-	-	-	376	—	526	—	150	-	530	154
4'-Cl	-	-	-	388	2.52	535	6.63	147	1200	539	151
4'-CF_3	379	-	15	394	2.13	535	6.54	141	1200	529	135
4'-CN	-	-	-	408	2.67	542	7.79	134	3000	537	129
4'-NO_2	-	-	-	422	2.55	547	7.28	125	3000	538	116
2'-CN,4'-NO_2	-	-	-	464	3.02	529	6.19	65	3500	527	63
(ii) Heterocyclic Dyes (65,66)											
65;6'-NO_2	-	-	-	500	4.61	604	8.86	104	1000	600	100
66;5'-NO_2	-	-	-	526	3.46	616	6.52	90	3000	612	86

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.10. Visible Spectra of Some Dyes Derived from N'-Ethyl-N-phenylpiperazine (59; Y = $-CH_2N(Et)CH_2-$).

										Modified Values[d]	
Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	389	-	2	391	-	562	-	171	-	-	-
4'-H	387	-	5	392	2.17	529	4.13	137	400	534	142
4'-Cl	398	-	2	400	2.48	536	6.29	136	600	539	139
4'-CF_3	407	-	1	408	2.55	535	6.46	127	800	527	119
4'-CN	420	-	5	425	2.93	543	7.02	118	1100	535	110
4'-NO_2	435	-	10	445	2.83	545	8.19	100	1500	536	91
2'-CN,4'-NO_2	488	-	16	504	3.08	526	7.11	22	9900	522	18
(ii) Heterocyclic Dyes (65,66)											
65;6'-NO_2	-	-	-	533	4.95	604	10.04	71	700	600	67
66;5'-NO_2	-	-	-	565	4.00	615	6.39	50	2000	614	49

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.11. Visible Spectra of Some Dyes Derived from N'-Methyl-N-phenylpiperazine (59; Y = $-CH_2(NMe)CH_2-$).

Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	Modified Values[d] λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	-	-	-	-	—	-	-	-	-	-	-
4'-H	-	-	-	-	—	-	-	-	-	-	-
4'-Cl	397	2.59	2	399	2.24	534	5.94	135	800	539	140
4'-CF_3	402	2.01	6	408	2.36	534	6.02	126	1000	528	120
4'-CN	419	2.73	4	423	2.61	541	7.12	118	1000	532	109
4'-NO_2	433	2.39	9	442	2.60	544	8.13	102	1600	535	93
2'-CN,4'-NO_2	484	2.92	17	501	3.26	522	6.92	21	9000	-	-
(ii) Heterocyclic Dyes (65,66)											
65;6'-NO_2	-	-	-	531	4.82	605	9.84	74	1500	600	69
66;5'-NO_2	-	-	-	-	—	-	-	-	-	-	-

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

[b] Difference between wavelengths of neutral dye and azonium cation

[c] No. of equivalents of acid required to produce optimum amount of azonium ion

[d] See footnote to tables, p.78

Table 2.12. Visible Spectra of Some Dyes Derived from N'-Acetyl-N-phenylpiperazine(59; Y = $-CH_2N(Ac)CH_2-$).

										Modified Values[d]	
Dye	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[a]	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	λ_{max}/nm	$10^{-4}\varepsilon_{max}$	$\Delta\lambda$/nm[b]	$10^{-3}E$[c]	λ_{max}/nm	$\Delta\lambda$/nm[b]
	(Cyclohexane)			(EtOH)		(EtOH/HCl)				(EtOH/HCl)	
(i) Benzenoid Dyes (64)											
4'-OMe	375	-	12	387	2.64	565	4.76	178	420	-	-
4'-H	373	-	14	387	2.47	535	5.92	148	500	-	-
4'-Cl	382	-	14	396	2.78	532	6.36	136	550	540	144
4'-CF_3	392	-	13	405	2.45	537	6.38	132	700	528	123
4'-CN	405	-	16	421	2.80	540	6.97	119	550	530	109
4'-NO_2	413	-	24	437	2.58	546	7.71	109	1000	537	100
2'-CN,4'-NO_2	466	-	32	498	3.01	519	6.68	21	7500	-	-
(ii) Heterocyclic Dyes (65,66)											
65;6'-NO_2	-	-	-	529	4.95	601	9.57	72	1150	598	69
66;5'-NO_2	-	-	-	557	4.16	614	6.13	57	1300	609	52

[a] Difference between wavelengths of neutral dye in cyclohexane and in ethanol

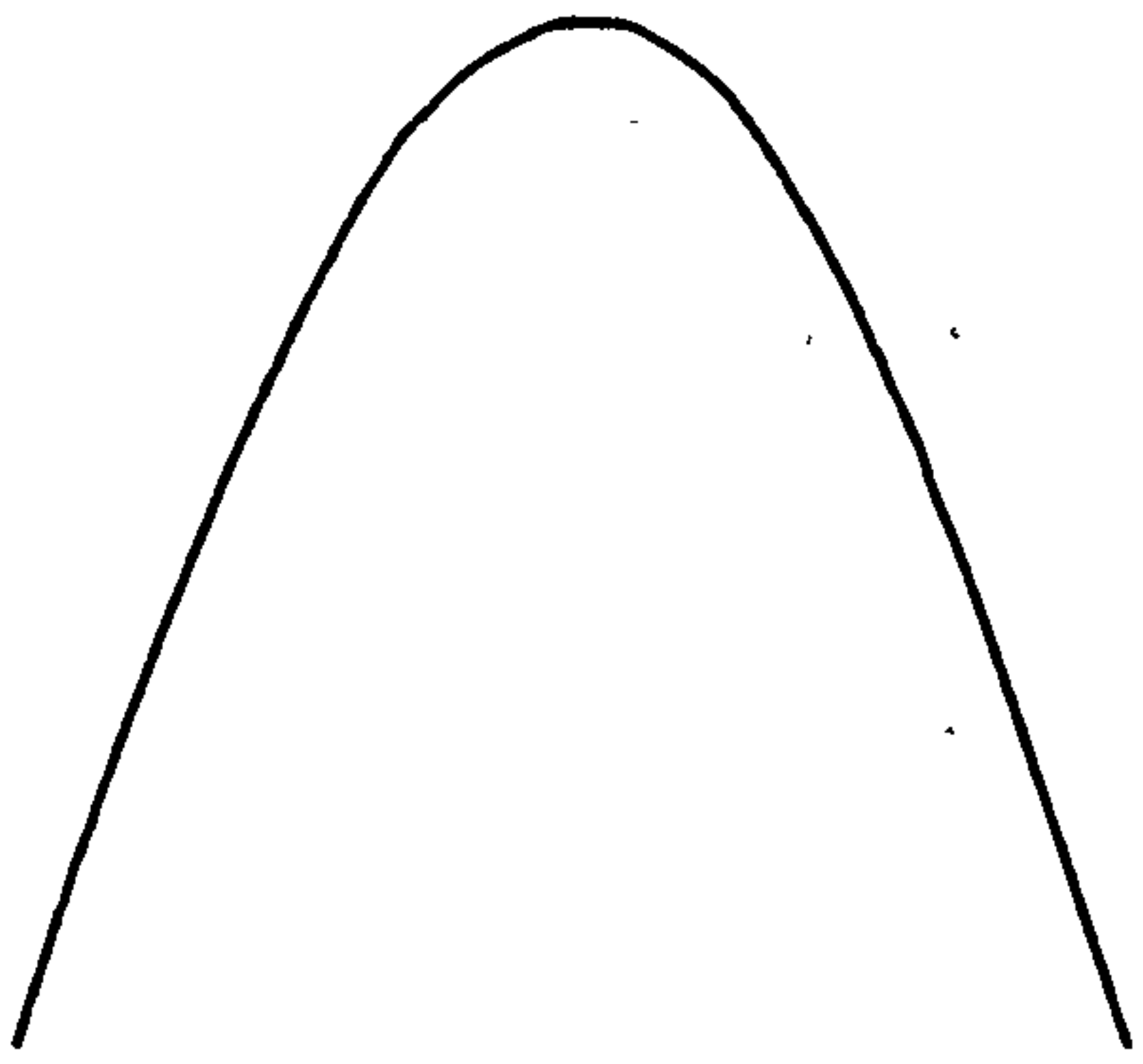
[b] Difference between wavelengths of neutral dye and azonium cation

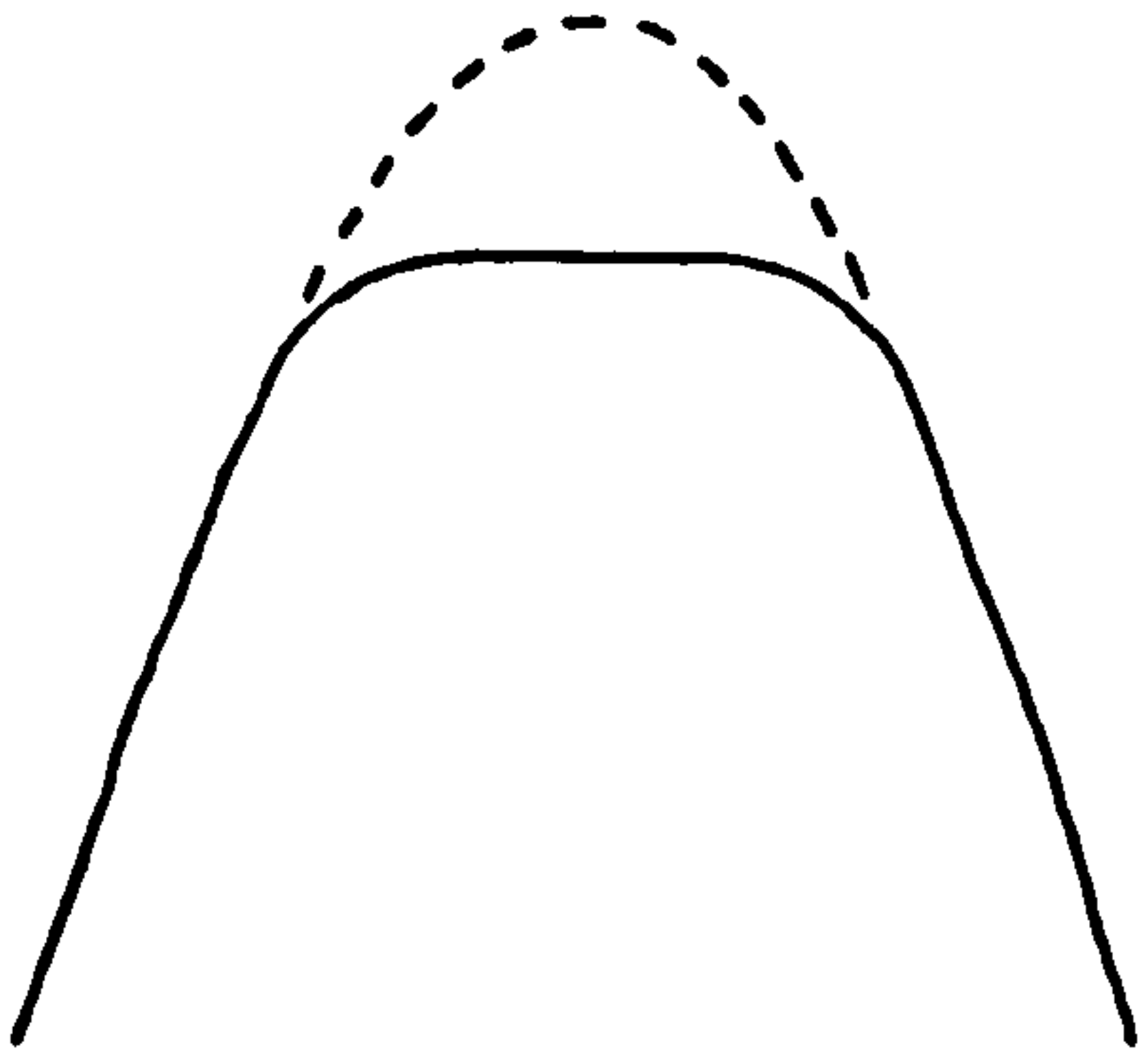
[c] No. of equivalents of acid required to produce optimum amount of azonium ion

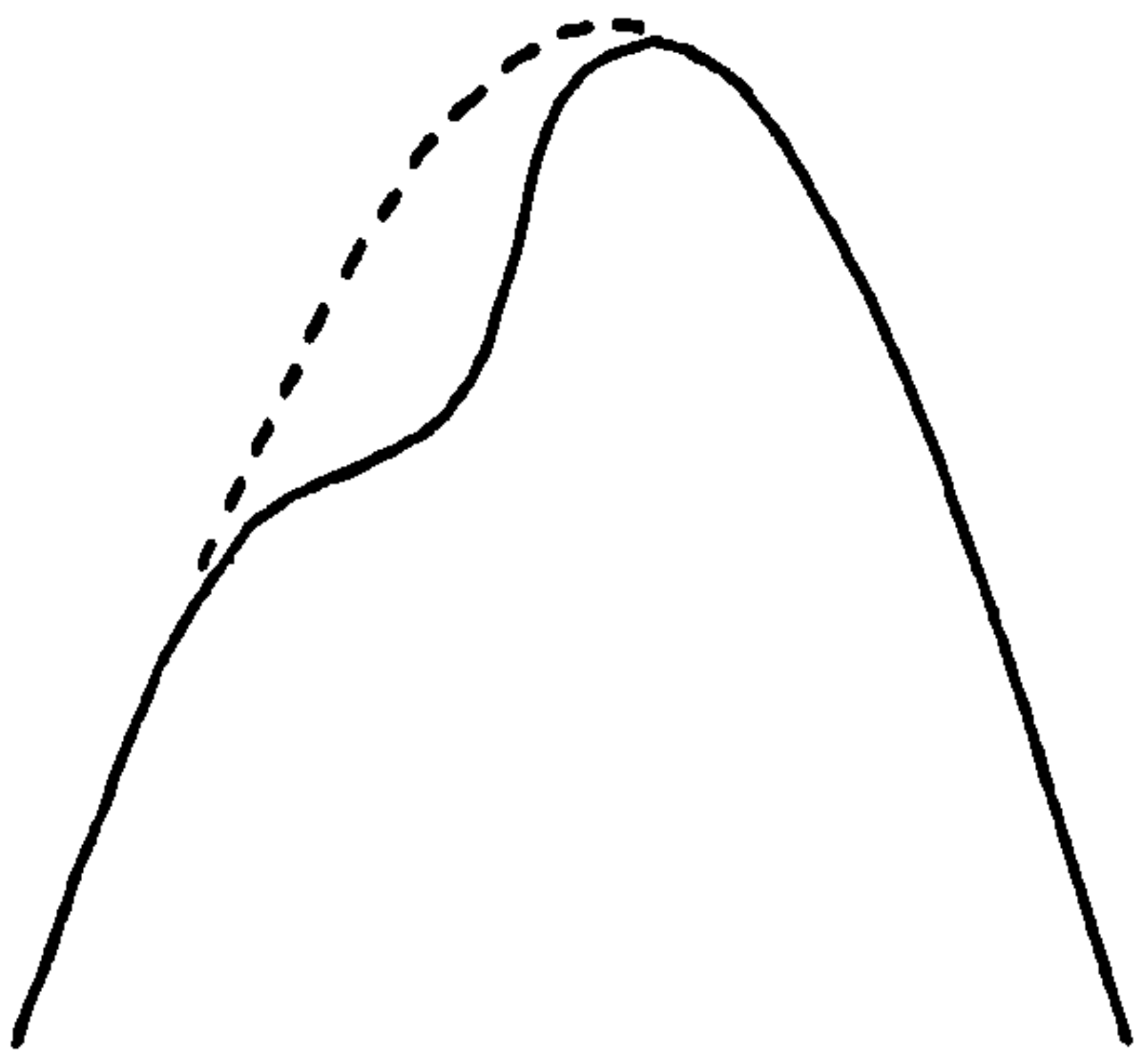
[d] See footnote to tables, p. 78

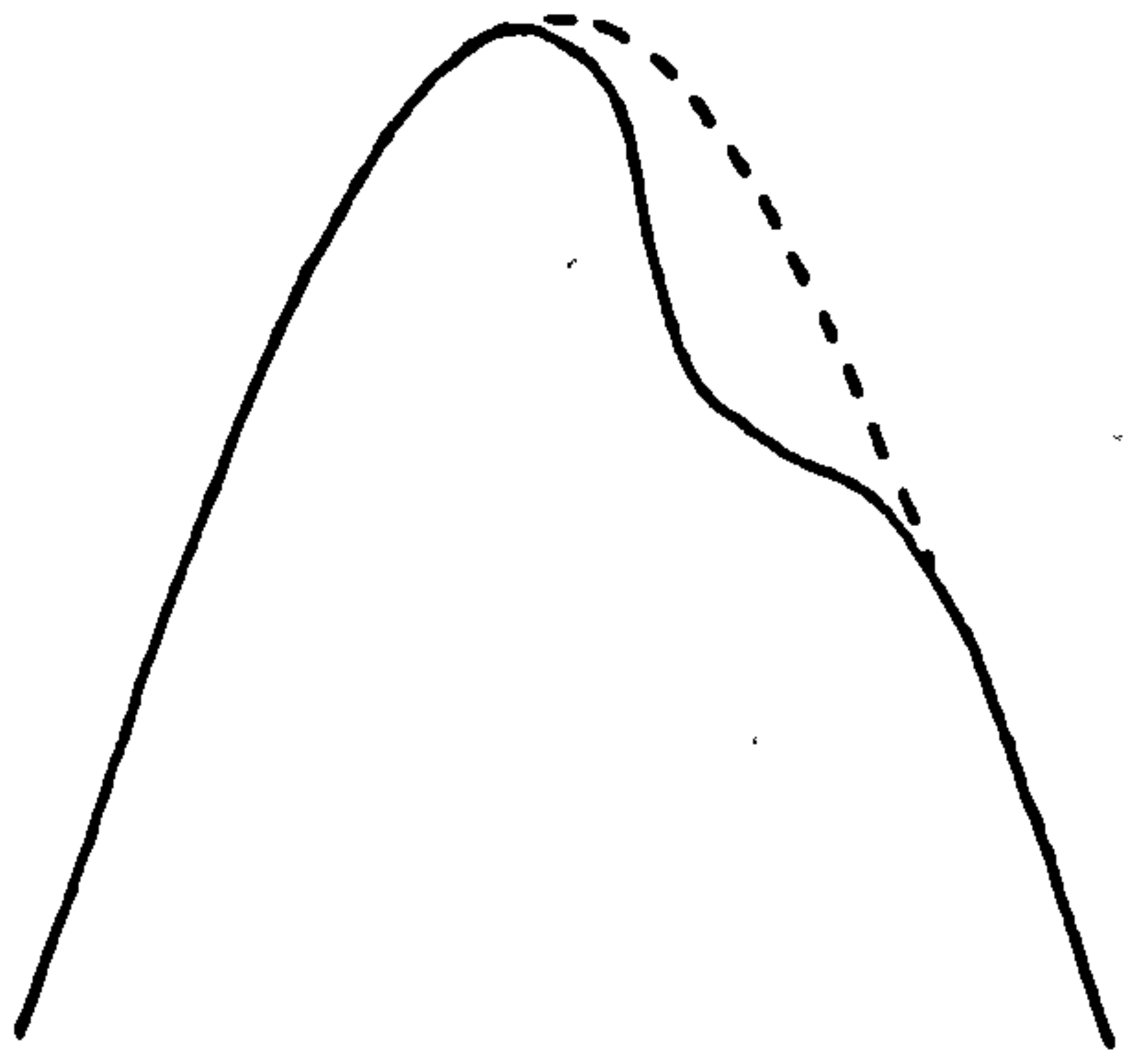
Footnote to Tables 2.5-2.12

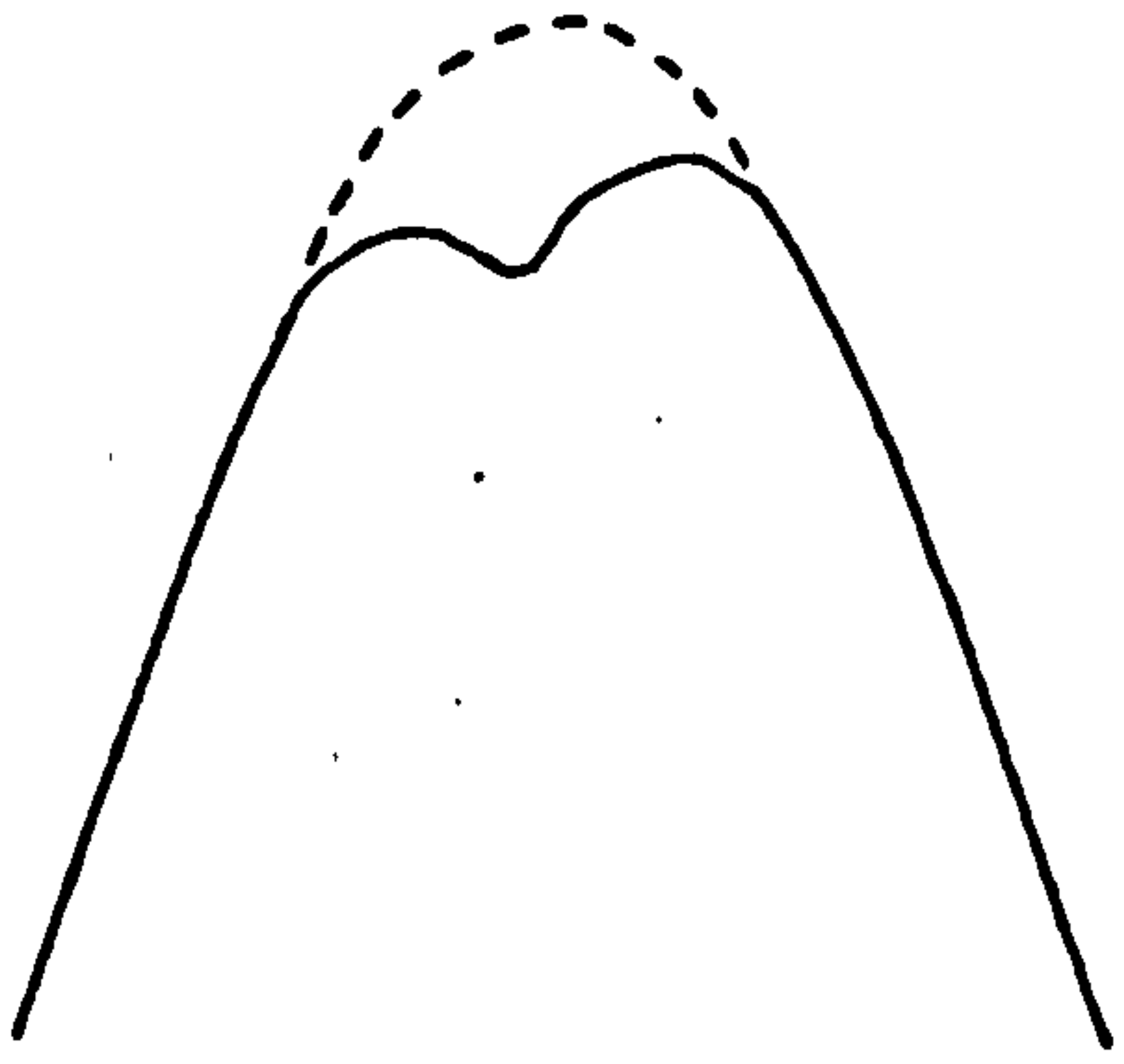
[d] The shape of the visible absorption band in acid solution is somewhat variable [(i) - (vi)] , due to fine structure. The modified λ_{max} values were obtained by completing a smooth band envelope (dotted line). This procedure appears to be advantageous in certain cases, both as regards comparison between dyes in the same series and in different series . Where modified values are not quoted, the curve is of type (i).

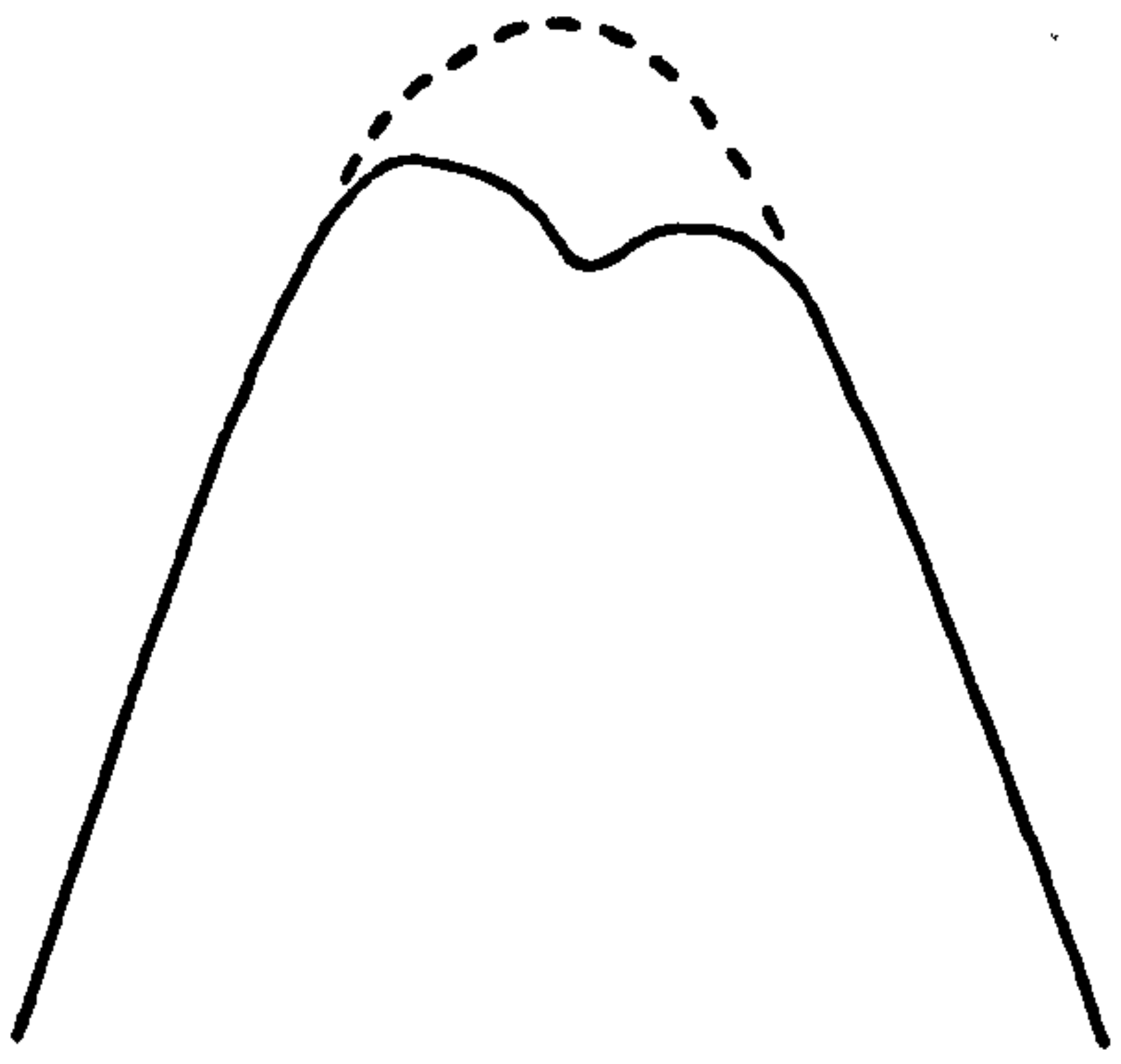

(i)


(ii)


(iii)


(iv)


(v)


(vi)

Within each dye series, the 4'-substituted-4-aminoazobenzene derivatives show the expected general bathochromic displacement of the visible absorption band as the electron withdrawing strength of the 4'-substituent increases, together with a somewhat variable but definite increase in the intensity of absorption. The wavelength range depends on the terminal amino group; in the 4-pyrrolidinoazobenzene series (64; Y = $-CH_2CH_2-$), for example, the 4'-nitro derivative is 75 nm more bathochromic than its parent, whereas the corresponding thiomorpholine-1,1-dioxide dyes (64; Y = $-CH_2SO_2CH_2-$) show a difference of only 46 nm. Electron releasing groups (Me, OMe) have little effect on the position of the first band, shifting λ_{max} from the parent dye value by only a few nanometres. Graphs of the wavelength shift produced by a 4'-substituent against the appropriate Hammett σ-constant are shown for the pyrrolidino-, piperidino- and morpholino-azo dyes in Figs. 2.3, 2.4 and 2.5, respectively.* The absence of a hypsochromic effect for the electron donor groups is reflected in their position relative to the straight line, and confirms previous findings (section 1.5) that, in general, only electron acceptors follow the Hammett relation, and then only approximately, since the substituent is directly involved in the excitation process and as a consequence will have different electronic properties (and hence different σ value) in the excited state.

It can be seen from the graphs that certain acceptor substituents (H, Cl, Br, Ac, CN) fall on or near the line while others (CF_3, NO_2) do not. These deviations appear to be consistent; thus, NO_2 is always somewhat above the straight line, although comparison of the three plots suggests that this upward deviation decreases as the electron donating power of the terminal amino group decreases. A similar distribution of points is found for the NN-dimethylamino- and NN-diethylaminoazobenzenes.

---

*See Table 2.20 for σ values

Fig. 2.3.

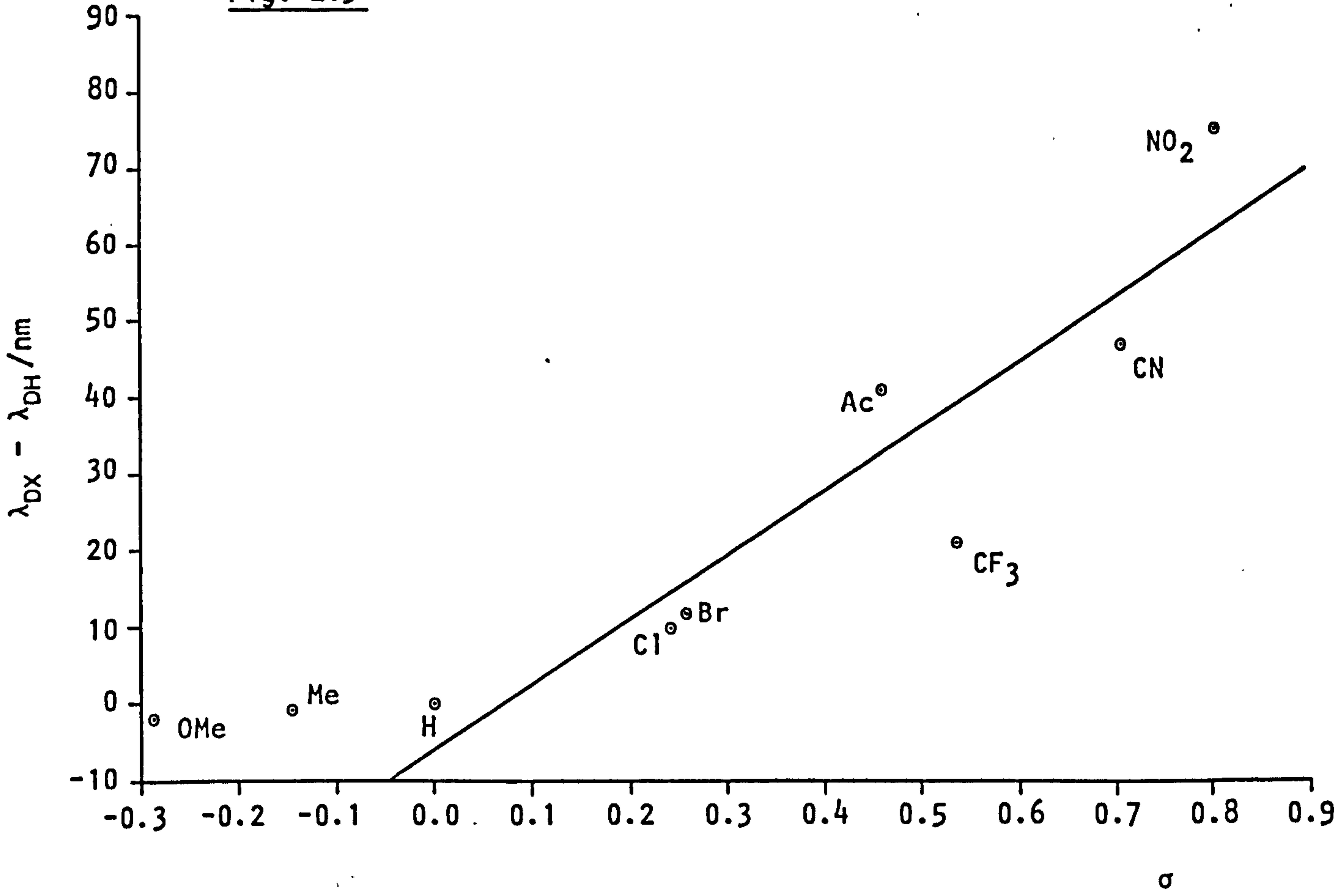
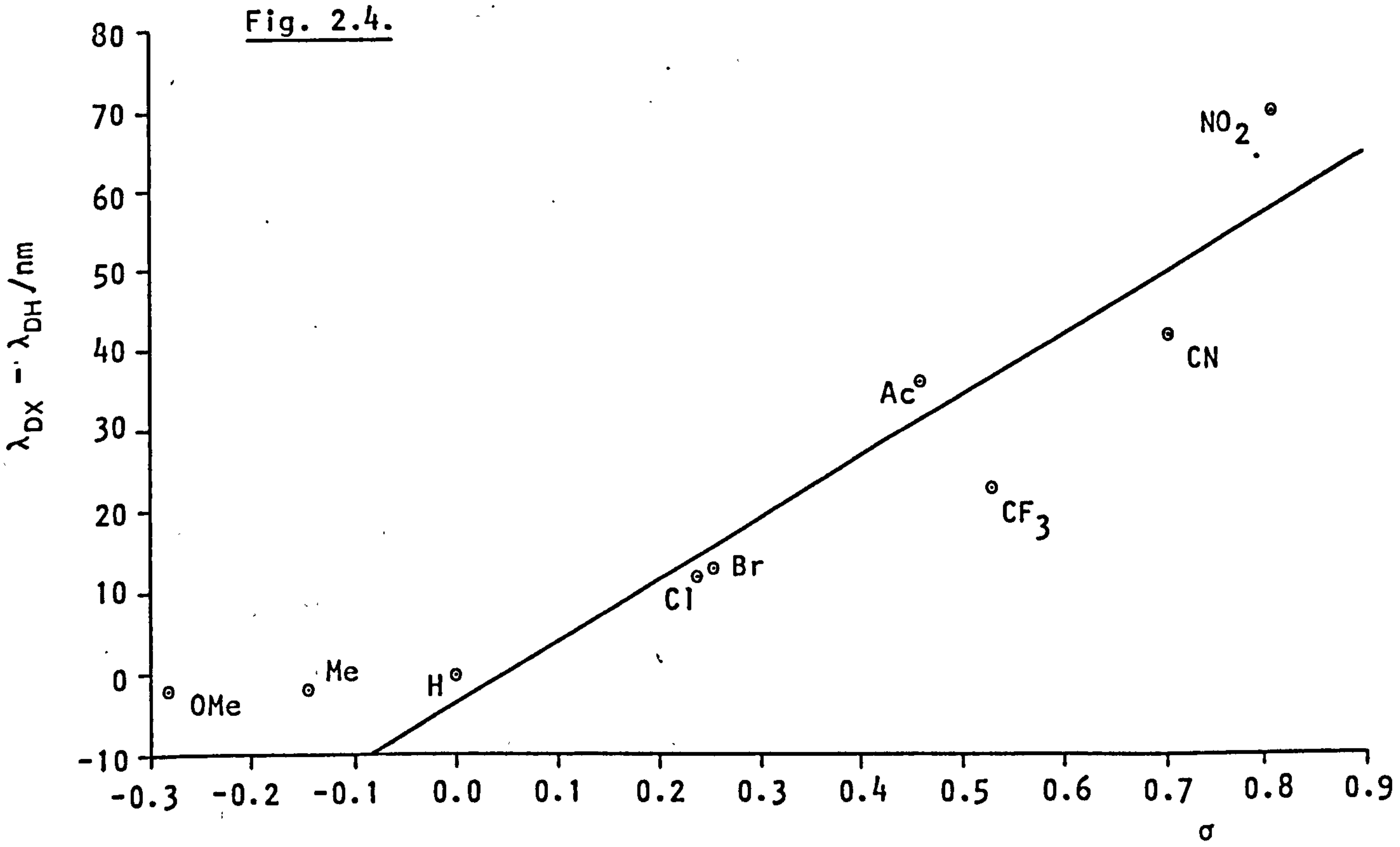


Fig. 2.4.



Relation between Hammett substituent constants (σ) and $\lambda_{DX} - \lambda_{DH}$ of derivatives of 4-pyrrolidinoazobenzene (Fig. 2.3) and 4-piperidinoazobenzene (Fig. 2.4) in ethanol (see Tables 2.5 and 2.6).

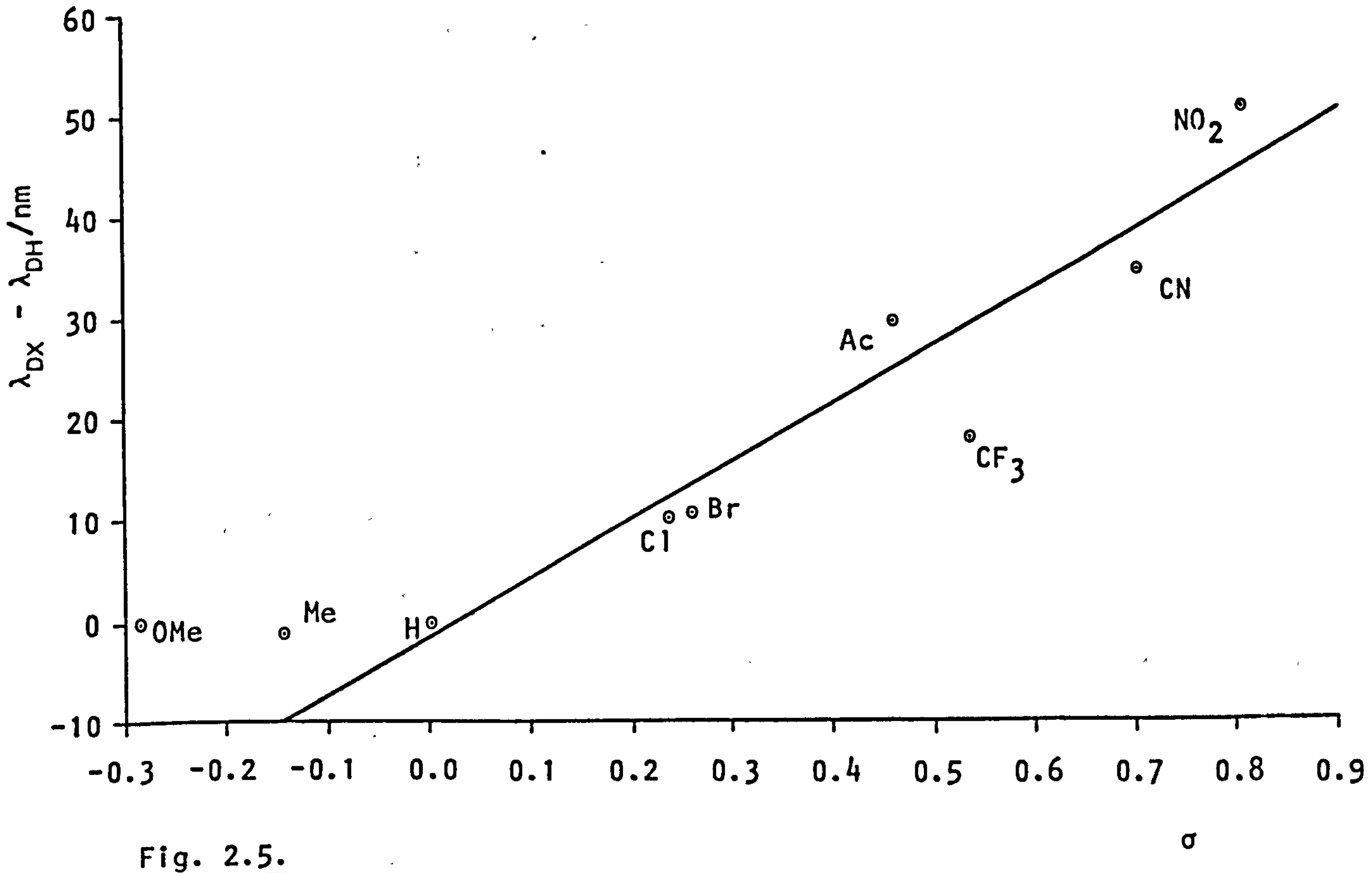


Fig. 2.5.

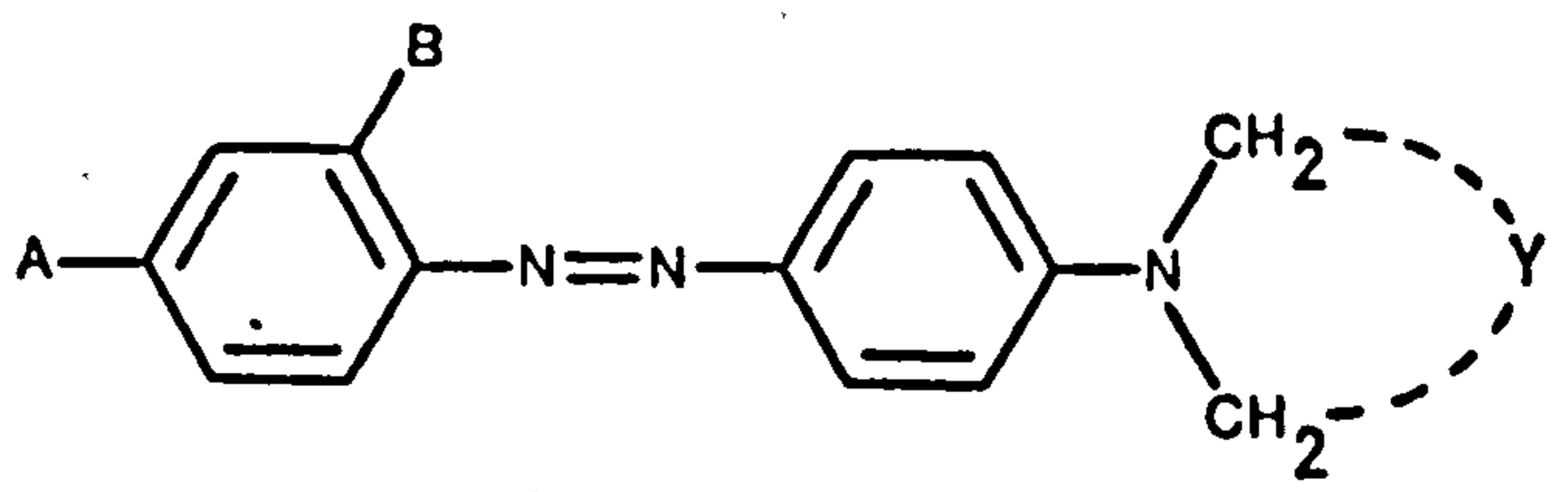
Relation between Hammett substituent constants (σ) and λ_{DX}-λ_{DH} of derivatives of 4-morpholinoazobenzene in ethanol (see Table 2.7).

Provided that the distribution pattern holds generally, it may be that graphs of this type could be used to predict λ_{max} values for 4'-acceptor-substituted dyes (and presumably in a similar manner for 3'-acceptors), having first related in some way the deviation from the line to the power of the 4-donor substituent. Unfortunately, the generality of this distribution is not known and it is necessary to correlate several series of dyes, containing as many different 4'-substituents as possible, in order to establish which substituents always appear close to the straight line. However, once the particular pattern is known, three or four dyes could be prepared in a new series and it would then be possible to calculate λ_{max} values with reasonable accuracy for other dyes in that series.

In cases where the 2'-cyano derivative has been prepared, it is found that the dye absorbs maximally at the same wavelength as the 4'-isomer, as expected for an ortho substituent which does not exert a crowding effect (section 1.5). N-[4-(2'-Cyano-4'-nitrophenylazo)-phenyl]pyrrolidine (72d) shows additivity of substituent effects,[27,68,140] such that the sum of the wavelength shifts of the 2'-cyano (72b) and of the 4'-nitro (72c) derivatives equals that produced by the disubstituted dye (Table 2.13). However, this additivity relationship does not hold for the corresponding dyes in which the terminal nitrogen atom forms part of a six-membered ring, as illustrated by the appropriate piperidinoazo dyes (72e-h). Presumably, this breakdown must be associated with the previously discussed steric factors inherent in dyes containing six-membered rings; the 2'-cyano-4'-nitro derivatives of these systems absorb at longer wavelengths than the additivity rule would suggest, again indicating that the powerful electron accepting residue of the molecule is forcing improved conjugation of the nitrogen lone pair at the expense of increased steric strain.

Of the other dyes of type (64) studied, the 3',5'-bistrifluoromethyl derivatives appear to cause wavelength shifts equivalent to dyes containing a 4'-cyano substituent. The pentafluoro dyes (64; 2',3',4',5',6'-F_5) are not quite as bathochromic as their 4'-Ac counterparts; the crowding effect of two fluorine atoms ortho to the azo link diminishes the overall electron withdrawing ability. It is apparent that, as a

Table 2.13. Visible Spectra[a] of Some Azo Dyes (72) which Illustrate the Additivity Rule.



(72)

Dye	A	B	Y	λ/nm	$\Delta\lambda$/nm[b]	
72a	H	H	$-(CH_2)_2-$	413	-	
72b	H	CN	$-(CH_2)_2-$	458	45	= 120
72c	NO_2	H	$-(CH_2)_2-$	488	75	
72d	NO_2	CN	$-(CH_2)_2-$	536	123	
72e	H	H	$-(CH_2)_3-$	400	-	
72f	H	CN	$-(CH_2)_3-$	442	42	= 112
72g	NO_2	H	$-(CH_2)_3-$	470	70	
72h	NO_2	CN	$-(CH_2)_3-$	529	129	

[a] Solvent ethanol

[b] Relative to A=B=H

general rule, the intensity of absorption increases gradually as the electron withdrawing strength of substituents in the diazo component increases; extinction coefficients are approximately the same in ethanol and in cyclohexane. Absorption bands in the latter solvent often contain shoulders on either side of the main peak. This feature is thought to be due to vibrational fine structure and is less common in polar solvents due to solvation effects.

In the case of the benzenoid dyes (64), the positive solvatochromism increases gradually as the electron withdrawing power of the 4'-substituent increases, due to a progressive increase in the stabilisation of the excited state (71b) by the polar solvent. The heterocyclic azo dyes (65-70) display a considerably bigger solvatochromic effect owing to the general polarity of these systems and of their excited states in particular, possibly owing to the diene character of the acceptor residue and, in some cases, also to the presence of electronegative heteroatoms. The marked bathochromic shifts produced by the various heterocyclic dyes are accompanied by significant increases in intensity of absorption, giving extinction coefficients which are exceptionally high for azo dyes. Of the aromatic heterocycles studied, the benzthiazole residue imparts the highest intensities; the 6'-nitrobenzthiazole derivative (65; $Y = -CH_2CH_2-$) has an ε_{max} of 64,800,in line with PPP-MO predictions (see Appendix 1). This situation may be a consequence of the relatively large number of π-electrons contributing to the electronic transition. However, the benzthiazole ring system does not necessarily produce the dye of longest wavelength. Comparing the phenyl (64), benzthiazole (65) and thiazole (66) residues (Table 2.14), the benzthiazole system produces the most bathochromic of the parent dyes whereas the thiazole ring is associated with the most bathochromic of the nitro-substituted dyes. The $\Delta\lambda$ values listed in Table 2.14 reflect the insulating effect of the benzthiazole ring, and the enhanced conjugative effect of the thiazole ring,relative to the phenyl nucleus, on the acceptor capacity of the nitro substituent.

Compared with the parent thiazolylazo dyes (73), the 1, 3, 4- and 1, 2, 4-thiadiazole analogues, (74) and (75) respectively, appear to show the order of bathochromicity anticipated on resonance and inductive grounds.

Table 2.14. The Effect of a Nitro Group on Some Pyrrolidinoazo Dye Systems.

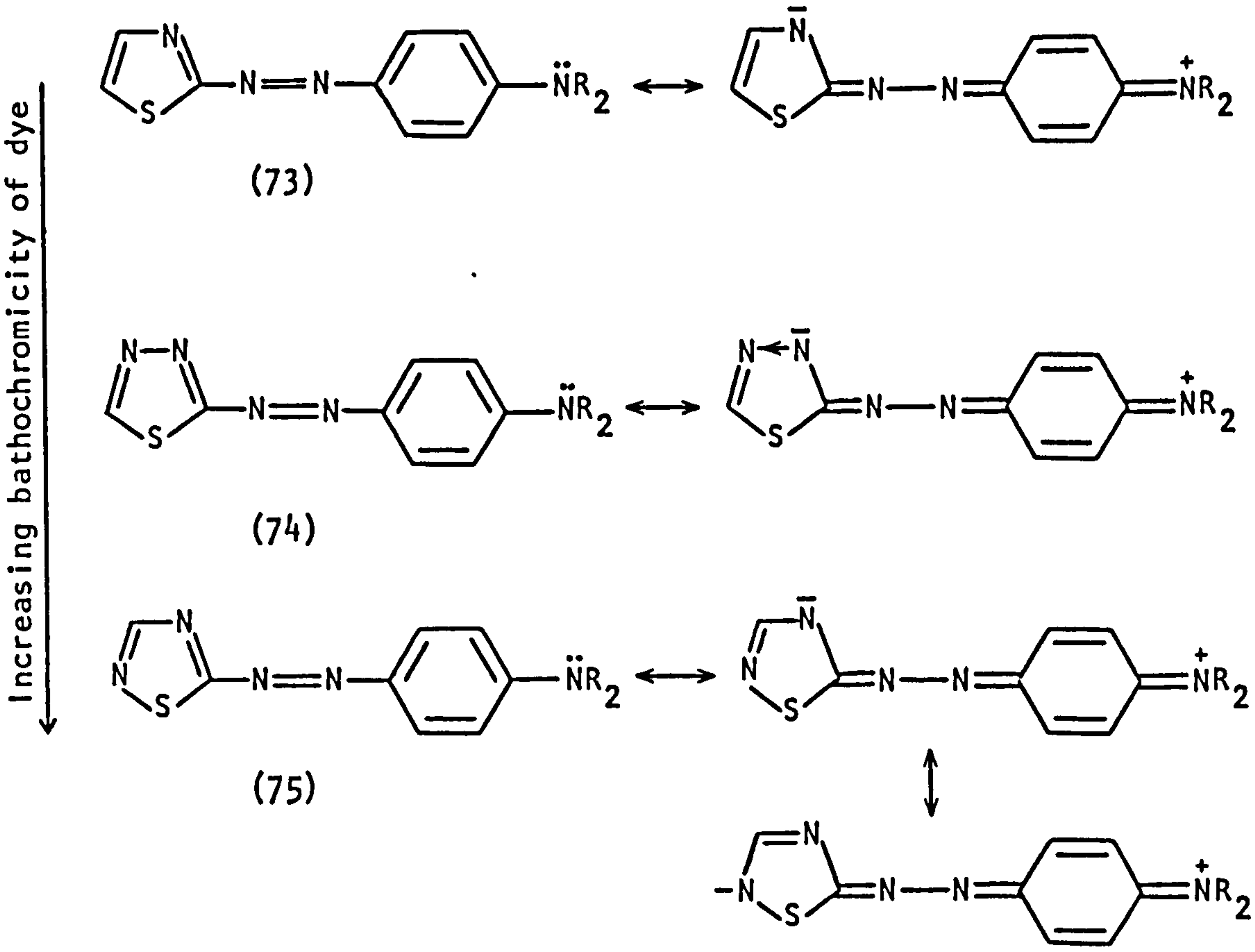
Dye	λ_{max}/nm[a]	$\Delta\lambda$/nm[b]
64(Y = $-CH_2CH_2-$);4'-H	413	—
;4'-NO_2	488	75
65(Y = $-CH_2CH_2-$);6'-H	514	—
;6'-NO_2	551	37
66(Y = $-CH_2CH_2-$);5'-H	494	—
;5'-NO_2	584	90

[a] Solvent ethanol

[b] Relative to the parent dye

Thiophene acceptor rings also show a substantial bathochromic shift when electron withdrawing substituents are present,although comparable dyes tend to absorb at shorter wavelengths than their thiazole counterparts owing to the absence of an electronegative nitrogen atom in the ring. Nevertheless, blue dyes are easily achieved using these systems (see Appendix II).

Comparison of the thiazolyl- and 6'-nitrothiazolyl-azo dyes derived from the coupling component of dye (76)[21] with those from N-phenylpyrrolidine (Table 2.5) suggest that the thienylazo dye (77a) should absorb at a wavelength of about 10-15 nm less than that of the dye (76), i.e. at about 510-15 nm. Dye (77b) might be expected to show a hypsochromic shift relative to (77a) owing to steric hindrance between the ortho-

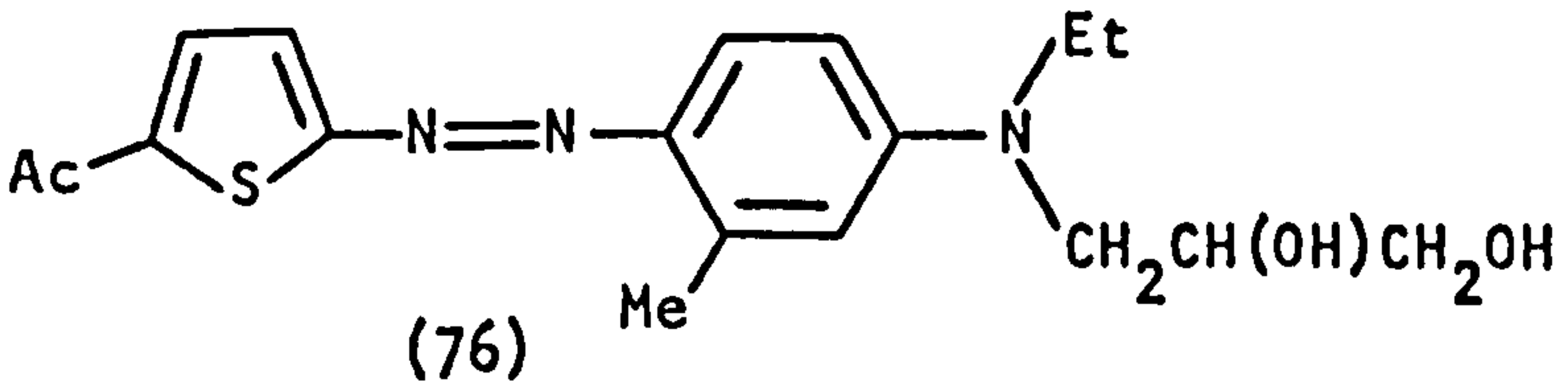


(73)

(74)

(75)

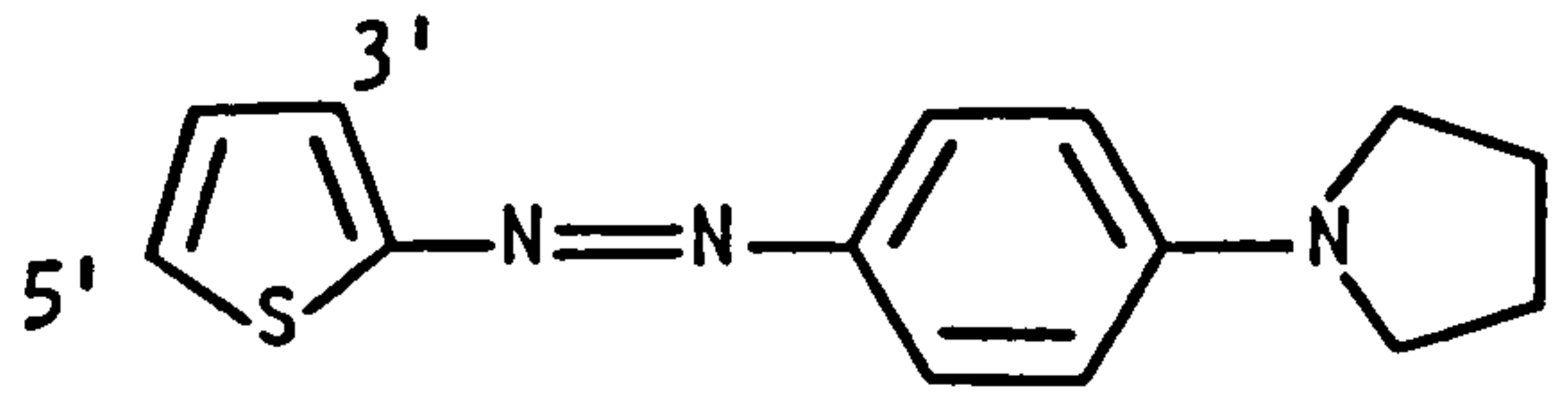
acetyl group and the lone pair of the α-azo nitrogen atom; even allowing for this clash, it is likely that the most bathochromic isomer will have the azo link in the 2'-position of the thiophene ring [dye (77b) should be more bathochromic than (78)]. This postulate assumes that conjugation of the acetyl group through four carbon atoms of the thiophene ring [(77a), <u>para</u>-substitution] does not hold any advantages over conjugation through two carbon atoms [(77b), <u>ortho</u>-substitution] apart from the steric factors previously discussed. Unfortunately, at the present time the required data for dyes (77) are not available. However, the hypothesis is supported by PPP-MO calculations; predicted λ_{max} values for dyes (77a), (77b), and (78), respectively, are 481 nm, 464 nm and 449 nm.



(76)

λ_{max} = 525 nm

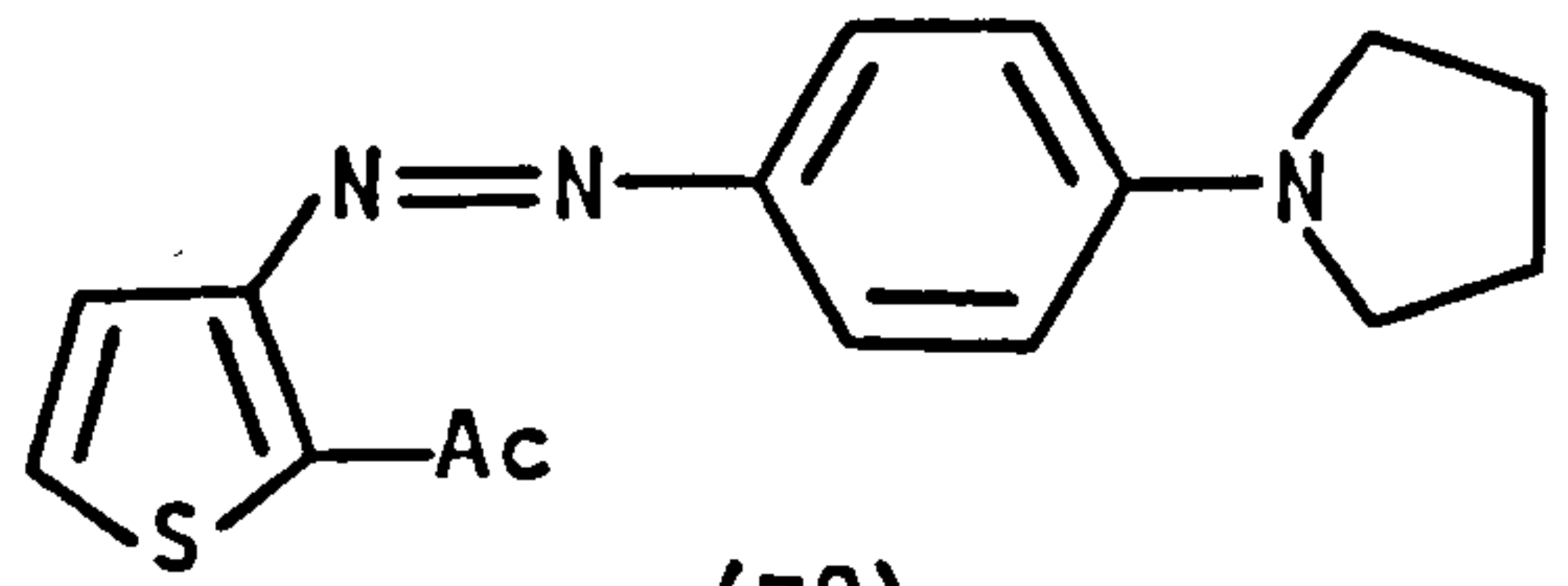
ε_{max} = 32500(MeOH)



(77)

(77a);5'-Ac

(77b);3'-Ac



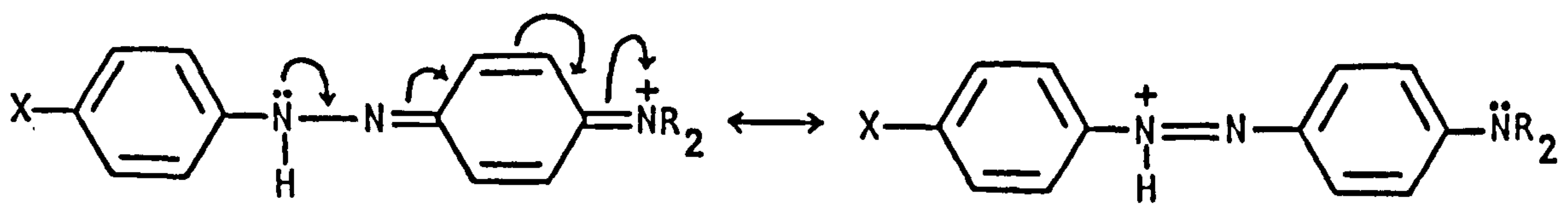
(78)

λ_{max} = 477 nm

ε_{max} = 27300 (EtOH)

2.3.2. Acidic Solution

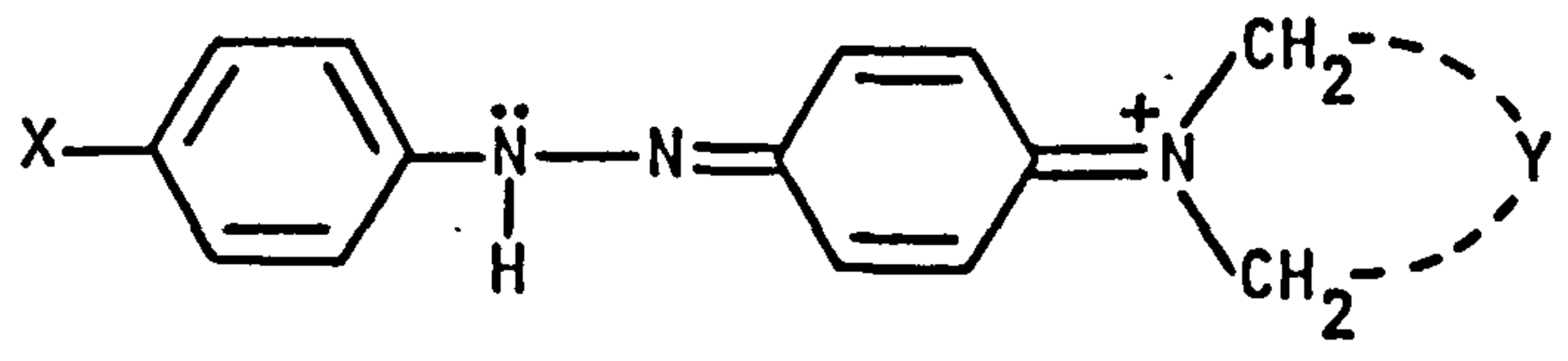
As discussed in the Introduction (Section 1.7), solutions of the mono-acid salt of derivatives of 4-aminoazobenzene show two long-wavelength absorption bands, due to the ammonium cation (at ∿320 nm) and the azonium cation (at ∿ 500-550 nm), the latter ion being responsible for the colour change of the dye in acid solution. Substituent effects can be interpreted in terms of their effect on the resonance canonicals (79a) and (79b) which correspond approximately to the ground and excited states, respectively,of the azonium cation. Qualitatively, the excited state will be increasingly stabilised as the electron-donating strength of X and the electron-accepting strength of $\overset{+}{N}R_2$ increase. Those terminal amino groups which exhibit the weakest donor properties in the neutral dye should show the strongest acceptor



(79a) (79b)

powers in the protonated dye, thereby shifting the azonium band to longer wavelengths. Experimental data (Tables 2.5-2.12) reveal a rather irregular trend, as illustrated by two examples in Table 2.15.

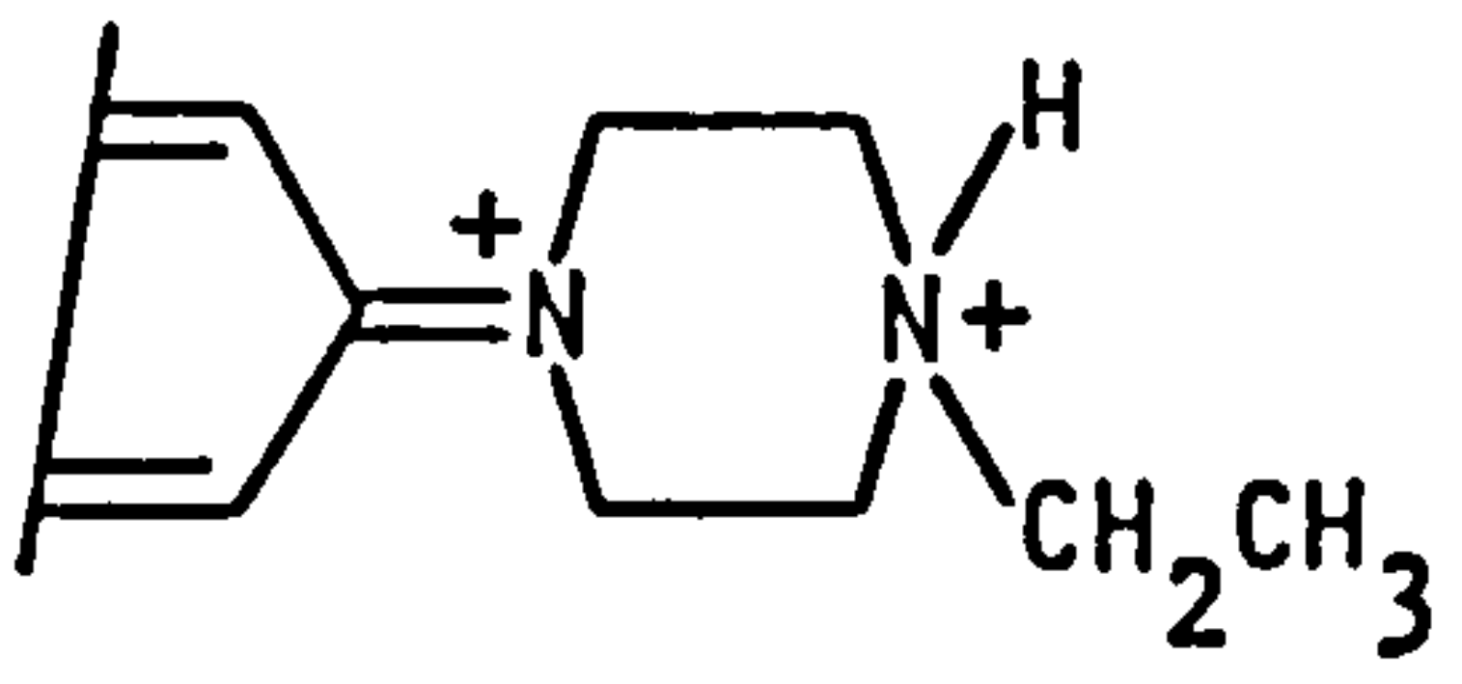
Table 2.15. Absorption Bands of Some Protonated Azo Dyes (80).



(80)

Y	X = H		X = NO_2	
	λ_{DH^+}/nm[a]	$(\lambda_{DH^+}-\lambda_D)$/nm[b]	λ_{DH^+}/nm	$(\lambda_{DH^+}-\lambda_D)$/nm
$-CH_2CH_2-$	530	117	512	30
$-CH_2CH_2CH_2-$	528	128	516	52
$-CH_2SCH_2$	536	141	531	79
$-CH_2N(Et)CH_2-$	534	142	545	91
$-CH_2OCH_2$	535	149	520	91
$-CH_2N(Ac)CH_2-$	535	148	546	100
$-CH_2SO_2CH_2-$	530	154	547	116

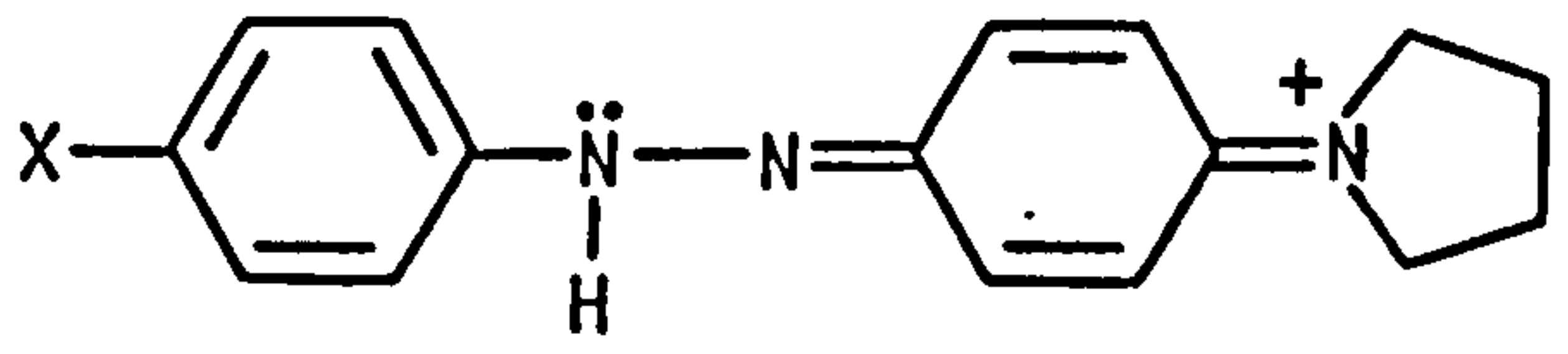
For dyes of type (80; X = H), variation of Y produces only small changes in protonated dye wavelength. Uncertainties in the measurement of protonated spectra due to their variable shape (see p.78) become more important in these cases and tend to make any trends less apparent. For the 4'-nitro derivatives (80; X = NO_2), however, where the changes in wavelength are larger, the expected trend is fairly clearly observed, although the effect of the morpholino group (80; Y = $-CH_2OCH_2-$) appears to be anomalous. The acceptor strength of the protonated N'-ethylpiperazinyl group is somewhat unclear; almost certainly, the aliphatic t-amino group will be protonated, thereby producing a large -I effect and increasing the electron withdrawing effect of the ring as a whole (81), but this situation is not always reflected in the wavelength shift.



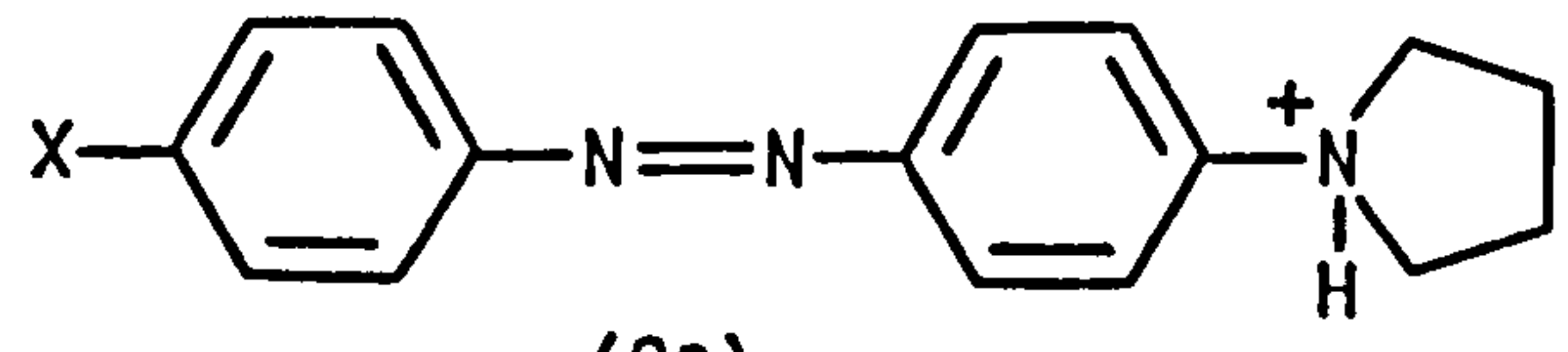
(81)

The difference in wavelength between protonated and unprotonated dye (Table 2.15, $\lambda_{DH^+}-\lambda_D$) does show a fairly regular increase for both series as the donor strength of the terminal amino group decreases. Interestingly, the position of the N'-ethylpiperazinyl dyes is that expected on the basis of an unprotonated aliphatic amino group.

The intensities of the absorption bands produced by the univalent cation vary both with coupling component and with acceptor residue. Although an equilibrium exists between ammonium and azonium tautomers, this equilibrium can be displaced significantly in favour of one or the other species. The 4-pyrrolidinoazobenzene dyes (64; Y = $-CH_2CH_2-$) exist almost entirely as the azonium form in acid solution, unlike their close relatives (in wavelength terms) the diethylaminoazo dyes, where the equilibrium favours the ammonium form.[89] This bias towards the azonium cation fits in with the generalisation of Brown et al.,[141] which states that reactions will proceed in such a manner as to favour the formation of an exo double bond in a five-membered ring (although it should be noted that Effenberger et al.[126] have expressed doubts about this generalisation). The azonium cation (82) contains an exo double bond whereas the ammonium form (83) does not.

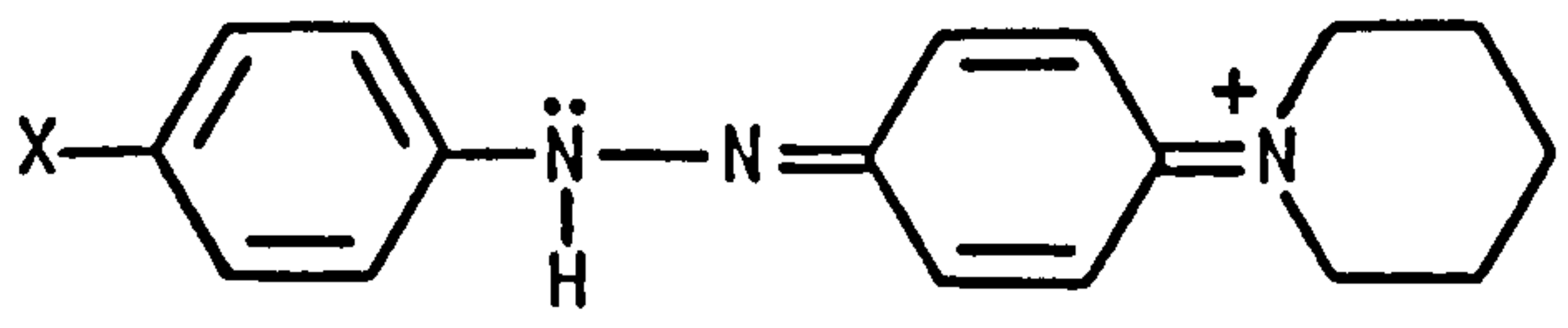


(82)



(83)

The above workers also postulated that an exo double bond will destabilise a six-membered ring, and indeed the 4-piperidinoazobenzene dyes prefer to exist as the ammonium form in acid solution. This result is to be expected, of course, since the loss of conjugation caused by steric hindrance between α-methylene and ortho-phenyl protons results in an increased electron density at the terminal nitrogen atom and a decreased electron density at the β-azo nitrogen atom. The former increase is such that only relatively low concentrations of acid are needed to effect full protonation of the neutral dye. Electron withdrawing groups in the 4'-position of the acceptor ring increase the amount of azonium ion (up to about 20%) by increasing the conjugation of the lone pair, as illustrated by 84(a) and 84(b). This increase is less noticeable in the case of the pyrrolidinoazo dyes, since the equilibrium already lies very heavily in favour of the azonium species.

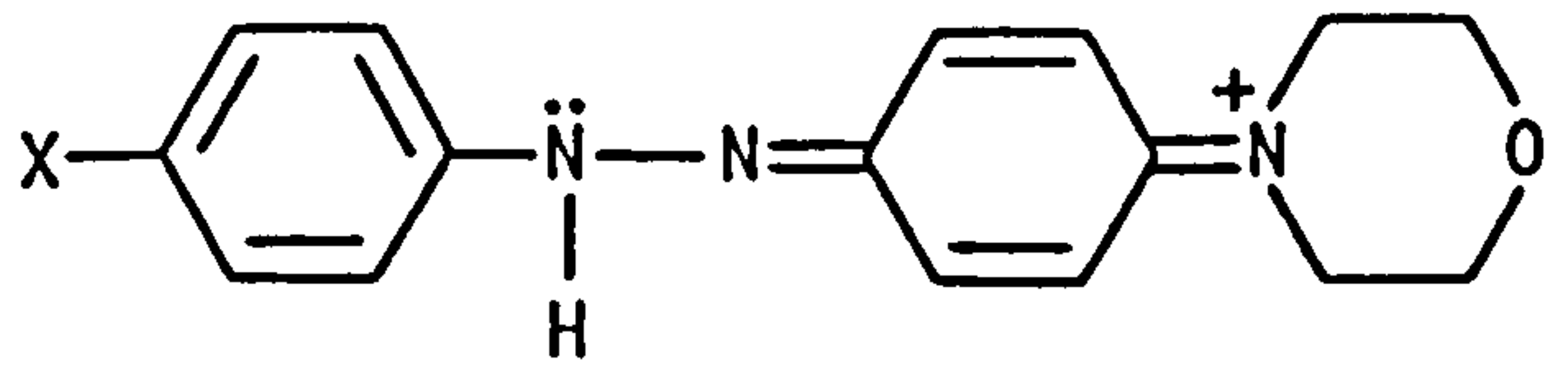


(84)

(a) X = OMe; ε_{max} = 1200

(b) X = NO_2; ε_{max} = 13250

The remaining six-membered terminal amino ring systems contain heteroatoms in the γ-position which withdraw electron density from the terminal nitrogen atom according to the strength of their -I effect. This withdrawal reduces the overall electron density at the two protonation sites and consequently increases the amount of acid needed to produce a cation. At the same time, the β-azo nitrogen atom becomes a relatively more favoured site for protonation, especially when the dye contains an electron withdrawing group in the 4'-position of the phenyl ring, and this situation is reflected in the ε_{max} values. The 4-morpholinoazobenzene dyes (64; Y = $-CH_2OCH_2-$) show a change in the equilibrium, as the acceptor strength of the 4'-substituent increases, from predominantly (about 80%) the ammonium form to predominantly (up to about 70%) the azonium form; this behaviour is illustrated by 85(a) and (b). The lowering of electron density at the



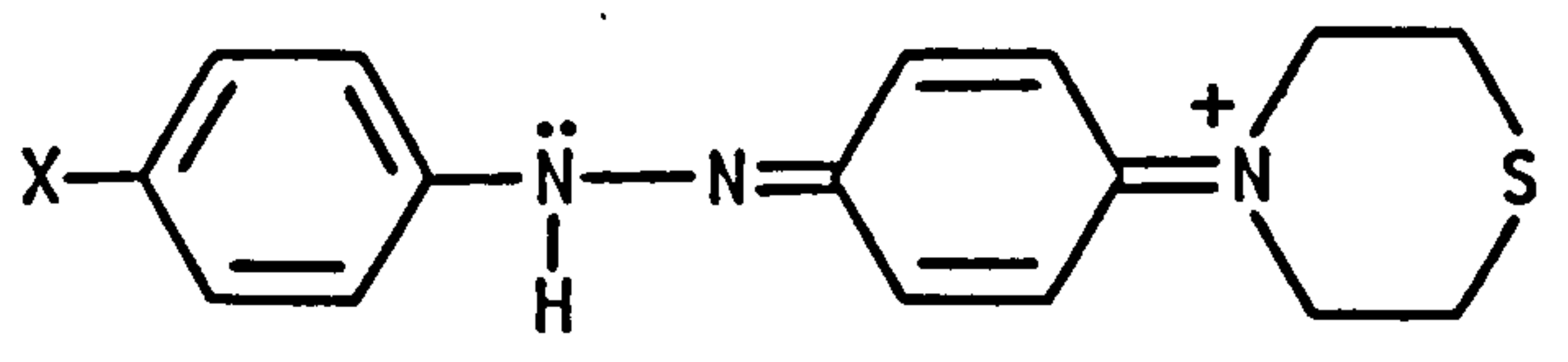
(85)

(a) X = OMe; ε_{max} = 10,400

(b) X = NO_2; ε_{max} = 47,800

terminal nitrogen atom by the electronegative oxygen atom is partly offset by partial deconjugation of the nitrogen lone pair, so that the ammonium form still predominates when substituent X is a donor or a weak acceptor. In the presence of a strong acceptor, however, this deconjugation is sufficiently resisted for the β-azo nitrogen atom to become the more favoured site for protonation.

A similar argument can be advanced for dyes in which the heteroatom is changed to the less electronegative sulphur such that relatively more of the ammonium cation is to be expected than for comparable dyes with an oxygen heteroatom. In fact, slightly more of the azonium form is observed [see 86(a) and (b)]; this result may be



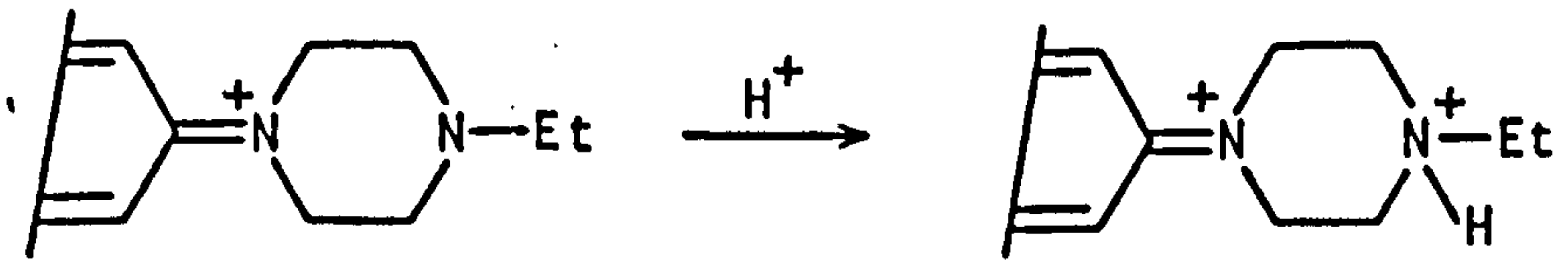
(a) X = OMe; ε_{max} = 15300

(b) X = NO_2; ε_{max} = 67400

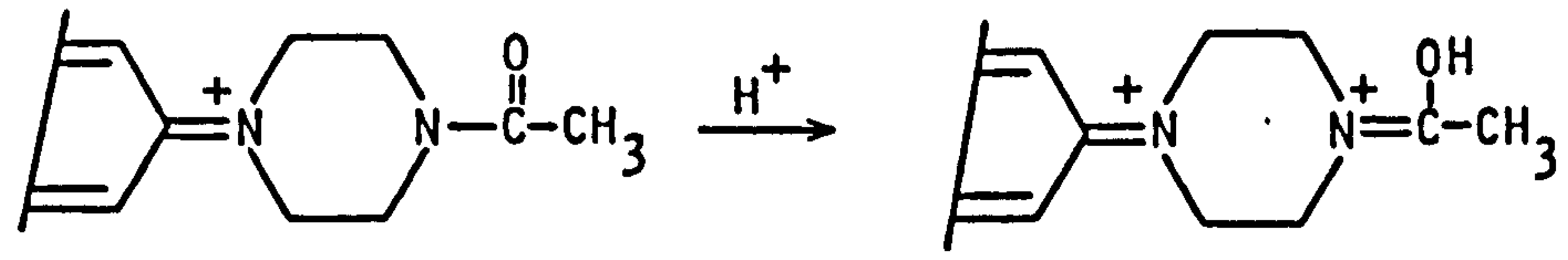
(86)

accounted for by the sulphur atom reducing the electron density at the β-azo atom relatively less than at the terminal atom, possibly by some involvement of the d-orbitals of the sulphur atom.

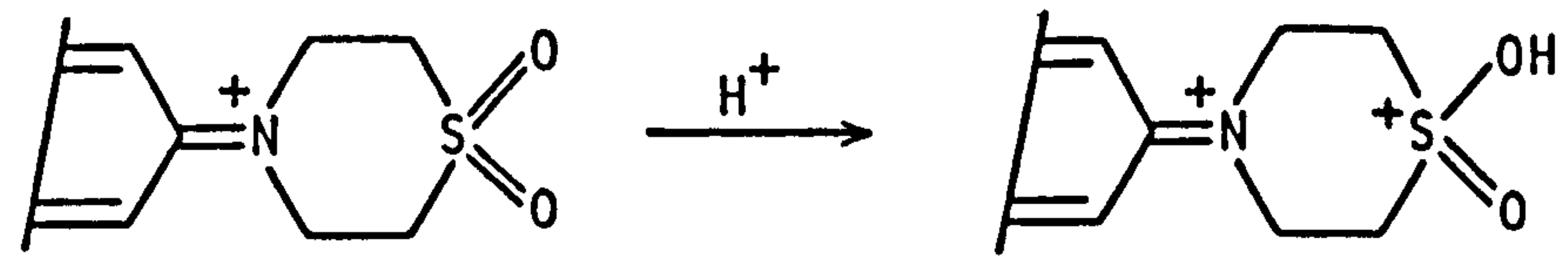
It is noticeable that the azo dyes derived from N'-ethyl- and N'-acetyl-N-phenylpiperazine (64; Y = $-CH_2N(Et)CH_2-$ and $-CH_2N(Ac)CH_2-$, respectively), and from N-phenylthiomorpholine-1,1-dioxide (64; Y = $-CH_2SO_2CH_2-$) exist in acid solution almost entirely as the azonium tautomers. These dyes probably interact with acid to develop a relatively high positive charge on the heteroatom due respectively to protonation at the heteroatom (87), at the N'-acetyl group as with (88) or at the sulphone linkage (89). In any event, the N'-acetyl group is an electron withdrawing substituent and the sulphur atom is relatively positive. The pronounced inductive effect in these cases reduces the electron density at the terminal nitrogen atom to such an extent that protonation takes place almost entirely at the β-azo nitrogen atom, even when electron donor groups are present [see for instance 90(a) and (b)], and high concentrations of acid are needed since the overall electron



(87)



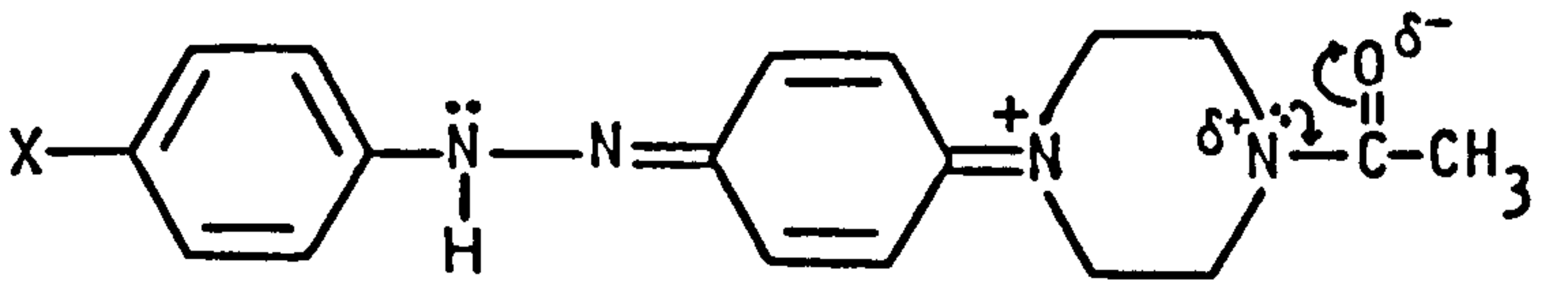
(88)



(89)

density at the two sites is much reduced.

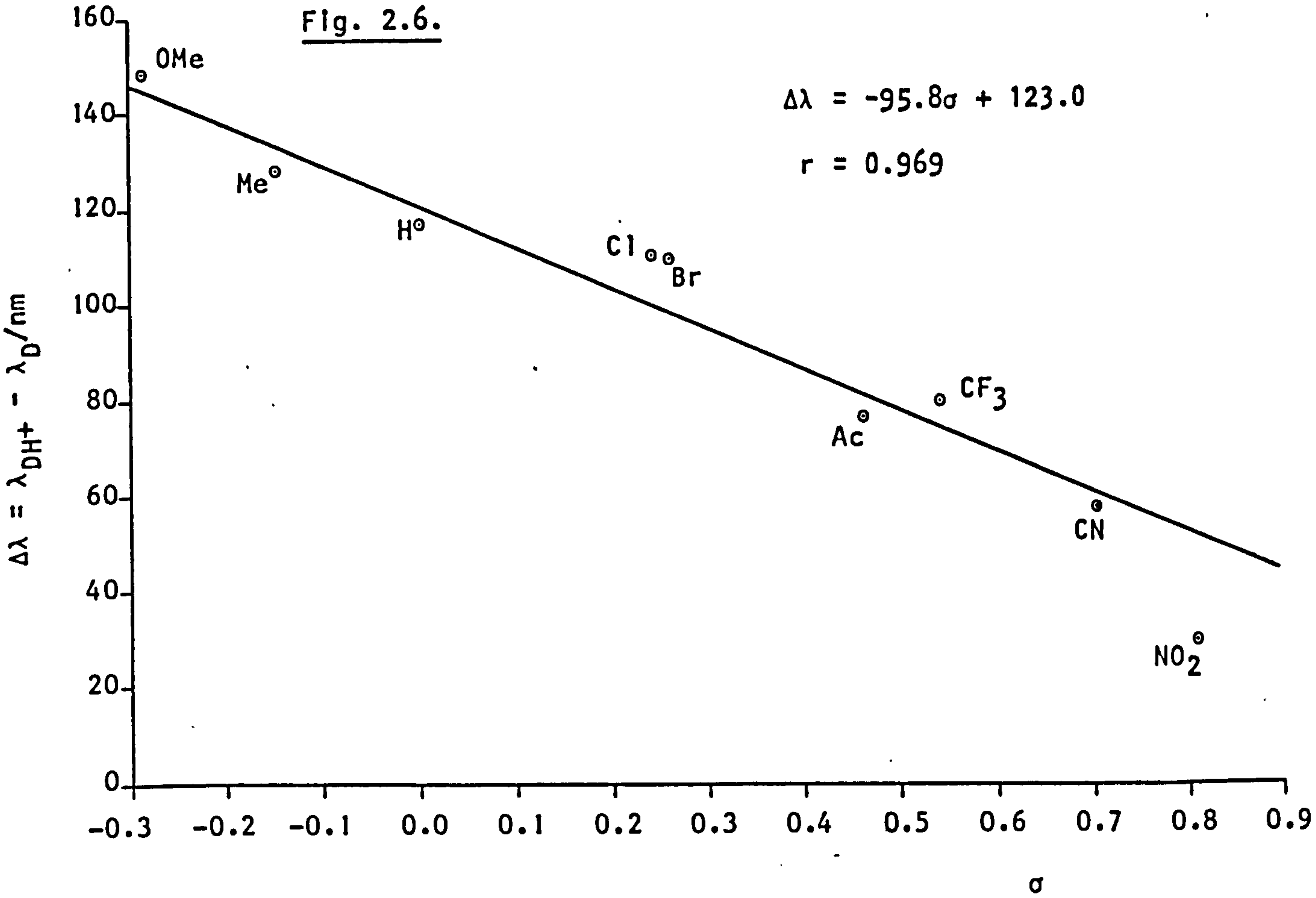
Good linear correlations are found between the wavelength shift of the dye on protonation ($\lambda_{DH^+}-\lambda_D$) and the Hammett σ value of the para-substituent (Figs. 2.6-2.13) for each of the benzenoid dye series (64). Similar correlations are found for the benzthiazol-2-yl dyes (65), although the number of points involved is rather small (e.g.,Fig. 2.14). These correlations confirm earlier work on related azo systems.[55] Donor groups in the para position produce bathochromic shifts of the first band

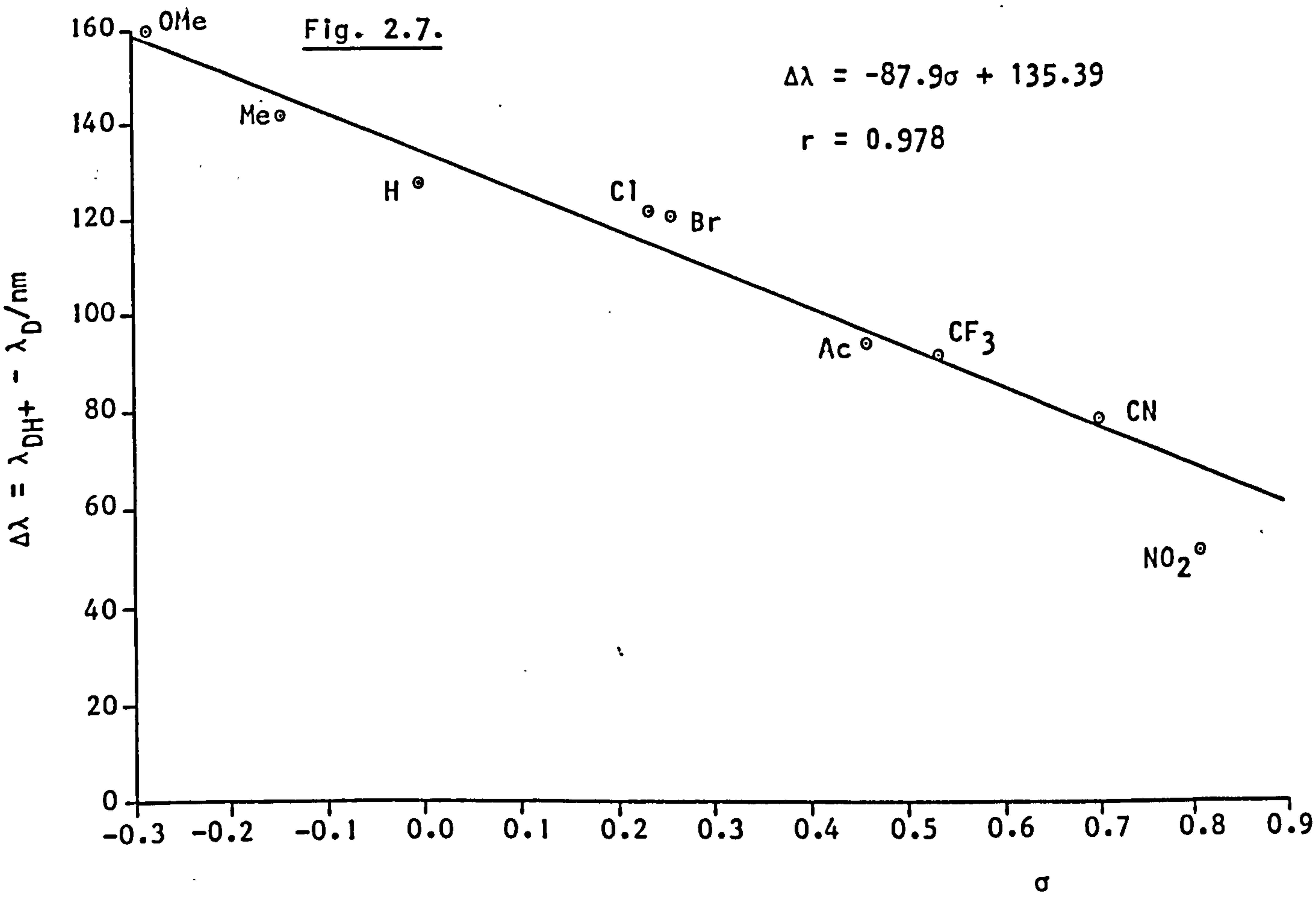


(90)

(a) X = OMe; ε_{max} = 47,600

(b) X = NO_2; ε_{max} = 77,100





Relation between Hammett substituent constants (σ) and $\lambda_{DH}+-\lambda_D$ of derivatives of 4-pyrrolidinoazobenzene (Fig. 2.6) and 4-piperidinoazobenzene (Fig.2.7) in ethanol and ethanolic hydrogen chloride (see Tables 2.5 and 2.6).

Fig. 2.8.

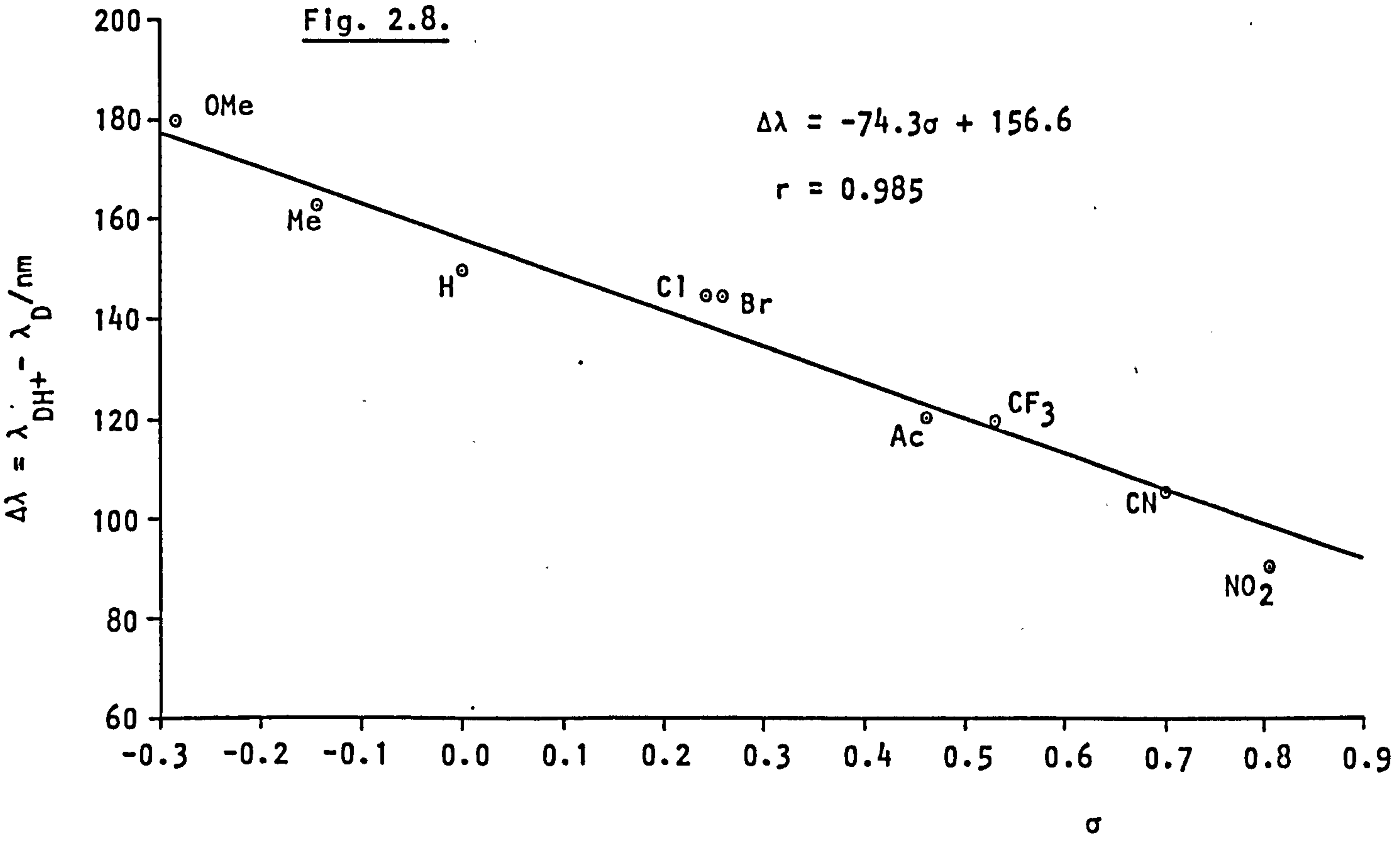
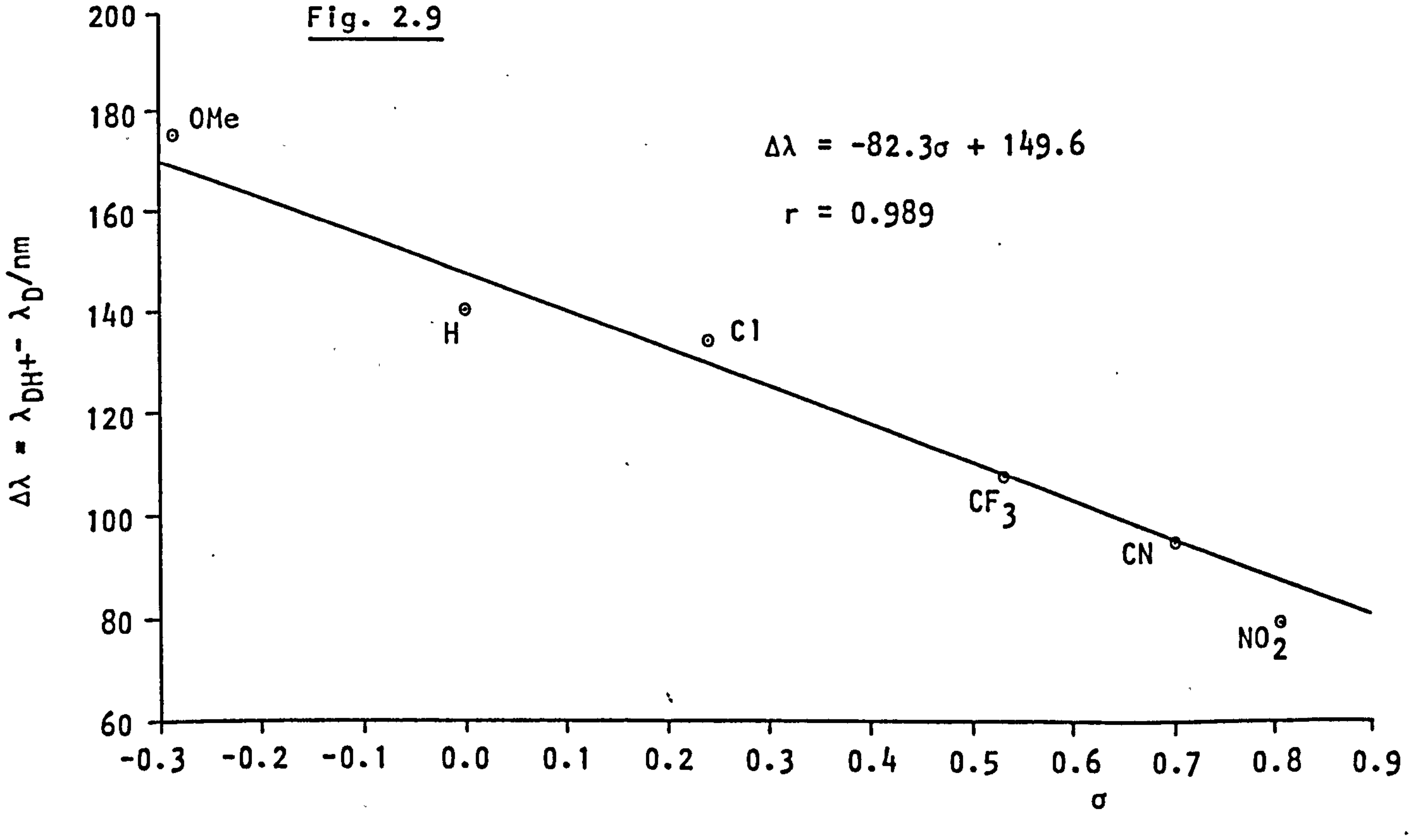


Fig. 2.9



Relation between Hammett substituent constant (σ) and $\lambda_{DH^+}-\lambda_D$ of derivatives of 4-morpholinoazobenzene (Fig. 2.8), and 4-thiomorpholinoazobenzene (Fig. 2.9) in ethanol and in ethanolic hydrogen chloride (see Tables 2.7 and 2.8).

Fig. 2.10.

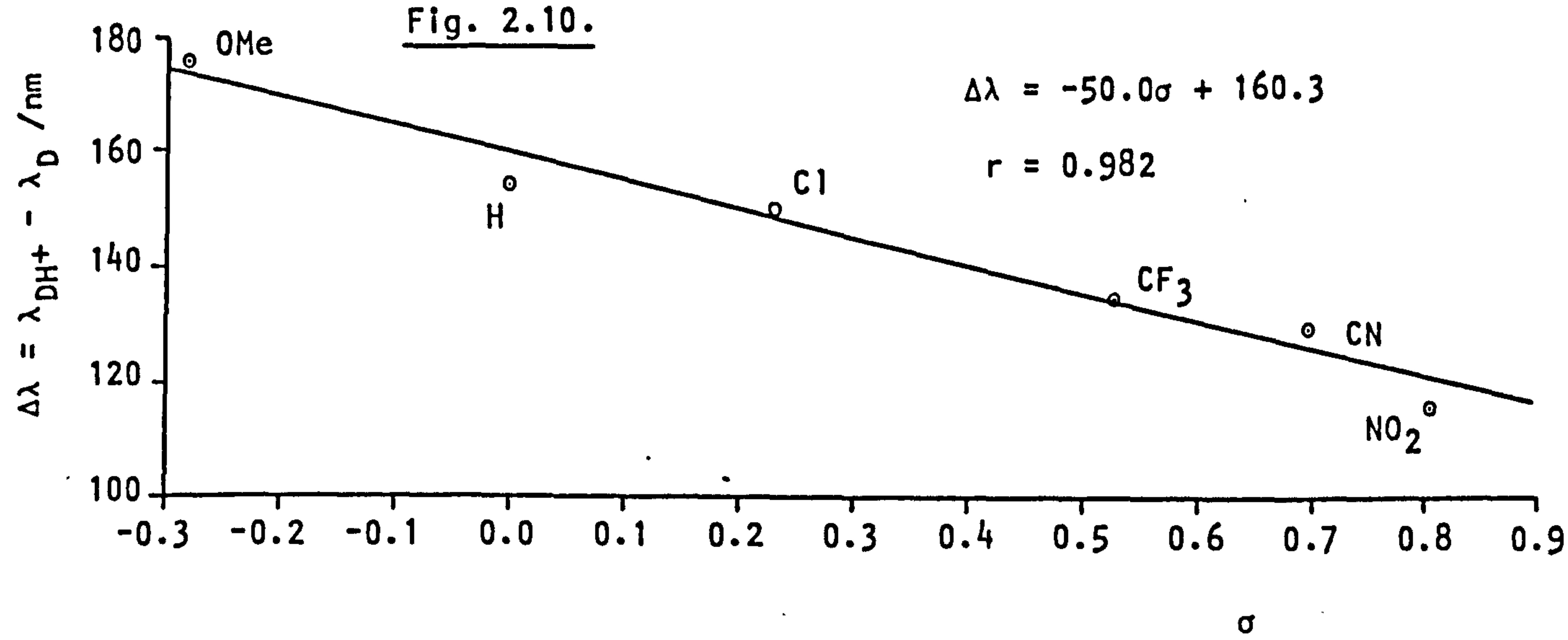


Fig. 2.11.

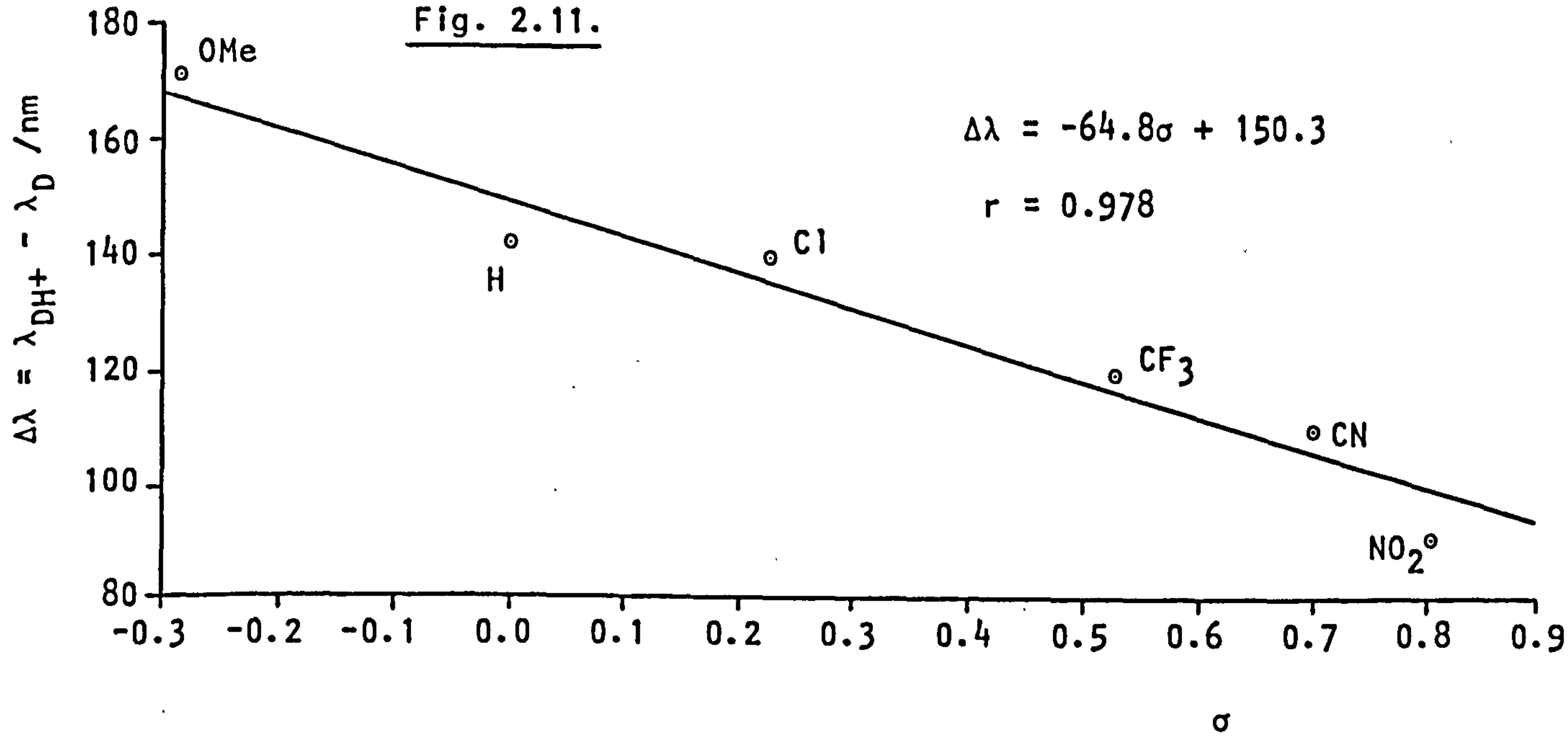
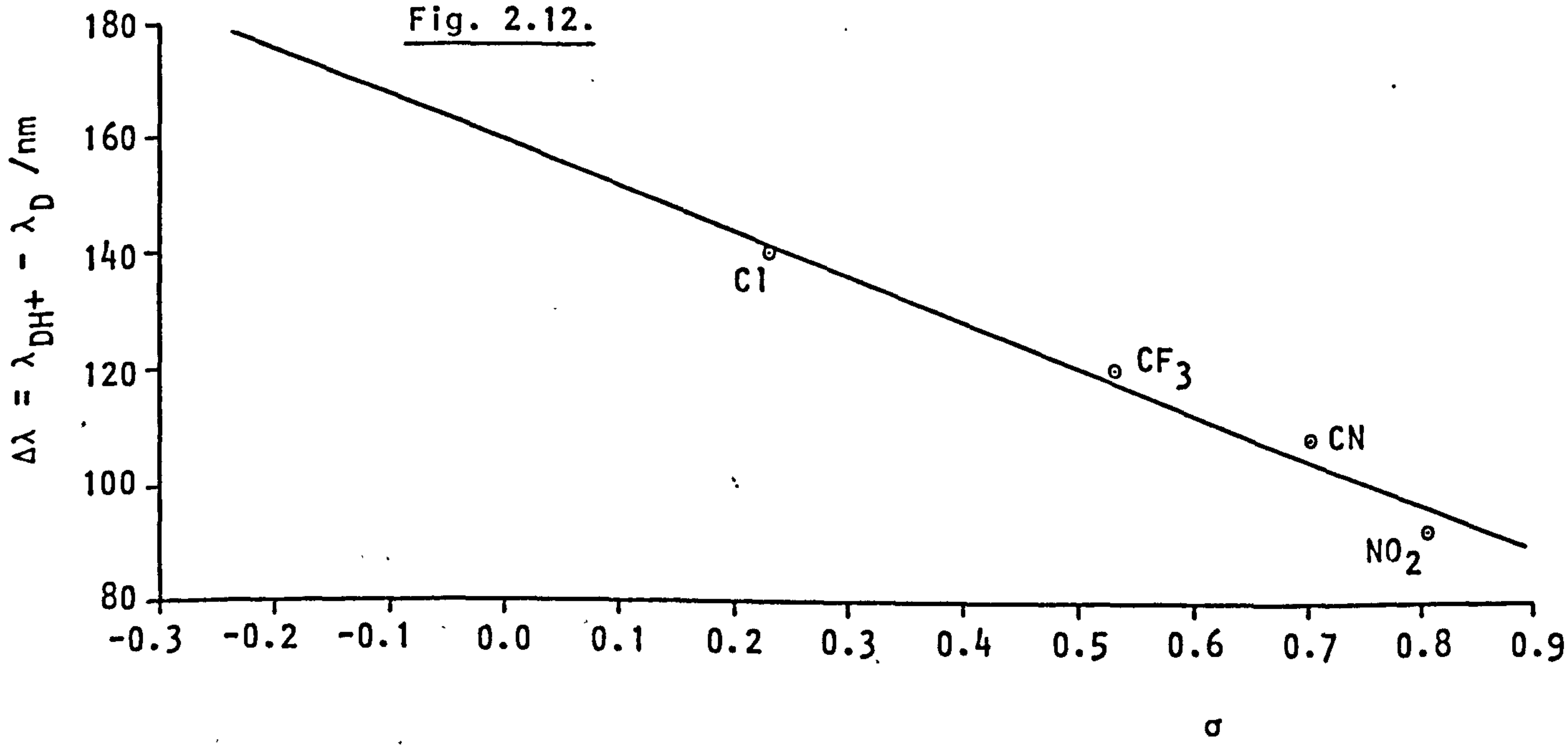


Fig. 2.12.



Relation between Hammett substituent constants (σ) and $\lambda_{DH+}-\lambda_D$ for 4,4'-disubstituted azobenzenes derived from N-phenylthiomorpholine-1,1-dioxide (Fig. 2.10), N'-ethyl-N-phenylpiperazine (Fig. 2.11) and N'-methyl-N-phenylpiperazine (Fig. 2.12) in ethanol and ethanolic hydrogen chloride (see Tables 2.9, 2.10 and 2.11, respectively).

Fig. 2.13.

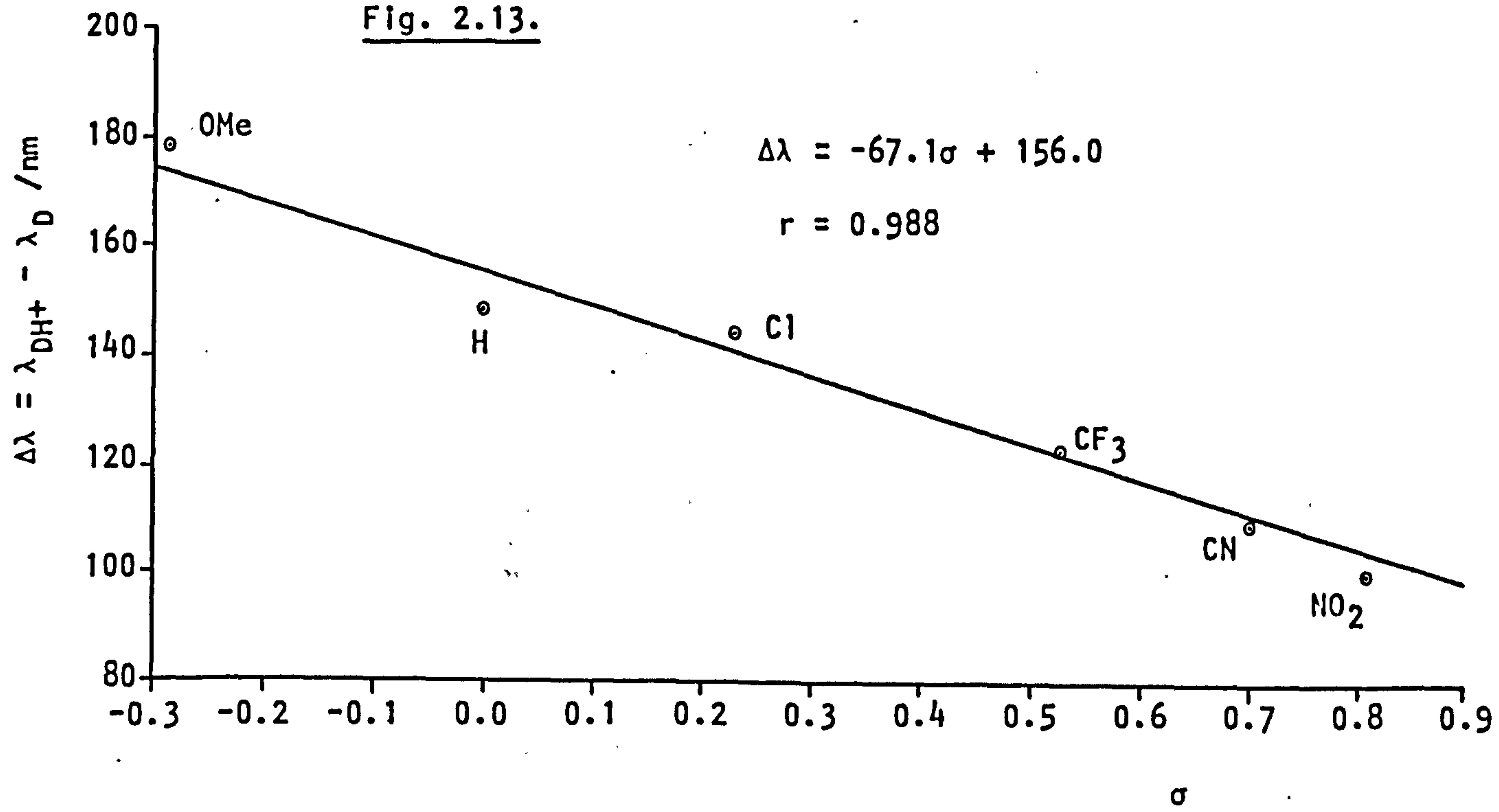
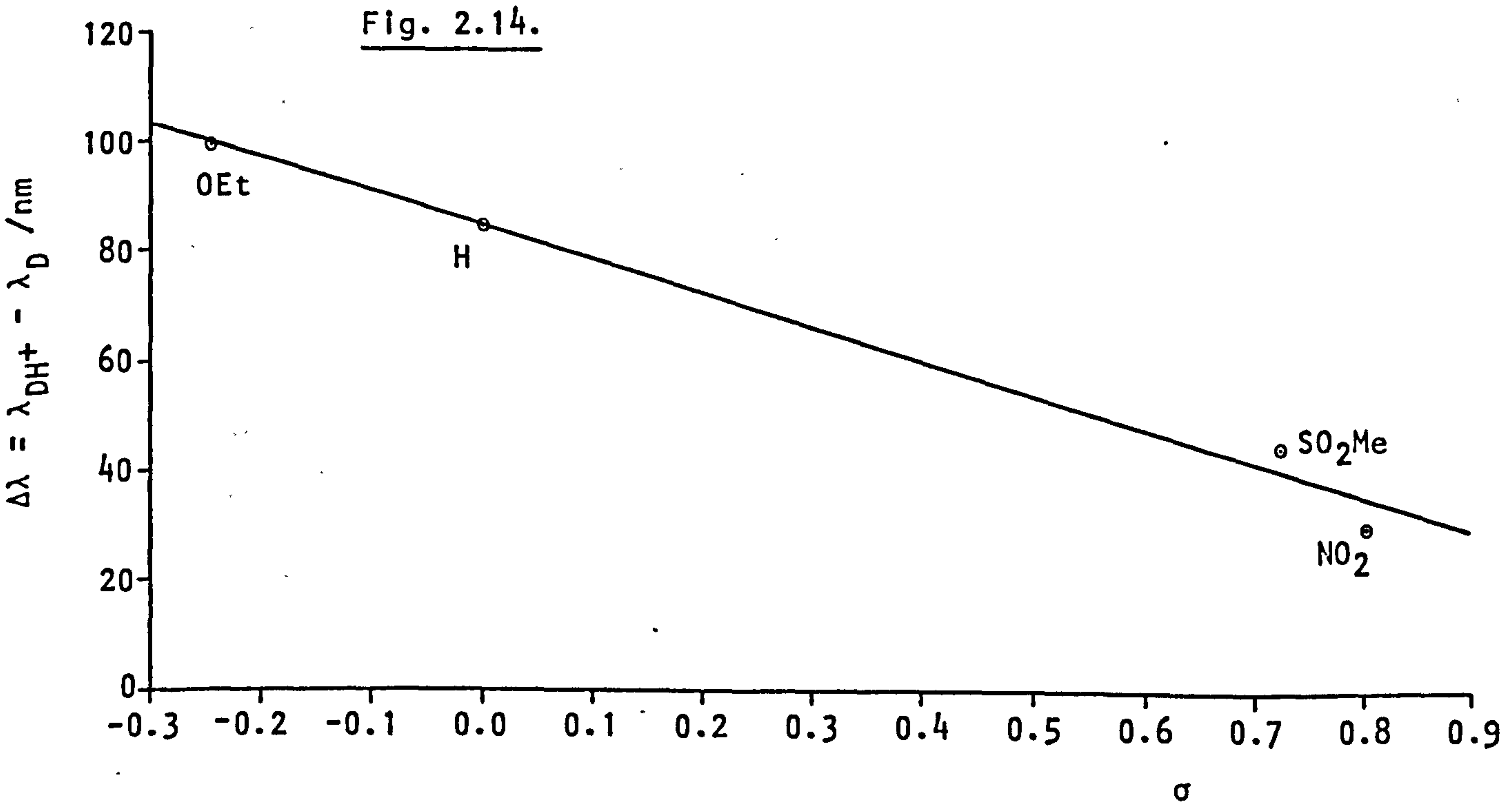


Fig. 2.14.



Relation between Hammett substituent constant (σ) and $\lambda_{DH+} - \lambda_D$ for 4,4'-disubstituted azobenzenes derived from N'-acetyl-N-phenylpiperazine (Fig. 2.13), and for N-[4-(6'-substituted-benzthiazol-2'-ylazo)phenyl]pyrrolidines (Fig. 2.14) in ethanol and ethanolic hydrogen chloride (see Tables 2.12 and 2.5, respectively).

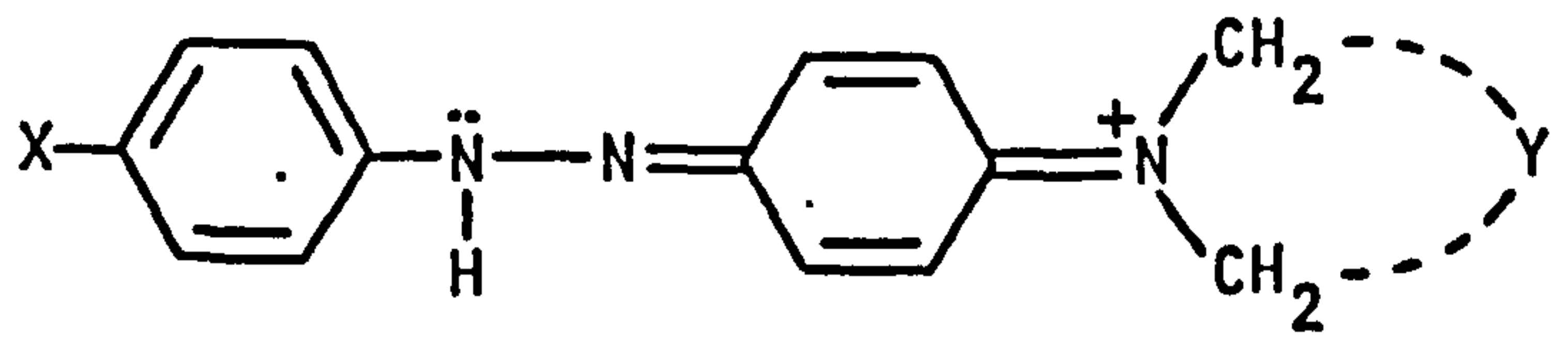
but the effect of electron withdrawing groups (as previously discussed in section 1.7) is less regular, varying both within and across the various series. The wavelength shift of the azonium cation (80) caused by the substituent X relative to its parent (X = H) appears to increase as the acceptor strength of the terminal amino group increases, when X is a strong acceptor, whereas it remains essentially constant when X is a donor group or a weak acceptor (Table 2.16). Identification of particular trends is again hampered by the irregular shapes of the azonium absorption bands.

Dyes containing a 2'-cyano substituent often show reduced intensities and absorb at slightly lower wavelengths than their 4'-isomers; this result may be due to interaction between the ortho-substituent and the protonated azo link. Much higher acid concentrations are needed to protonate these dyes and this reflects the shielding of the β-azo nitrogen lone pair of electrons by the adjacent substituent.

The pentafluoro derivatives (91) also hinder protonation at the β-azo nitrogen atom. A new band appears at ca. 470 nm; the origin of the absorption is uncertain, but may arise from protonation at the α-azo nitrogen atom.[142,143]

It is noteworthy that the azonium tautomers of dyes of types (64), (67) and (68) absorb in the region 500-565 nm [for example, dyes 92(a) and (b)], whereas the analogous bands of types (65), (66), (69) and (70) are found in the region 570-620 nm [for example, dyes 93(a) and (b)]. The diazahemicyanine cations of the latter groups are protonated at the ring nitrogen atom ortho to the azo link, leading to an extended conjugated system (95),[73,95] and thereby producing a bathochromic shift of 60-80 nm relative to the phenyl azonium system (94). It is

Table 2.16. Wavelength Shifts Produced by Substituents X in the Azonium Cation (80).



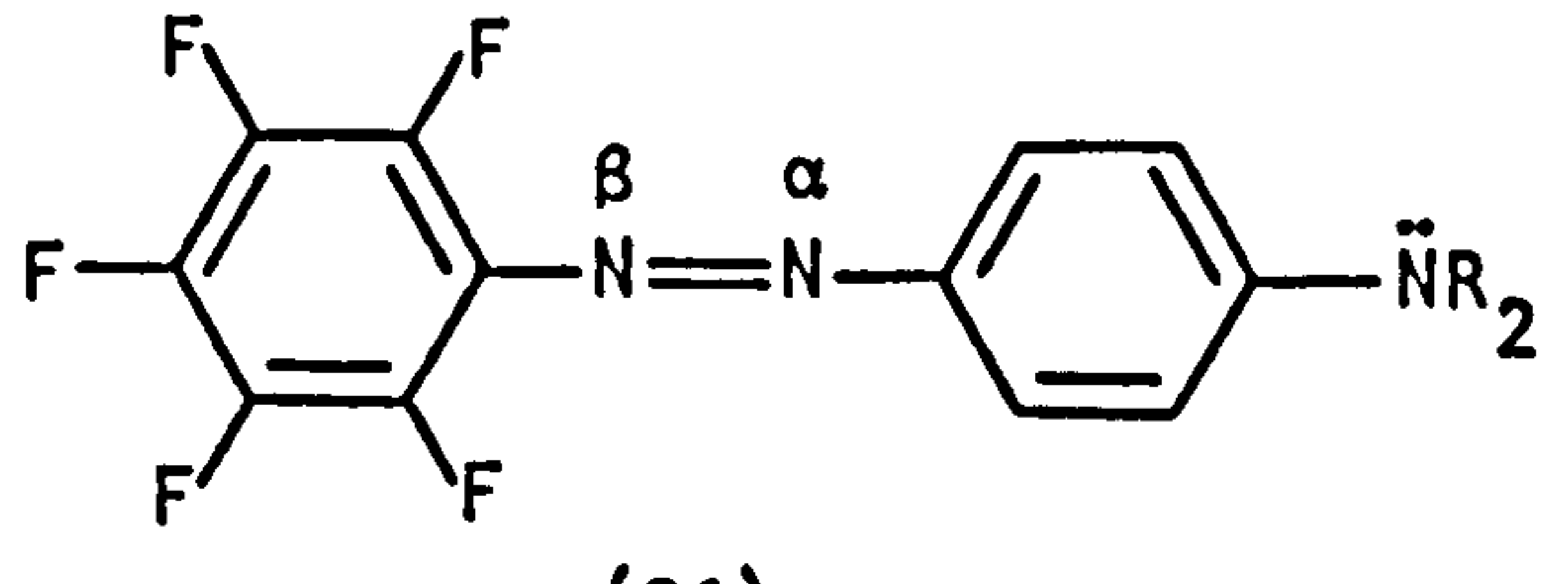
(80)

Y	X = OMe		X = Cl		X = NO_2	
	$\Delta\lambda^a$	$\Delta\lambda_m^b$	$\Delta\lambda^a$	$\Delta\lambda_m^b$	$\Delta\lambda^a$	$\Delta\lambda_m^b$
$-CH_2CH_2-$	+40	+29	+5	+4	-7	-12
$-CH_2CH_2CH_2-$	+37	+30	+3	+6	-5	-6
$-CH_2SCH_2-$	+38	+33	+3	+5	-5	-1
$-CH_2N(Et)CH_2-$[c]	+33	+28	+7	+5	+16	+2
$-CH_2OCH_2-$	+41	+31	+5	+5	-5	-7
$-CH_2N(Ac)CH_2-$	+30	+30	-3	+5	+11	+2
$-CH_2SO_2CH_2-$	+32	+28	+9	+9	+21	+8

[a] $\Delta\lambda$ = Difference between wavelengths of protonated azo dyes with substituents X and H

[b] $\Delta\lambda_m$ = As above, but with modified spectral curve (see p.78)

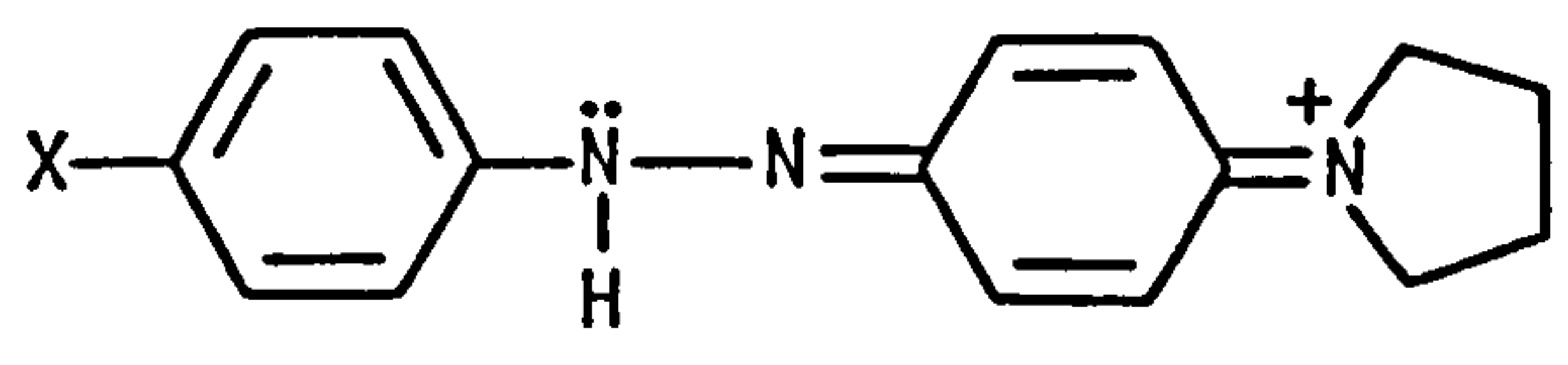
[c] Probably protonated at the t-amino group



(91)

evident that protonated benzthiazolyl dyes of the type (93) will absorb in the same region as the related commercial basic dyes (96). Hammett correlations of the types previously discussed will be of considerable use in the prediction of λ_{max} values for these dyes.

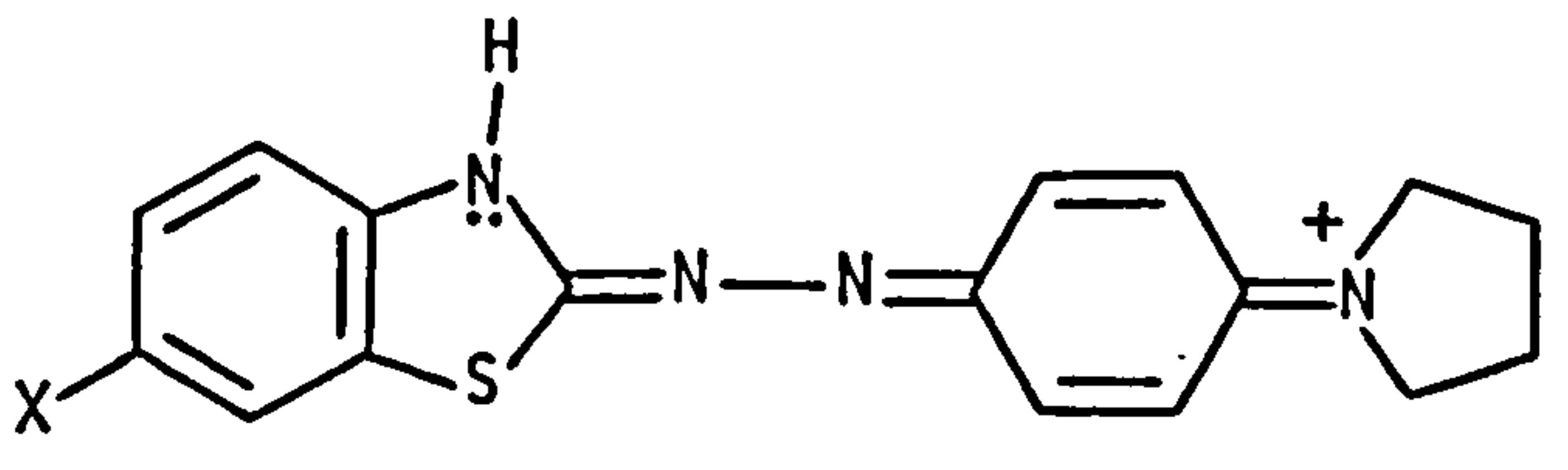
In the dyes studied, examples of negative halochromism occur only in the pyrrolidine and piperidine series, being greatest in the former group (which contains the most powerful terminal amino donor group). The positive halochromism of 4'-nitro-4-pyrrolidinoazobenzene confirms that the production of a hypsochromic shift on protonation with only one acceptor substituent present is very difficult, and requires an



(a) X = OMe; λ_{max} = 559 nm

(b) X = NO_2; λ_{max} = 512 nm

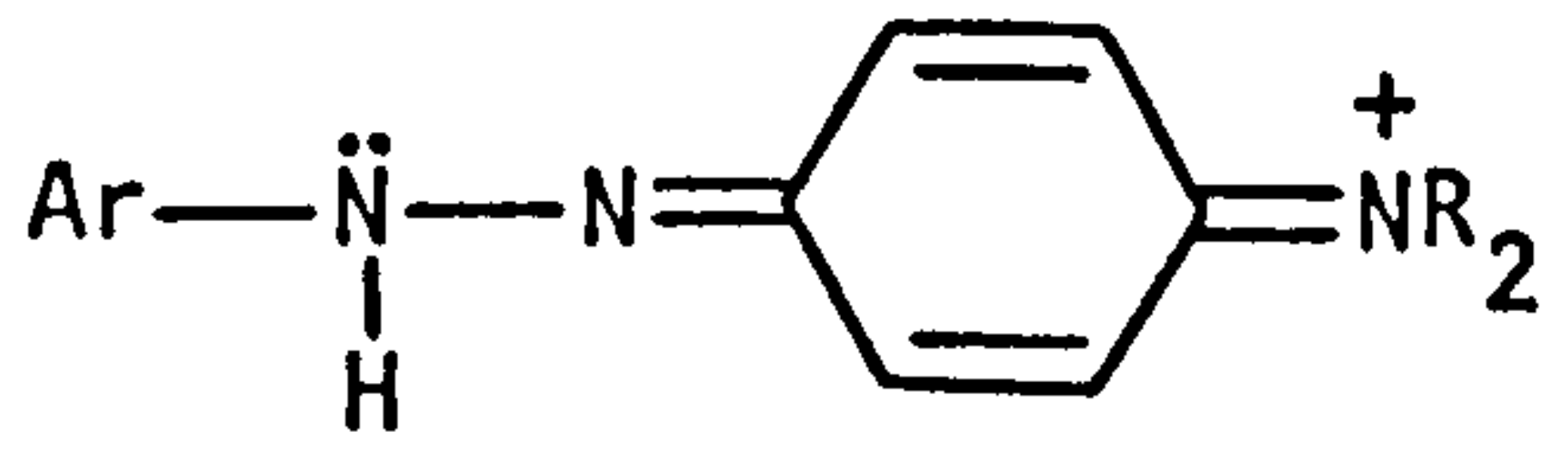
(92)

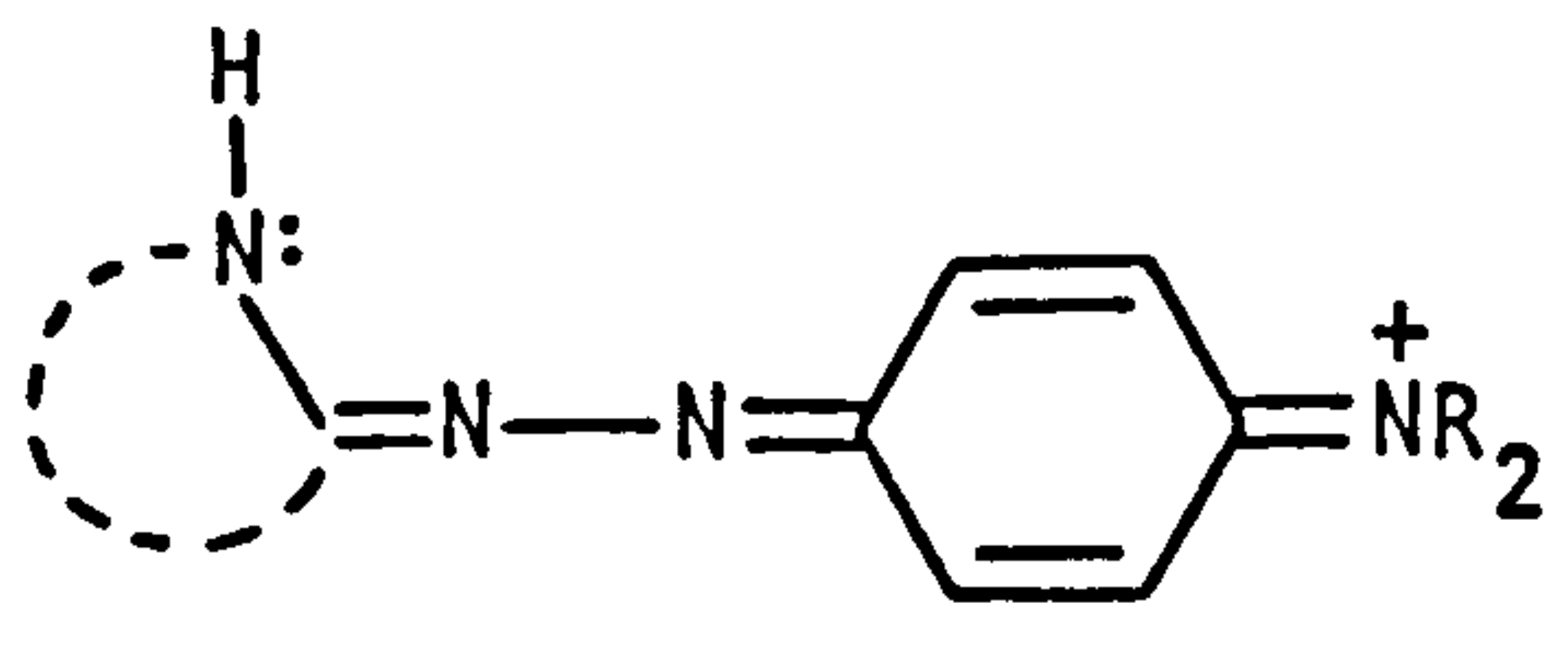


(a) X = OEt; λ_{max} = 618 nm

(b) X = NO_2; λ_{max} = 585 nm

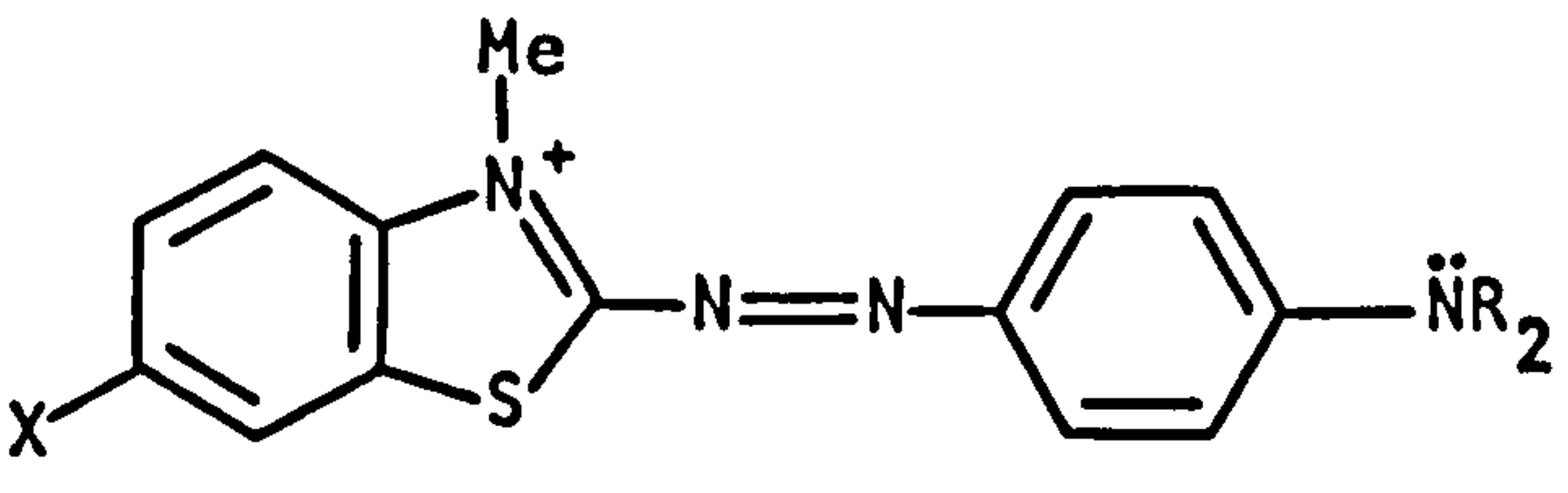
(93)



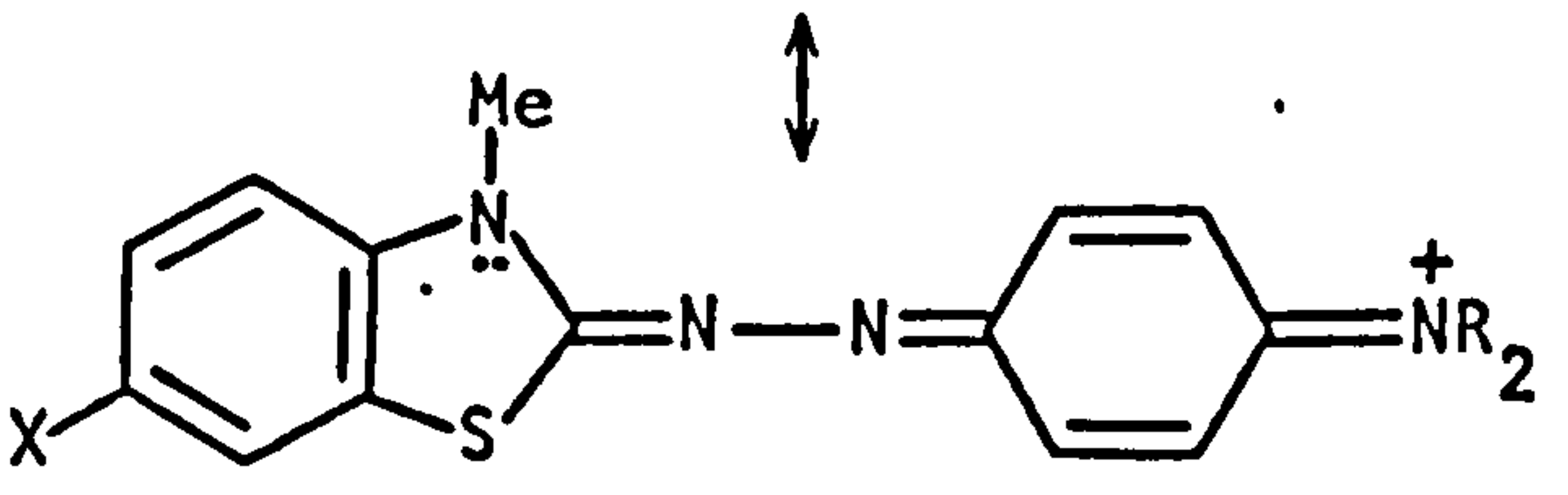


(94)

(95)

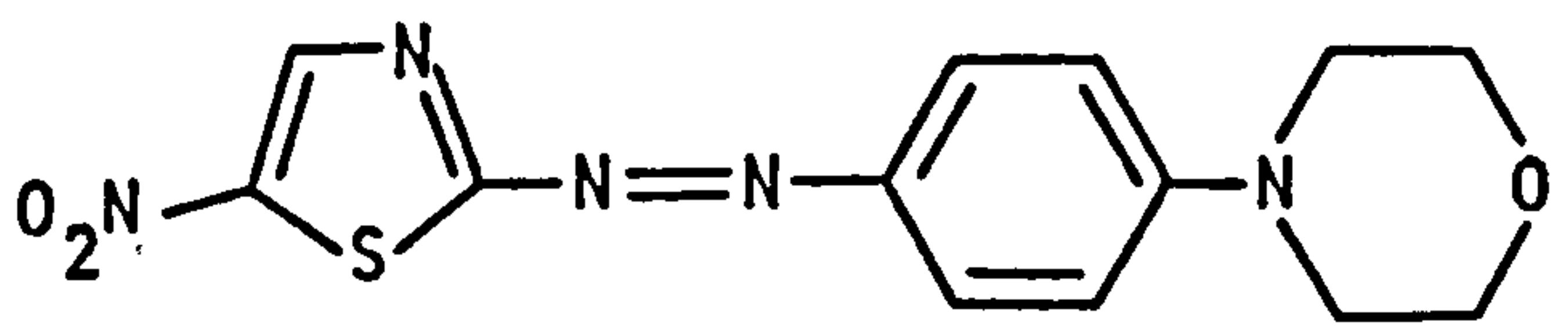


(96a)



(96b)

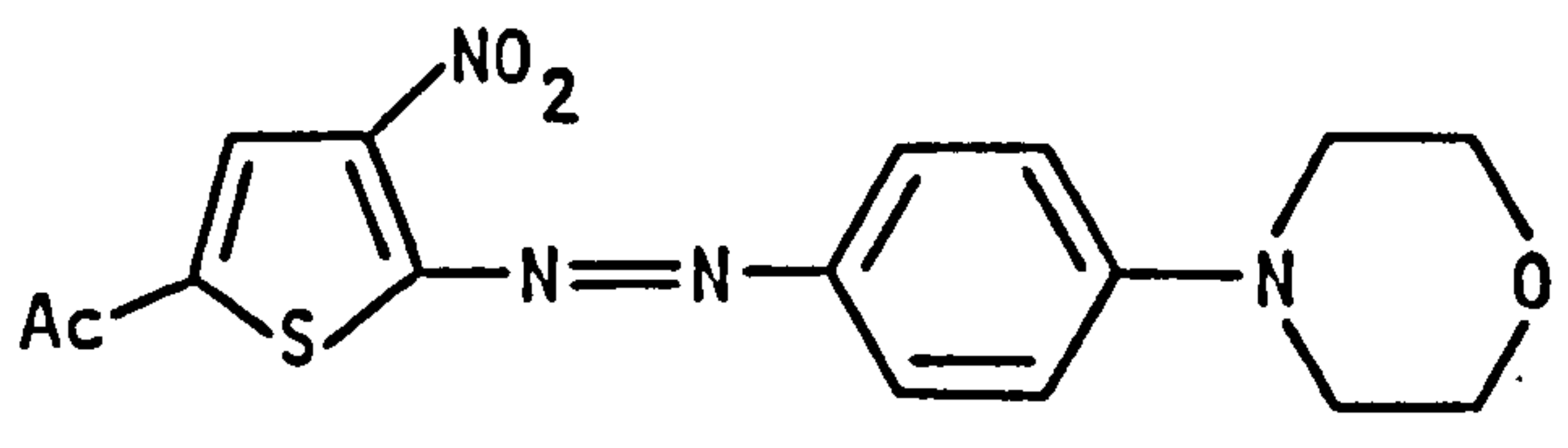
extremely strong acceptor such as tricyanovinyl.[96]. On the other hand, the presence of two acceptor groups makes this effect much easier to obtain, as for example in 2'-cyano-4'-nitro-4-pyrrolidinoazobenzene (64; 2'-CN,4'-NO_2, Y = $-CH_2CH_2-$; $\lambda_{DH^+}-\lambda_D$ = -38 nm). The long wavelength shift produced by the neutral heterocyclic dyes does not automatically produce negative halochromism; this result depends on the species involved. Thus, the two dyes (97) and (98) show similar wavelengths in neutral solution but are markedly different in acid, since they belong to the different systems (95) and (94), respectively. An extreme example of negative halochromism is provided by dye (99).



(97)

λ_{max} = 558 nm (EtOH)

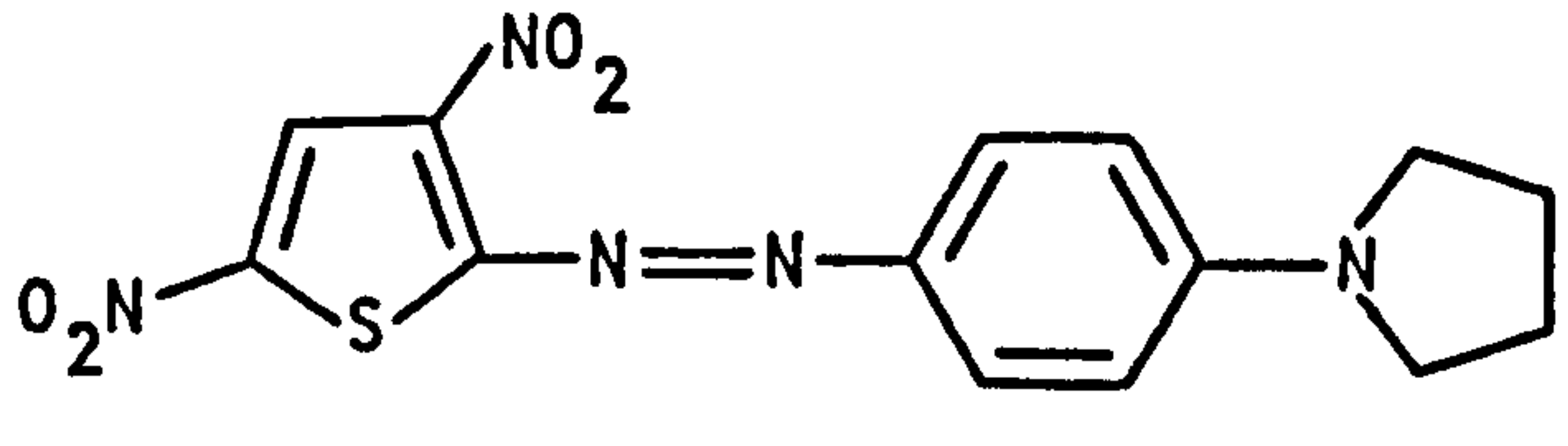
$\lambda_{DH^+}-\lambda_D$ = +46 nm



(98)

λ_{max} = 555 nm (EtOH)

$\lambda_{DH^+}-\lambda_D$ = -15 nm

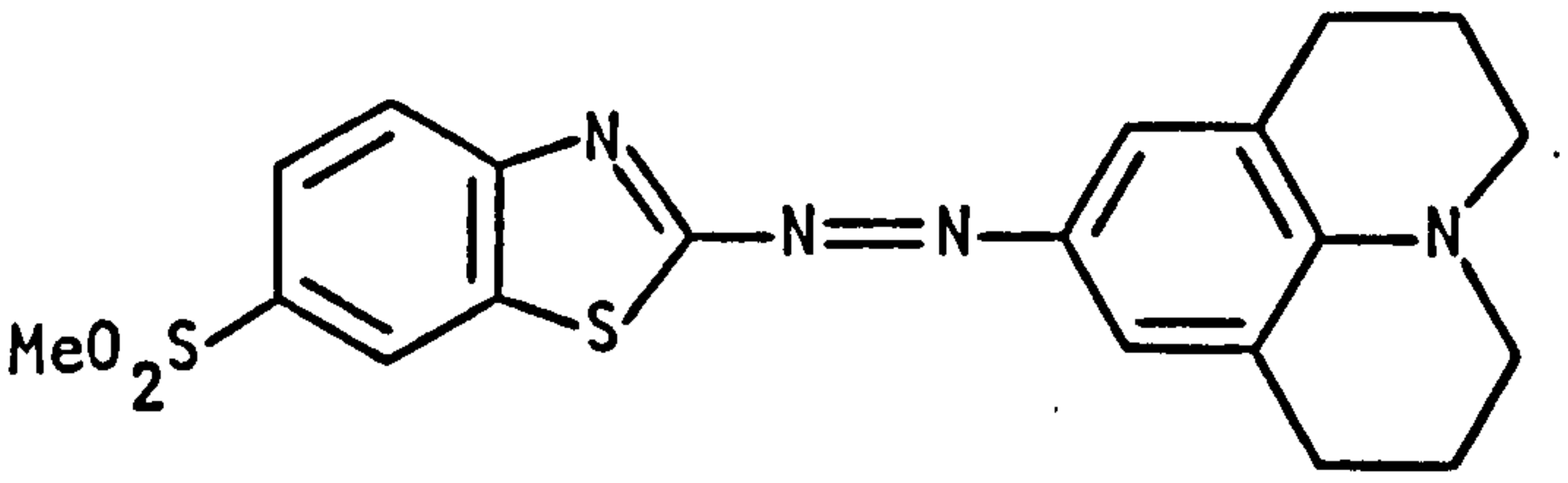


λ_{max} = 639 nm (EtOH)

$\lambda_{DH^+}-\lambda_D$ = -120 nm

(99)

Analogous benzthiazolyl azo dyes show negative halochromism only when the terminal amino group is optimally conjugated (e.g., 100),[68] due to the insulating effect of the annellated ring.

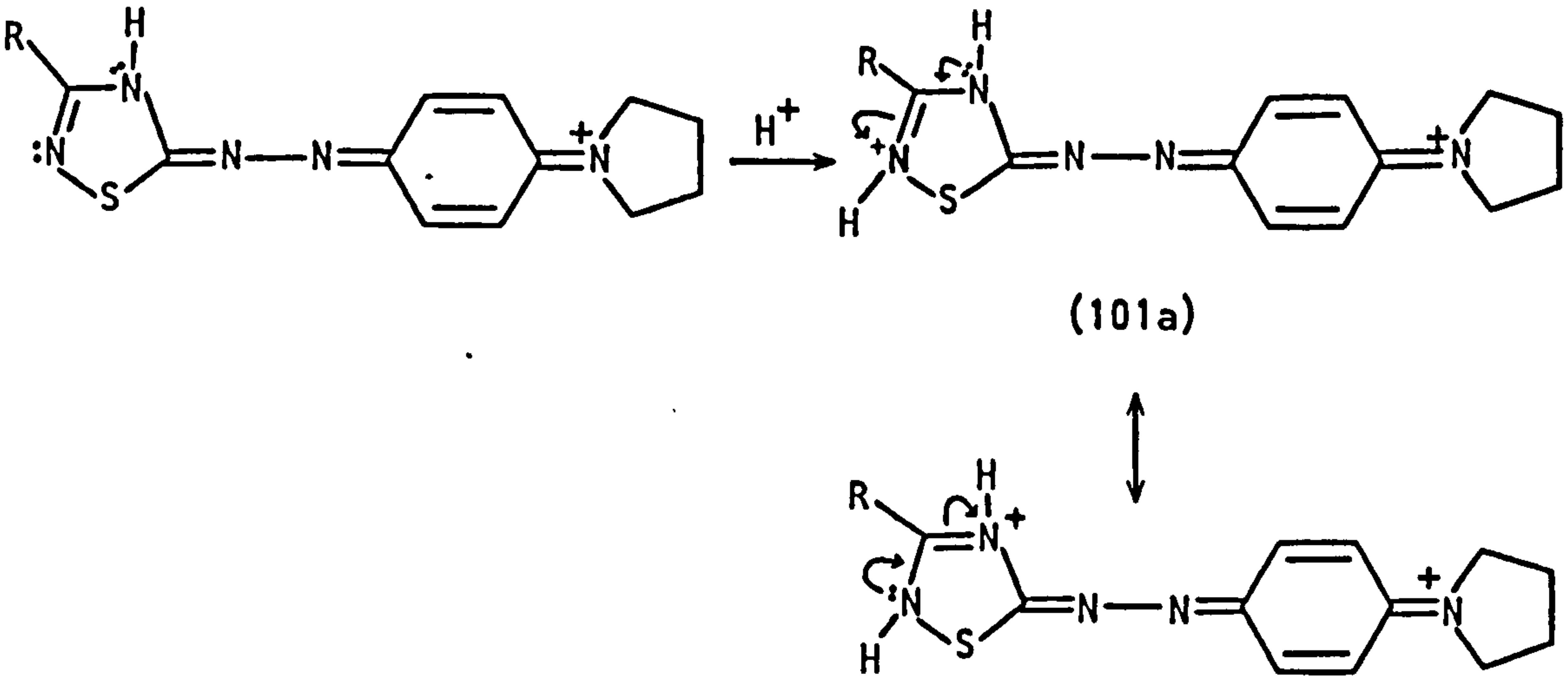


λ_{max} = 574 nm (EtOH)

$\lambda_{DH^+}-\lambda_D$ = -10 nm

(100)

The intensities of the visible band of the protonated heterocyclic azo dyes are generally high, showing the preference for this form over the ammonium form, although in some cases protonation is hampered by the presence of an <u>ortho</u>-substituent (particularly in the thienylazo dyes). Additionally, attachment of a second proton, presumably at the β-azo nitrogen atom, can reduce the apparent intensity of the univalent cation. Such protonation produces a new band at <u>ca</u>. 430-460 nm, and occurs to such an extent with the 1',2',4'-thiadiazolyl types (69) that the diazahemicyanine absorption is observed only as a shoulder on the main band of the neutral dye. As this latter band decreases, so too does the shoulder since the dication forms immediately. This anomalous ease of diprotonation is probably related to the involvement of the second nitrogen atom of the heteroaromatic ring, perhaps by the formation of (101), particularly since the 1',3',4'-thiadiazolyl dye (70; 5'-SEt) does form an intense diazahemicyanine band.



(101a)

(101b)

The univalent cations of the benzthiazol-2-ylazophenylamino dyes (65) show remarkably high ε_{max} values, exceeding 100,000 in some cases. These values are of the same order as those of the triarylmethane dyes and are reflected in the commercial development of related basic dyes (96).

2.4. Fastness Properties of the Azo Dyes

2.4.1. Light Fastness

The light fastness ratings for each series of azo dyes, together with those of some NN-diethylaminoazobenzene derivatives dyed under the same conditions, are given in Tables 2.17-2.19. Fastness to light appears to improve as the strength of the -I effect of the terminal amino ring heteroatom increases, in accordance with findings in related dyes;[16,27,68] the pyrrolidino- and piperidinoazo dyes, in which the heteroatom is absent, are rather fugitive. Light fastness ratings also increase as the electron withdrawing strength of substituents in the diazo residue increases, a trend previously observed by some workers[14] but not by others,[67,140] who found little change in ratings with variation in diazo ring substituents. It can be concluded that strong

Table 2.17. Light Fastness Ratings on Polyester[a] of some Azo Dyes Derived from (a) N-Phenylpyrrolidine (64-70; [b] Y = $-CH_2CH_2-$), (b) N-Phenylpiperidine (64-67; [b] Y = $-CH_2CH_2CH_2-$) and (c) N-Phenylmorpholine (64-67; [b] Y = $-CH_2OCH_2-$).

Dye	Light Fastness Ratings		
	(a) Y = $-CH_2CH_2-$	(b) Y = $-CH_2CH_2CH_2-$	(c) Y = $-CH_2OCH_2-$
(i) Benzenoid Dyes (64)			
4'-OMe	1-2	2-3	3-4
4'-Me	1-2	2-3	3-4
4'-H	2	3	4
4'-Cl	2	3-4	4
4'-Br	2	3-4	3-4
4'-CF_3	2	2-3	4-5
4'-Ac	3-4	3	4-5
2'-CN	3-4	3-4	4-5
4'-CN	3-4	3-4	5
4'-NO_2	3-4	3-4	4-5
2'-CN,4'-NO_2	3-4	4	5
3',5'-$(CF_3)_2$	2	2-3	4-5
F_5	3-4	3	4-5

continued/ ....

Table 2.17. continued/ ....

Dye	Light Fastness Ratings		
	(a) Y = $-CH_2CH_2-$	(b) Y = $-CH_2CH_2CH_2-$	(c) Y = $-CH_2OCH_2-$
(ii) Heterocyclic Dyes (65-70)			
65;6'-OEt	1-2	1-2	2-3
65;6'-H	1-2	1-2	2-3
65;6'-SO_2Me	2	2	2-3
65;6'-NO_2	3	2-3	3-4
66;5'-H	2-3	2-3	2-3
66;5'-NO_2	3	3-4	3
67;3',5'-$(CN)_2$, 4'-Me	2-3		
67;3'-NO_2,5'-Ac	3	3-4	4
67;3',5'-$(NO_2)_2$	3-4		
68;2'-CO_2Me	3-4		
68;2'-COMe	3		
69;3'-Ph	2-3		
69;3'-SMe	2-3		
70;5'-SEt	2-3		

[a] 2% dyeing

[b] See p.66

Table 2.18. Light Fastness Ratings on Polyester[a] of Some Azo Dyes Derived from (a) N-Phenylthiomorpholine (64-66;[b] Y = $-CH_2SCH_2-$), (b) N'-Ethyl-N-phenylpiperazine (64-66;[b] Y = $-CH_2N(Et)CH_2-$), and (c) N'-Acetyl-N-phenylpiperazine (64-66;[b] Y = $-CH_2N(Ac)CH_2-$).

Dye	Light Fastness Ratings		
	(a) Y = $-CH_2SCH_2-$	(b) Y = $-CH_2N(Et)CH_2-$	(c) Y = $-CH_2N(Ac)CH_2-$
(i) Benzenoid Dyes (64)			
4'-OMe	1-2		2
4'-H	2		3
4'-Cl	2		4-5
4'-CF_3	2-3	3	4-5
4'-CN	3	3	4
4'-NO_2	2-3	3	4
2'-CN,4'-NO_2	3-4	3	4
(ii) Heterocyclic Dyes (65,66)			
65;6'-NO_2	2-3		3
66;5'-NO_2	2		

[a] 2% dyeing

[b] See p.66

Table 2.19. Light Fastness Ratings on Polyester[a] of Some Azo Dyes Derived from (a) N-Phenylthiomorpholine-1,1-dioxide (64;[b] Y = $-CH_2SO_2CH_2-$), and (b) NN-Diethylaniline (30).[c]

Dye	Light Fastness Ratings (a) 64; Y = $-CH_2SO_2CH_2-$	(b) 30
4'-OMe		1-2
4'-Me		2
4'-H		2
4'-Cl	4	3-4
4'-Br		3-4
4'-CF_3	5	3-4
4'-Ac		4
4'-CN	4	4-5
4'-NO_2	4	4-5

[a] 2% dyeing

[b] See p.66

[c] See p. 57

acceptor groups are associated with improved stability to light. The suggestion that meta-substitution in the diazo component increases stability to light[144,145] is not borne out by the various 3',5'-bistrifluoromethyl-substituted dyes (which give the same fastness ratings as the corresponding 4'-trifluoromethyl compounds), in agreement with the work of Mehta and Peters.[67]

It is widely assumed, largely on the basis of indirect evidence gained from comparative studies of fading rates, that the irreversible fading in light of azo dyes on polyester (where there is little interaction between dye and fibre) is associated with oxidative cleavage of the azo linkage.[146] PPP calculations (see Appendix I) show that the electron density at the β-nitrogen atom in the ground state of the dye is higher than that at the α-nitrogen atom, suggesting that oxidative attack will occur at the former site. However, the calculations also show that the electron density at the β-nitrogen atom (and, hence, the rate of attack by oxygen) increases in the ground state as the electron-withdrawing strength of a substituent in the 4'-position increases, leading to lower fastness to light, a result in contrast with the experimental findings. The excited state of the dye molecule shows a large build up of electron density at the α-azo nitrogen atom such that oxidative attack might well occur here rather than at the β-nitrogen atom (as resonance considerations imply). Electron withdrawing substituents in the diazo component do in fact reduce the electron density at the α-nitrogen atom in the excited state, leading to the observed fastness trend. Improved conjugation of the terminal amino group, which is also predicted to increase the electron density at the α-nitrogen atom in the excited state, should also lead to low stability to light. This is indeed the case for the optimally conjugated azo-julolidine (32) and azolilolidine (33) dyes, which have fastness ratings of only 1-2, and also for the pyrrolidinoazo dyes

(Table 2.17). It can therefore be concluded that the oxidative fading of azo dyes is initiated at the α-nitrogen atom when the dye is in the excited state. This proposal implies a fairly high stability to light in the case of the piperidinoazo dyes in which steric crowding results in a relatively low electron density at the α-azo nitrogen atom, and a relatively high density at the terminal nitrogen atom, owing to inefficient conjugation of the terminal nitrogen lone pair, as witnessed by the predominance of the ammonium form over the azonium form in acid solution. However, the observed fastness ratings are somewhat inferior to those of the NN-diethylaminoazobenzenes containing acceptor groups, and the dyes are almost as fugitive as the pyrrolidino analogues.

Griffiths has suggested,[147] by analogy with the susceptibility of many simple amino compounds towards photo-oxidation, that the oxidative degradation of aminoazo dyes occurs at the amino group rather than at the azo linkage, and that reaction occurs through the ground state of the molecule since the excited state may be too short lived (on the basis of the lack of fluorescence of azo dyes) for an attack to take place. In recent work on the fading of NN-diethylaminoazobenzene derivatives,[148] preliminary findings indicate that dealkylation of the substituted amino group takes place, thereby supporting this theory. The effect of electron-withdrawing substituents in the diazo residue or when incorporated into the terminal amino group can be explained in terms of their reduction of the electron density at the amino nitrogen atom. Similarly, the low light fastness values for the piperidinoazo dyes can be accounted for by the increased electron density at the terminal nitrogen atom. However, the high fading rates of efficiently conjugated dyes, such as the previously mentioned julolidine types, are less easily explained, although it can be argued that this conjugation is much less important in the ground state of the dye, compared with the excited state, and that a relatively high electron density exists at the terminal nitrogen atom even in well conjugated dyes.

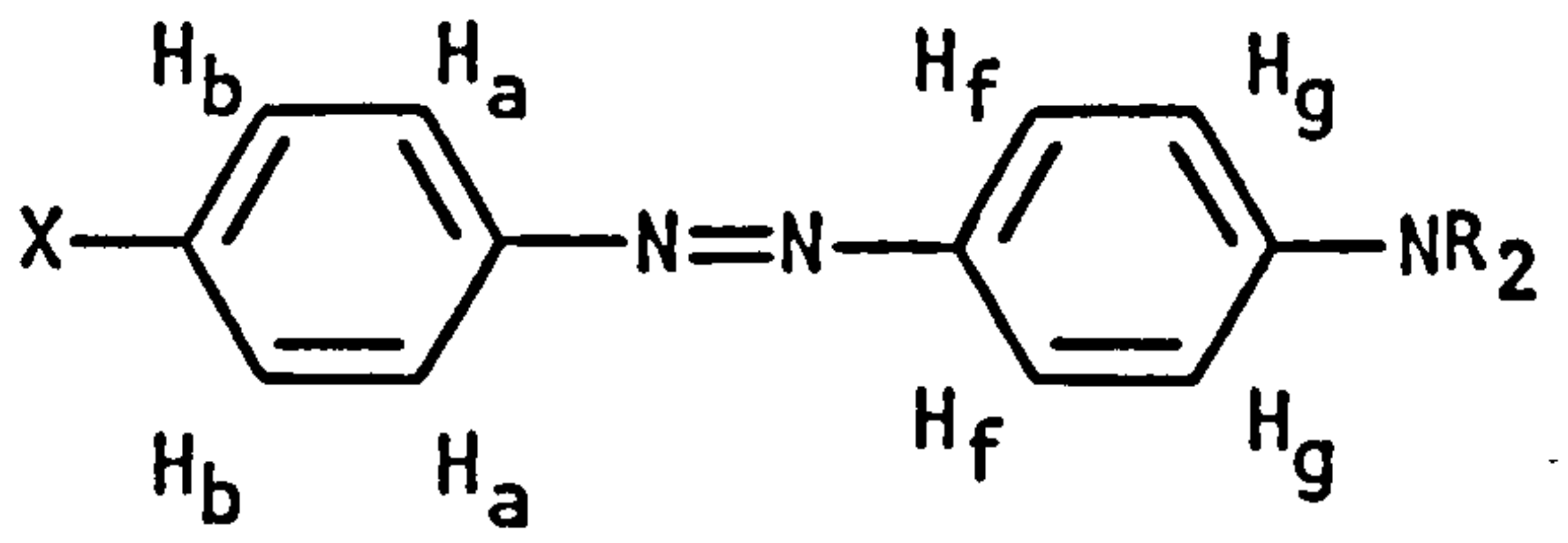
It seems likely that the oxidative fading of azo dyes can take place via attack at both the azo linkage and the amino nitrogen atom, the relative importance of each mechanism depending on the relative electron densities, in their appropriate states, of the atoms in question. It is significant that dyes with low fastness ratings are those in which either the azo linkage or the amino nitrogen atom has a relatively high electron density. The inclusion of substituents which simultaneously reduce the electron density at both sites, namely electron acceptors in the diazo residue or incorporated into terminal alkyl chains, almost always results in higher light-fastness values. On the other hand, electronic or steric effects which favour a build up of electron density at one site, at the expense of the other, invariably result in low light-fastness ratings.

2.4.2. Wash Fastness

Of the dyes tested on polyester, all had wash fastness ratings of 5 to bleeding and staining, with the exception of one compound which had a value of 4-5 for bleeding; wash fastness appears to be independent of any substituents present. The excellent values are not unexpected, however; the after treatment removes any dye left on the surface of the fibre and the dye molecules within the fibre cannot escape since the washing test takes place at temperatures, below 100°C, at which the polyester remains unswollen.

2.5. Proton Nuclear Magnetic Resonance Spectra of the Azo Dyes.

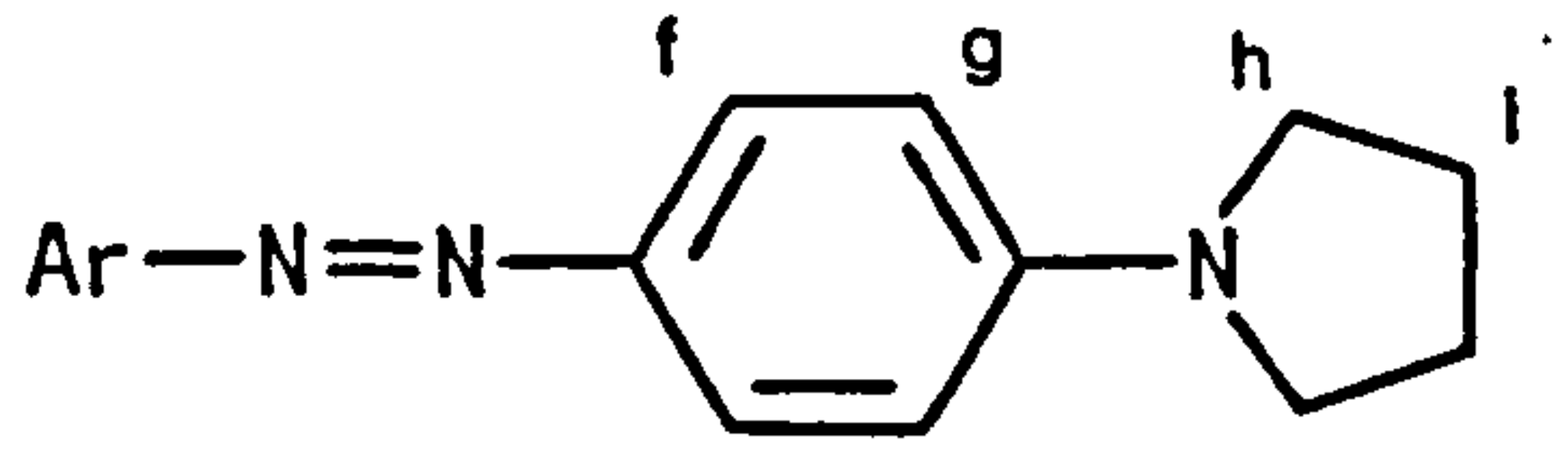
The ^{1}H-n.m.r. assignments are given in Tables 2.20-2.25, together with a footnote on p.121. The spectra of the 4,4'-disubstituted azobenzene types are easily analysed since, in most cases, four superimposed AB systems attributable to the four pairs of protons H_a, H_b, H_f and H_g (102) can be distinguished. The relative shifts of each pair can be inferred from the shape of the doublets and the observed constancy, or otherwise, of chemical shifts when the para substituents are varied. PPP molecular orbital predictions are also useful, based on the well established assumption[149-151] that within a class of compounds the chemical shift of a specific proton is determined primarily by the π-electron density at the carbon atom to which it is attached. For instance, they reveal that the H_a protons are usually more shielded than the H_f protons, even though the latter are in the ring containing the donor substituent (see Appendix 1).



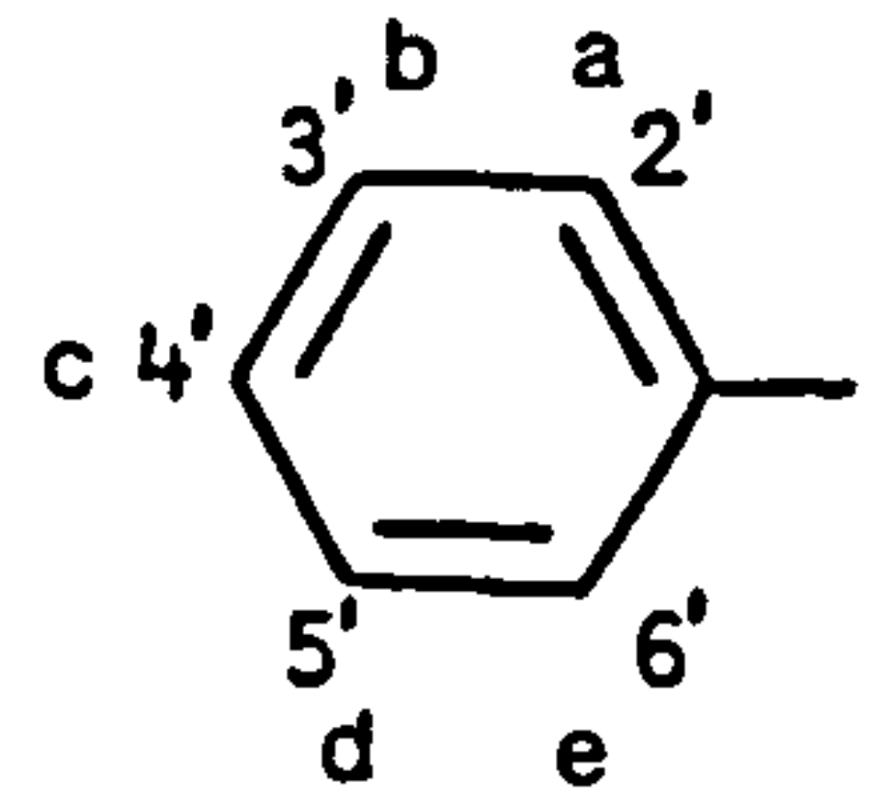
(102)

For a given substituent X, protons H_a and H_b effectively retain constant chemical shift values as the terminal amino donor group is changed (and vice-versa for H_f and H_g), thereby indicating the insulating effect of the azo linkage. Variation of X, however, causes H_b to move downfield, from δ ca. 7.0 (X=OMe) to δ ca. 8.35 (X=NO_2), approaching and eventually passing the signal of the proton (H_a) to which it is coupled. This movement reflects the reduction of electron density at the carbon atom to which H_b is attached, by the acceptor group X. The

Table 2.20. ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from N-Phenylpyrrolidine.



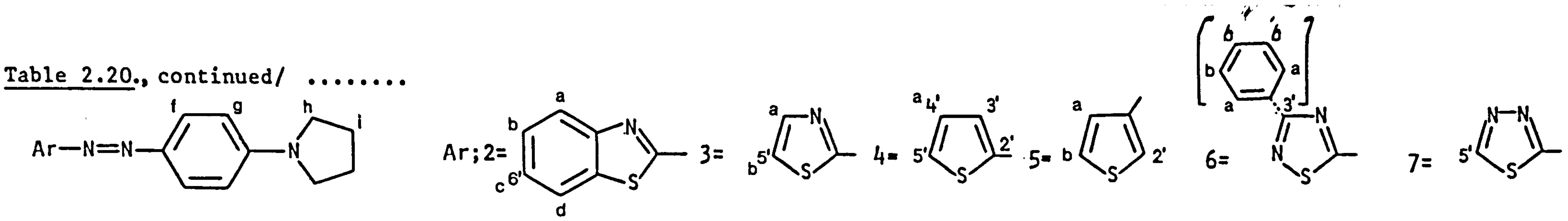
Ar; 1 =



Ar(1)	a	b	c	d	e	f	g	h	i	Other Protons	$\sigma_p{}^a$	Δδ=a-b
4'-OMe	7.86	7.00	-	7.00	7.86	7.86	6.64	3.25-3.6	1.9—2.2	OMe,3.87,s	-0.28	0.86
4'-Me	7.78	7.28	-	7.28	7.78	7.89	6.63	3.25-3.55	1.9—2.2	Me,2.42,s	-0.14	0.50
4'-H	7.90,dd	b, c, d, 7.35-7.7, m^b			7.90,dd	7.90	6.65	3.3—3.6	1.9—2.2		0.00	0.40
4'-Cl	7.82	7.43	-	7.43	7.82	7.90	6.63	3.3—3.55	1.9—2.2		0.24	0.39
4'-Br	7.78	7.58	-	7.58	7.78	7.90	6.62	3.3—3.6	1.9—2.2		0.26	0.20
4'-CF_3	7.72	7.95	-	7.95	7.72	7.92	6.64	3.3—3.6	1.9—2.2		0.53	-0.23
4'-Ac	7.86	8.09	-	8.09	7.86	7.92	6.64	3.3—3.55	1.9—2.2	COMe,2.64,s	0.47	-0.23
4'-CN	7.70	7.91	-	7.91	7.70	7.90	6.63	3.3—3.6	1.9—2.2		0.70	-0.21
4'-NO_2	7.92	8.33	-	8.33	7.92	7.92	6.64	3.3—3.6	1.95-2.2		0.81	-0.41
2'-CN	—	b,c,d,e, 7.2-8.1 (complex)				7.98	6.62	3.25-3.6	1.9—2.2			
2'-CN,4'-NO_2	—	8.59	-	8.41,dd	7.97	8.00	6.66	3.4—3.65	2.0—2.3			
3',5'-$(CF_3)_2$	8.29,s	-	7.85,s	-	8.29,s	7.93	6.66	3.3-3.6	1.95-2.25			(e-b=)-0.62
F_5	—	-	-	-	-	7.88	6.63	3.3-3.6	1.95-2.25			

continued/ ....

Table 2.20., continued/ ....



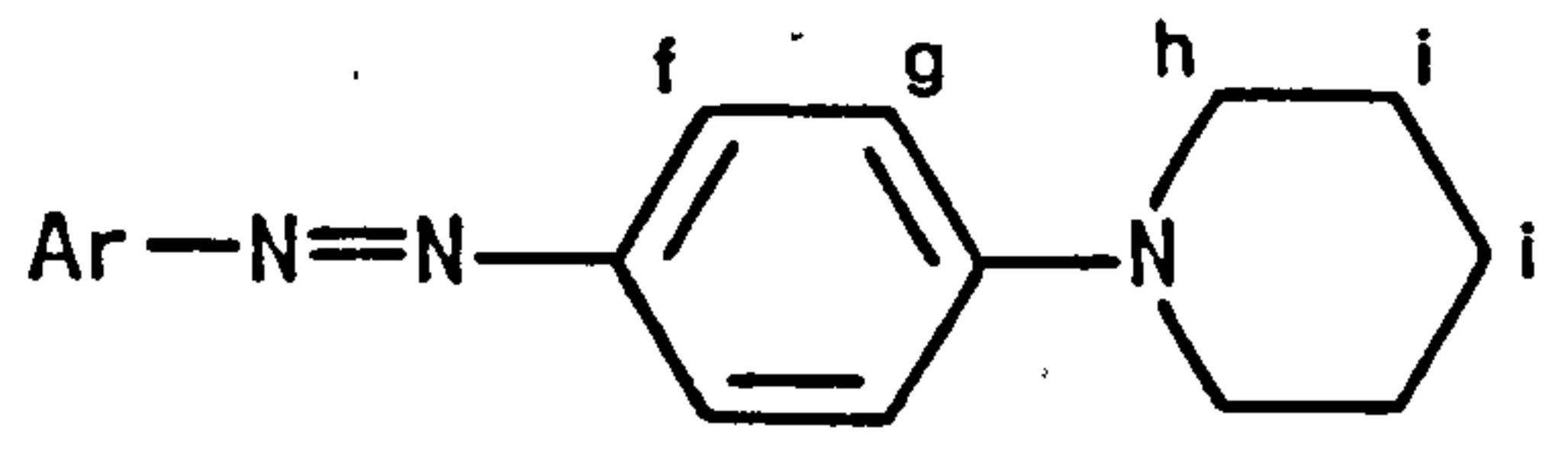
Ar	a	b	c	d	e	f	g	h	i	Other Protons
2;6'-OEt	7.38?	7.06,dd?	-	~7.27?	-	7.98	6.64	3.2—3.65	1.8—2.2	OCH_2,4.12,q;Me,1.43,t
2;6'-H	a,b,c,d, 7.2-8.2,m(complex)				-	8.02	6.65	3.4—3.7	2.0—2.35	
2;6'-SO_2Me	8.18	7.94,dd	-	8.44	-	8.04	6.68	3.4—3.7	2.0—2.3	SO_2Me,3.13,s
2;6'-NO_2	8.07	8.33,dd	-	8.73	-	8.02	6.67	3.4—3.7	2.0—2.3	
3;5'-H	7.97	7.34	-	-	-	8.01	6.68	3.35-3.65	2.0—2.25	
3;5'-NO_2	8.60,s	-	-	-	-	7.97	6.68	3.3—3.7	1.9—2.3	
4;3'-NO_2,5'-Ac	8.13,s	-	-	-	-	7.97	6.65	3.4—3.7	2.0—2.3	COMe,2.57,s
4;3',5'-$(CN)_2$, 4'-Me	-	-	-	-	-	7.91	6.63	3.4—3.65	2.0—2.25	Me,2.55,s
4;3',5'-$(NO_2)_2$	8.37,s	-	-	-	-	7.97	6.69	3.4—3.8	2.0—2.4	
5;2'-CO_2Me	7.40	7.53	-	-	-	7.95	6.64	3.3—3.6	1.9—2.2	CO_2Me,3.96,s
5;2'-COMe	7.48,s[c]	7.48,s[c]	-	-	-	7.87	6.63	3.25-3.55	1.9—2.2	COMe, 2.89,s
6;3'-Ph	8.40,dd	7.4-7.6,m	-	-	-	7.95	6.60	3.3—3.6	1.95-2.2	
6;3'-SMe	-	-	-	-	-	7.95	6.65	3.3—3.65	1.9—2.25	SMe, 2.71,s
7;5'-SEt	-	-	-	-	-	7.91	6.62	3.3—3.6	1.9—2.25	SCH_2,3.40,q;Me,1.50,t

[a] Values taken from 'Correlation Analysis in Chemistry - Recent Advances', Ed. N.B. Chapman and J. Shorter, Plenum Press, London, 1978, p.455.

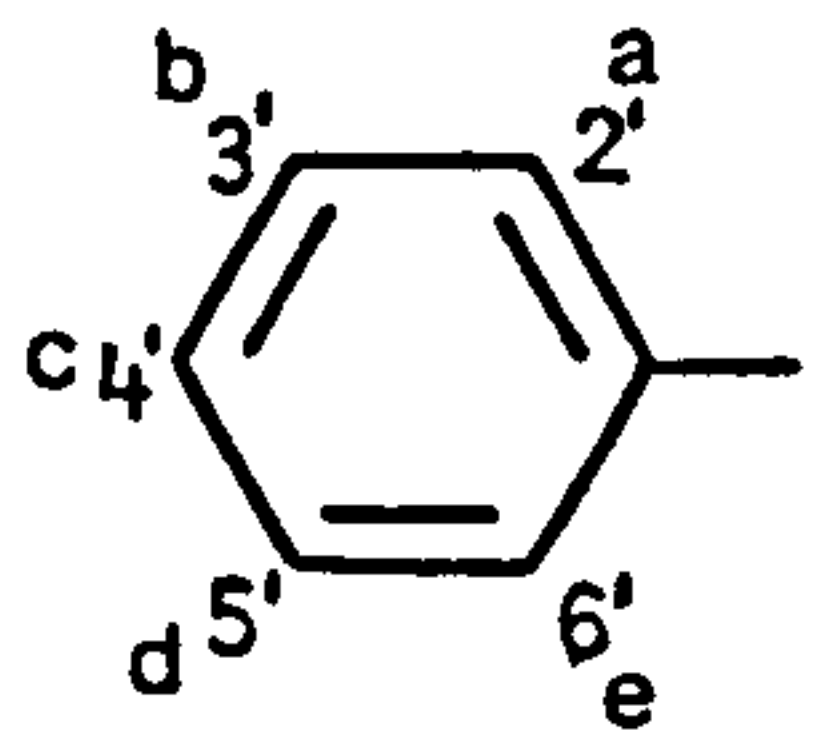
[b] H_b assigned at 7.5

[c] Collapsed doublet

Table 2.21. ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from N-Phenylpiperidine.



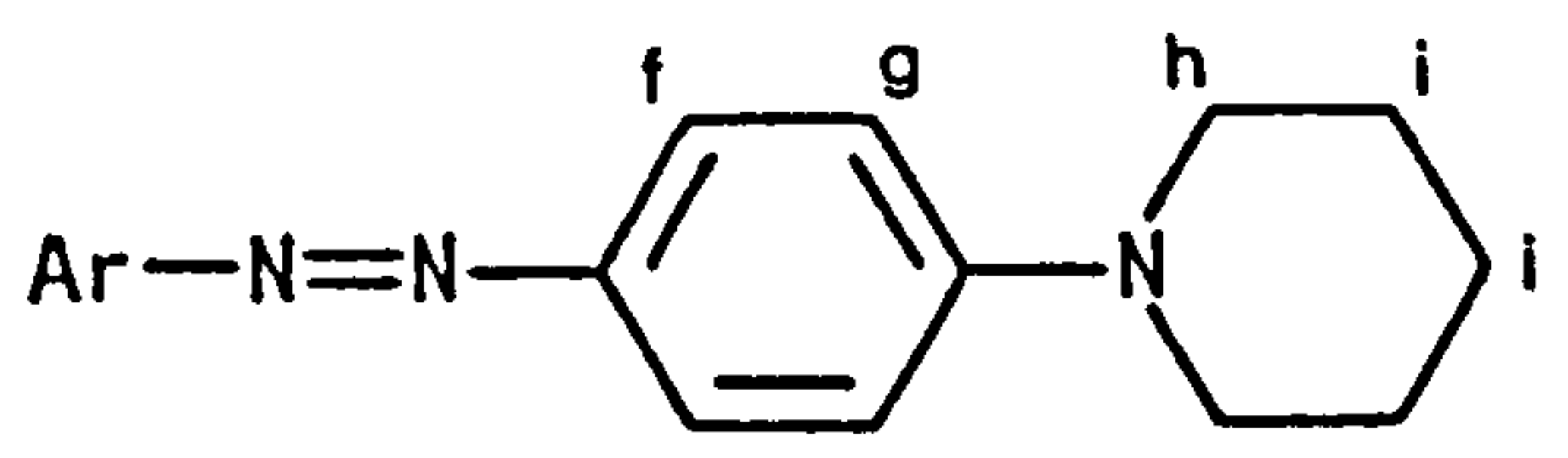
Ar; 1 =



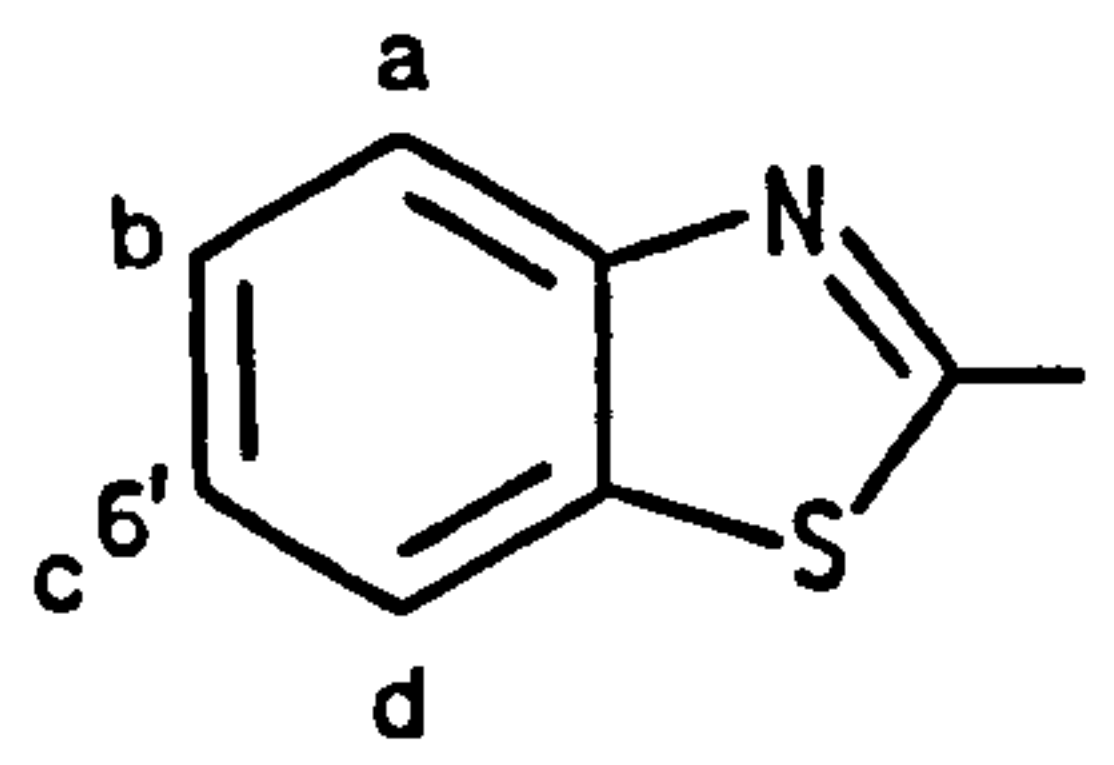
Ar (1)	a	b	c	d	e	f	g	h	i	Other Protons	Δδ=a-b
4'-OMe	7.85	7.00	-	7.00	7.85	7.87	6.97	3.35,bs	1.68,bs	OMe,3.87,s	0.85
4'-Me	7.81	7.29	-	7.29	7.81	7.88	6.98	3.38,bs	1.68,bs	Me,2.43,s	0.52
4'-H	7.90	b,c,d,7.3-7.7, (complex)^a			7.90	7.90	6.98	3.37,bs	1.66,bs		0.42
4'-Cl	7.84	7.44	-	7.44	7.84	7.90	6.97	3.41,bs	1.72,bs		0.40
4'-Br	7.77	7.59	-	7.59	7.77	7.88	6.96	3.40,bs	1.68,bs		0.18
4'-CF_3	7.73	7.96	-	7.96	7.73	7.90	6.97	3.41,bs	1.70,bs		-0.23
4'-Ac	7.87	8.10	-	8.10	7.87	7.90	6.96	3.43,bs	1.71,bs	COMe,2.66,s	-0.23
4'-CN	7.72	7.92	-	7.92	7.72	7.88	6.94	3.44,bs	1.69,bs		-0.20
4'-NO_2	7.95	8.36	-	8.36	7.95	7.95	6.98	3.47,bs	1.73,bs		-0.41
2'-CN	—	b,c,d,e,7.3-8.1 (complex)				7.97	6.94	3.43,bs	1.67,bs		
2'-CN,4'-NO_2	—	8.57	-	8.40,dd	7.93	7.93	6.90	3.50,bs	1.70,bs		(e-b=)-0.64
3',5'-$(CF_3)_2$	8.31,s	—	7.85,s	-	8.31,s	7.91	6.96	3.45,bs	1.70,bs		
F_5	—	—	-	-	-	7.87	6.93	3.45,bs	1.69,bs		

continued/ ....

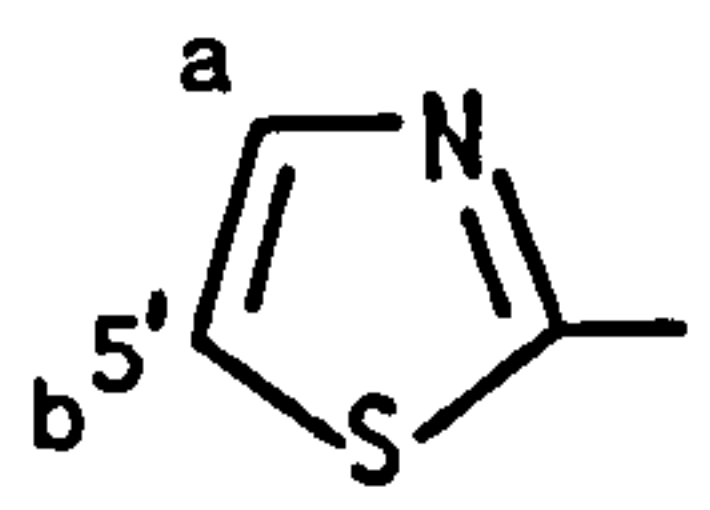
Table. 2.21., continued/.......



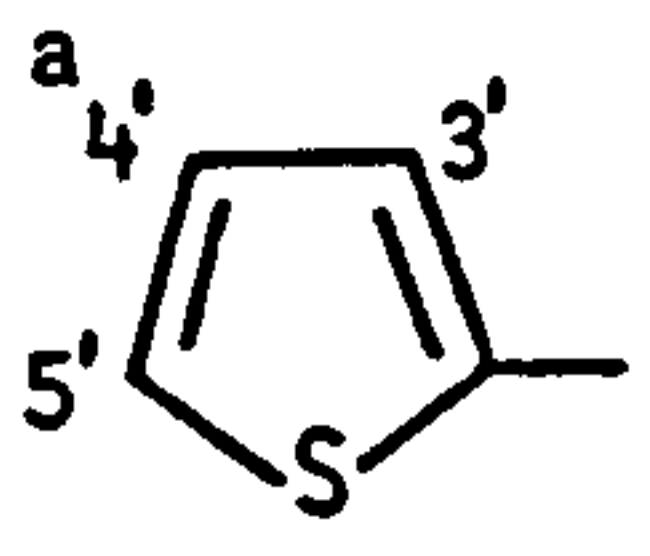
Ar; 2 =



3 =



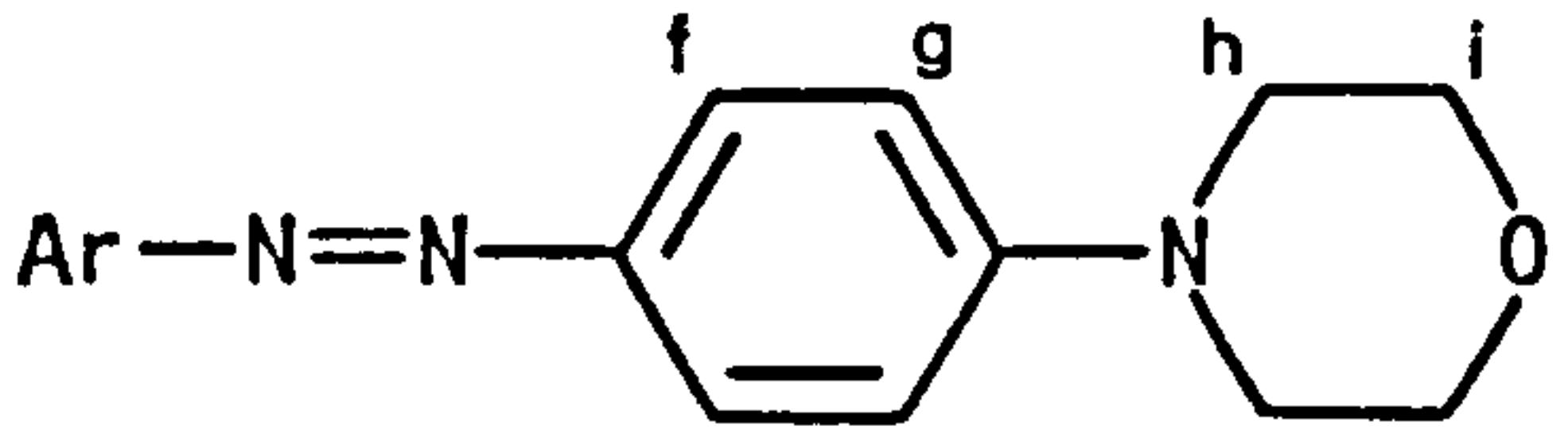
4 =



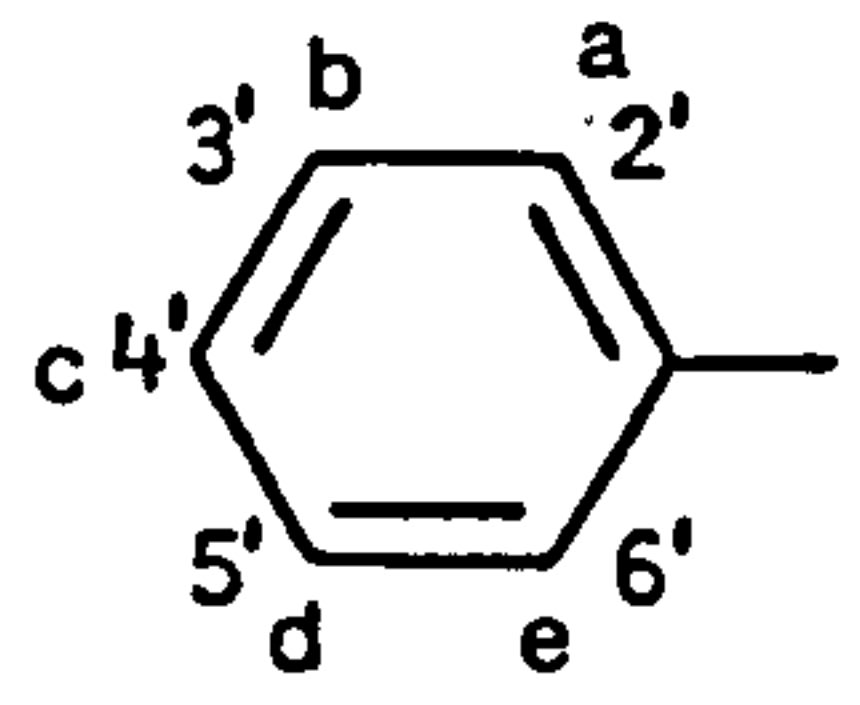
Ar	a	b	c	d	e	f	g	h	i	Other Protons
2;6'-OEt	7.37?	7.05,dd?	-	∿7.27?	-	7.95	6.92	3.46,bs	1.68,bs	OCH_2,4.11,q;Me,1.44,t
2;6'-H	a,b,c,d, 7.2-8.2, m (complex)				-	8.00	6.93	3.49,bs	1.69,bs	
2;6'-SO_2Me	8.19	7.95,dd	-	8.44	-	7.97	6.91	3.54,bs	1.70,bs	SO_2Me,3.11,s
2;6'-NO_2	8.09	8.35,dd	-	8.75	-	8.00	6.94	3.58,bs	1.73,bs	
3;5'-H	7.96	7.30	-	—	-	7.97	6.95	3.48,bs	1.70,bs	
3;5'-NO_2	8.60,s	—	-	—	-	7.97	6.93	3.60,bs	1.74,bs	
4;3'-NO_2,5'-Ac	8.13,s	—	-	—	-	7.94	6.90	3.57,bs	1.73,bs	COMe,2.57,s

[a] H_b assigned at 7.48

Table 2.22. ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from N-Phenylmorpholine.



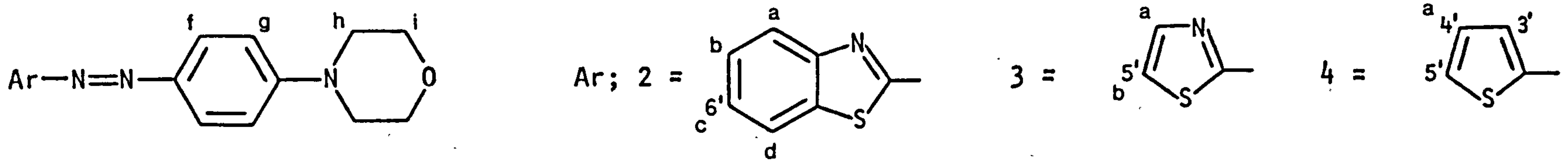
Ar;1=



Ar(1)	a	b	c	d	e	f	g	h	i	Other Protons	Δδ=a-b
4'-OMe	7.87	7.00	-	7.00	7.87	7.87	6.97	3.2—3.55	3.75–4.05	OMe,3.98,s	0.87
4'-Me	7.82	7.30	-	7.30	7.82	7.91	6.98	3.2—3.5	3.75–4.0	Me,2.42,s	0.52
4'-H	7.93	—7.3-7.7,m (complex)—^{a}			7.93	7.93	6.98	3.2—3.4	3.75–4.0		0.44
4'-Cl	7.85	7.45	-	7.45	7.85	7.91	6.97	3.2—3.45	3.7—4.0		0.40
4'-Br	7.78	7.59	-	7.59	7.78	7.90	6.96	3.2—3.45	3.7—4.0		0.19
4'-CF_3	7.74	7.97	-	7.97	7.74	7.94	6.98	3.25-3.45	3.7—4.0		-0.23
4'-Ac	7.90	8.11	-	8.11	7.90	7.94	6.98	3.2—3.45	3.7—4.0	COMe,2.64,s	-0.21
4'-CN	7.75	7.93	-	7.93	7.75	7.92	7.00	3.2—3.5	3.7—4.0		-0.18
4'-NO_2	7.95	8.36	-	8.36	7.95	7.95	6.88	3.2—3.6	3.75–4.0		-0.14
2'-CN	-	—7.3-8.1 (complex)—				8.00	6.95	3.2—3.6	3.7—4.0		
2'-CN,4'-NO_2	-	8.59	-	8.43,dd	7.95	7.98	6.93	3.3—3.6	3.75–4.05		(e-b=)-0.64
3',5'-$(CF_3)_2$	8.32,s	-	7.90,s	-	8.32,s	7.95	6.98	3.2—3.6	3.7—4.0		
F_5	-	-	-	-	-	7.90	6.95	3.3—3.6	3.7—4.0		

Continued/ ....

Table 2.22.,continued/ ....

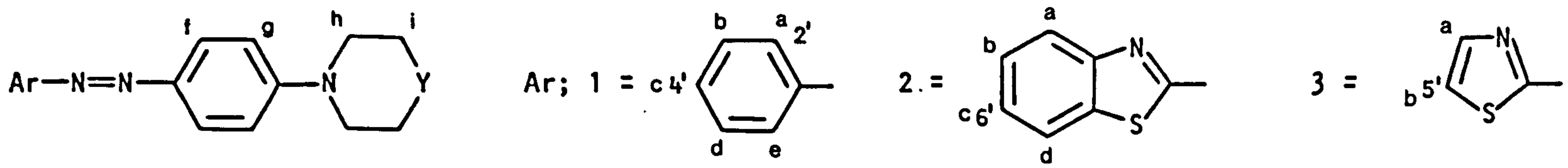


Ar	a	b	c	d	e	f	g	h	i	Other Protons
2;6'-OEt	7.38?	7.11,dd?	-	7.27?	-	7.99	6.95	3.3—3.55	3.7—4.05	OCH_2,4.13,q;Me,1.45,t
2;6'-H	a,b,c,d, 7.2-8.2,m (complex)				-	8.05	6.98	3.35-3.6	3.8—4.0	
2;6'-SO_2Me	8.25	7.97,dd	-	8.48,s[b]	-	8.05	6.96	3.4—3.6	3.75-3.95	SO_2Me,3.13,s
2;6'-NO_2	8.13	8.37,dd	-	8.76	-	8.02	6.96	3.4—3.6	3.8—4.0	
3;5'-H	7.95	7.30	-	-	-	7.97	6.94	3.4—3.6	3.75-4.0	
3;5'-NO_2	8.63,s	-	-	-	-	7.99	6.92	3.4—3.6	3.8—4.0	
4;3'-NO_2,5'-Ac	8.14,s	-	-	-	-	7.98	6.91	3.35-3.6	3.75-4.0	COMe,2.59,s

[a] H_b assigned at 7.49

[b] Collapsed doublet

Table 2.23. ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from (a) N-Phenylthiomorpholine (Y = -S-) and (b) N—Phenylthiomorpholine-1,1-dioxide (Y=-SO_2-).

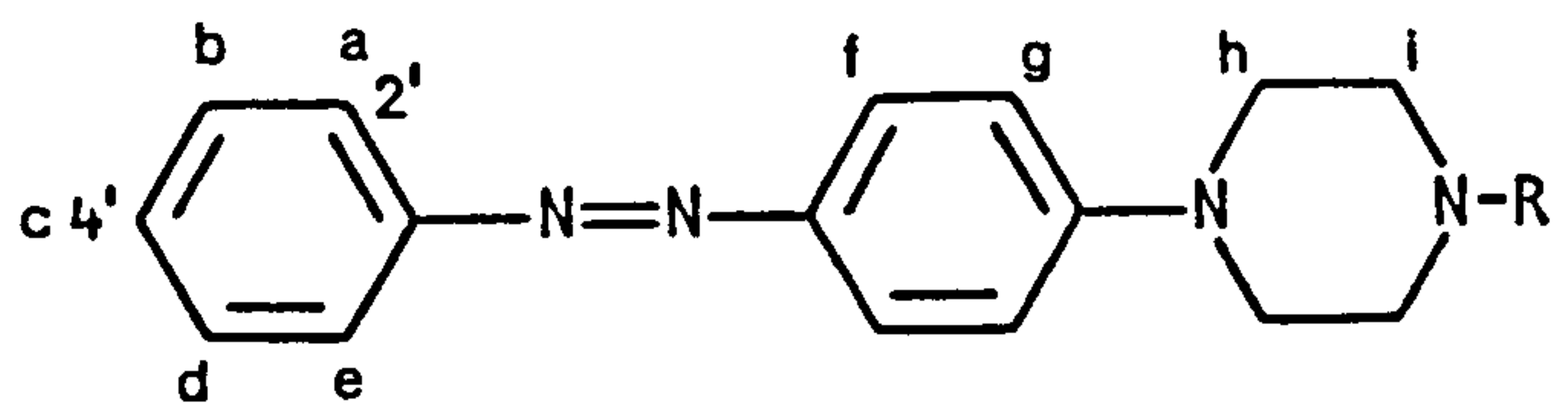


Ar	a	b	c	d	e	f	g	h	i	Other Protons	Δδ=a-b
a)1;4'-OMe	7.85	7.00	-	7.00	7.85	7.88	6.92	3.6—3.9	2.6—2.95	OMe,3.85,s	0.85
1;4'-H	7.90	b,c,d,7.3-7.65,m (complex)[a]			7.90	7.90	6.93	3.65-3.9	2.6—2.9		0.42
1;4'-Cl	7.84	7.46	-	7.46	7.84	7.89	6.94	3.65-3.9	2.6—2.9		0.38
1;4'-CF_3	7.73	7.96	-	7.96	7.73	7.91	6.93	3.6—4.0	2.6—2.9		-0.23
1;4'-CN	7.74	7.94	-	7.94	7.74	7.91	6.92	3.7—4.0	2.6—2.9		-0.20
1;4'-NO_2	7.95	8.37	-	8.37	7.95	7.95	6.95	3.75-4.0	2.65-2.9		-0.42
1;2'-CN, 4'-NO_2	—	8.58	-	8.41,dd	7.94	7.97	6.89	3.8—4.1	2.65-2.9		(e-b=)-0.64
2;6'-NO_2	8.14	8.39,dd	-	8.79	—	8.05	6.95	3.9—4.2	2.7—2.95		
3;5'-NO_2	8.63,s	—	-	—	—	7.98	6.90	3.8—4.1	2.6—2.9		
(b)1;4'-OMe	7.89	7.02	-	7.02	7.89	7.89	6.99	3.9—4.15	3.0—3.3	OMe,3.90,s	0.87
1;4'-Cl	7.85	7.47	-	7.47	7.85	7.93	7.01	3.9—4.2	3.0—3.3		0.38
1;4'-CF_3	7.76	7.97	-	7.97	7.76	7.97	7.02	3.9—4.2	3.0—3.3		-0.21
1;4'-NO_2[b]	—	—	-	—	—	—	—	-	-		—

[a] H_b assigned at 7.48

[b] Solubility too low

Table 2.24 ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from (a) N'-Ethyl-N-phenylpiperazine (R=Et) and (b) N'-Acetyl-N-phenylpiperazine (R=Ac).

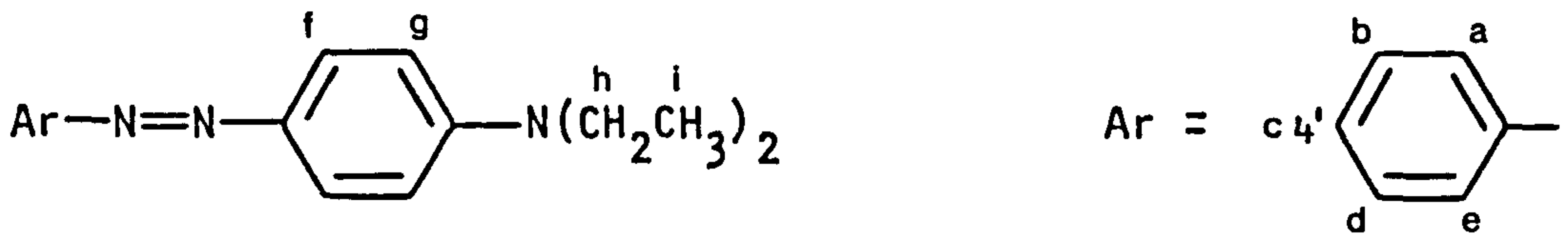


(a) R = $\overset{j}{CH_2}\overset{k}{CH_3}$ (b) R = COMe

Ar	a	b	c	d	e	f	g	h	i	Other Protons	Δδ=a-b
(a);4'-CF_3	7.73	7.97	-	7.97	7.73	7.92	6.98	3.3—3.6	2.45-2.75	j,2.49,q;k,1.11,t	-0.24
4'-CN	7.73	7.93	-	7.93	7.73	7.90	6.96	3.3—3.55	2.5—2.75	j,2.49,q;k,1.11,t	-0.20
4'-NO_2	7.92	8.34	-	8.34	7.92	7.92	6.97	3.35-3.6	2.5—2.8	j,2.50,q;k,1.13,t	-0.42
2'-CN,4'-NO_2	-	8.58	-	8.41,dd	7.93	7.95	6.93	3.4—3.7	2.5—2.8	j,2.50,q;k,1.11,t	(e-b=)-0.65
(b);4'-OMe	7.87	7.00	-	7.00	7.87	7.87	6.96	3.6—4.0?	3.2—3.5?	COMe,2.14,s;OMe,3.87,s	0.87
4'-H	7.91	b,c,d,7.3-7.6,m[a]			7.91	7.91	6.98	3.5—3.95?	3.25-3.5?	COMe,2.14,s	0.43
4'-Cl	7.84	7.45	-	7.45	7.84	7.90	6.98	3.6—3.95?	3.25-3.5?	COMe,2.16,s	0.39
4'-CF_3	7.73	7.96	-	7.96	7.73	7.93	6.97	3.6—3.9?	3.25-3.6?	COMe,2.15,s	-0.23
4'-CN	7.72	7.91	-	7.91	7.72	7.90	6.96	3.55-3.9?	3.25-3.6?	COMe,2.14,s	-0.19
4'-NO_2	7.94	8.36	-	8.36	7.94	7.94	6.97	3.65-4.0?	3.4—3.65?	COMe,2.17,s	-0.42
2'-CN,4'-NO_2	-	8.56	-	8.42,dd	7.94	7.97	6.92	3.60,bs	3.60,bs	COMe,2.15,s	(e-b=)-0.62

[a] H_b assigned at 7.48

Table 2.25. ^{1}H-NMR Assignments (δ) of Some Azo Dyes Derived from NN-Diethylaniline.



Ar	a	b	c	d	e	f	g	h	i	Other Protons	Δδ=a-b
4'-Me	7.81	7.30	-	7.30	7.81	7.90	6.75	3.48,q	1.26,t	Me,2.46,s	0.51
4'-H	7.90	b,c,d, 7.3-7.7, m[a]			7.90	7.90	6.74	3.46,q	1.24,t		0.43
4'-F[b]	7.88,dd	7.16,t	-	7.16,t	7.88,dd	7.88	6.74	3.48,q	1.25,t		0.72
4'-Cl	7.81	7.43	-	7.43	7.81	7.88	6.73	3.47,q	1.25,t		0.38
4'-Br	7.76	7.57	-	7.57	7.76	7.87	6.71	3.47,q	1.25,t		0.19
4'-I[c]	7.82	7.58	-	7.58	7.82	7.88	6.73	3.48,q	1.26,t		0.24
4'-CF$_3$	7.72	7.96	-	7.96	7.72	7.92	6.74	3.48,q	1.25,t		-0.24
4'-CN	7.71	7.91	-	7.91	7.71	7.89	6.73	3.49,q	1.26,t		-0.20
4'-NO$_2$	7.90	8.33	-	8.33	7.90	7.90	6.74	3.49,q	1.27,t		-0.42

[a] H_b assigned at 7.47

[b] $\sigma = 0.15$

[c] $\sigma = 0.28$

Footnote to n.m.r. data:

s = singlet

bs = broad singlet

dd = double doublet

t = triplet

q = quartet

m = multiplet

H_a-H_g: doublets unless otherwise stated

H_h-H_i: multiplets unless otherwise stated

Coupling Constants: J_{ortho} = 9.0 ± 0.6Hz

J_{meta} = 3.0 ± 0.6Hz

J_{45} = 3.5 ± 0.6Hz, thiazole ring (lit.,[152a] 3.1-3.6Hz)

J_{23} = 5.4 ± 0.6Hz, thiophene ring (lit.,[153] 4.9-6.2Hz)

J_{vic} = 7.2 ± 0.6Hz, alkyl chains

The ^1H-n.m.r. spectra were all measured for solutions in $[^2H]$chloroform at 60 MHz and ca. 40 °C.

effect of the latter group upon H_a is somewhat irregular, causing random chemical shifts within the region δ 7.7-7.95.

The chemical shift of H_b shows a rough correlation with the Hammett σ constant for substituent X; F and Cl appear to be anomalous, in that they cause H_b to absorb upfield relative to X=H. A similar situation is evident with the cyano group relative to $X=CF_3$. Much better correlations are obtained when σ is plotted against the difference in chemical shift between H_a and H_b ($\Delta\delta$)[154] as in Figs. 2.15 and 2.16. A similar correlation has been found in a series of 6'-(benzthiazolyl-2'-azo)-phenyl-NN-dimethylanilines.[155] Examination of the relevant data reveals that $\Delta\delta$ values are the same, regardless of the terminal amino donor group. This constancy may be of some use in the analysis of 4'-substituted azo dyes. Fluorine and chlorine again seem to be anomalous (Fig. 2.16); it is evident that the halogens produce quite different shifts for the protons H_b. The gradients of the two plots agree well with those found in the azojulolidine and azolilolidine analogues,[156] as expected since the sensitivity of H_b to variation in the 4'-substituent is independent of the 4-donor group.

Of the other aminoazobenzene derivatives studied the pentafluoro derivatives are useful in that they give unambiguous assignments to the donor ring protons. The parent and 2'-CN dyes show complex signals in the aromatic region which are too complicated to analyse on a first-order basis. The 2'-cyano-4'-nitro derivatives can be readily assigned, however, and it is noteworthy that an additive relationship[157] exists between the $\Delta\delta$ values of the disubstituted dyes (103; $\Delta\delta$ = e-b = ca. -0.63) and those of the monosubstituted dyes (102:$X=NO_2$, $\Delta\delta$ = a-b = e-b = ca. -0.41) and (102; X=CN, $\Delta\delta$ = a-b = e-b = ca. -0.20). This relationship implies that in dyes of structure (104) the cyano group has the same effect on

Fig. 2.5.

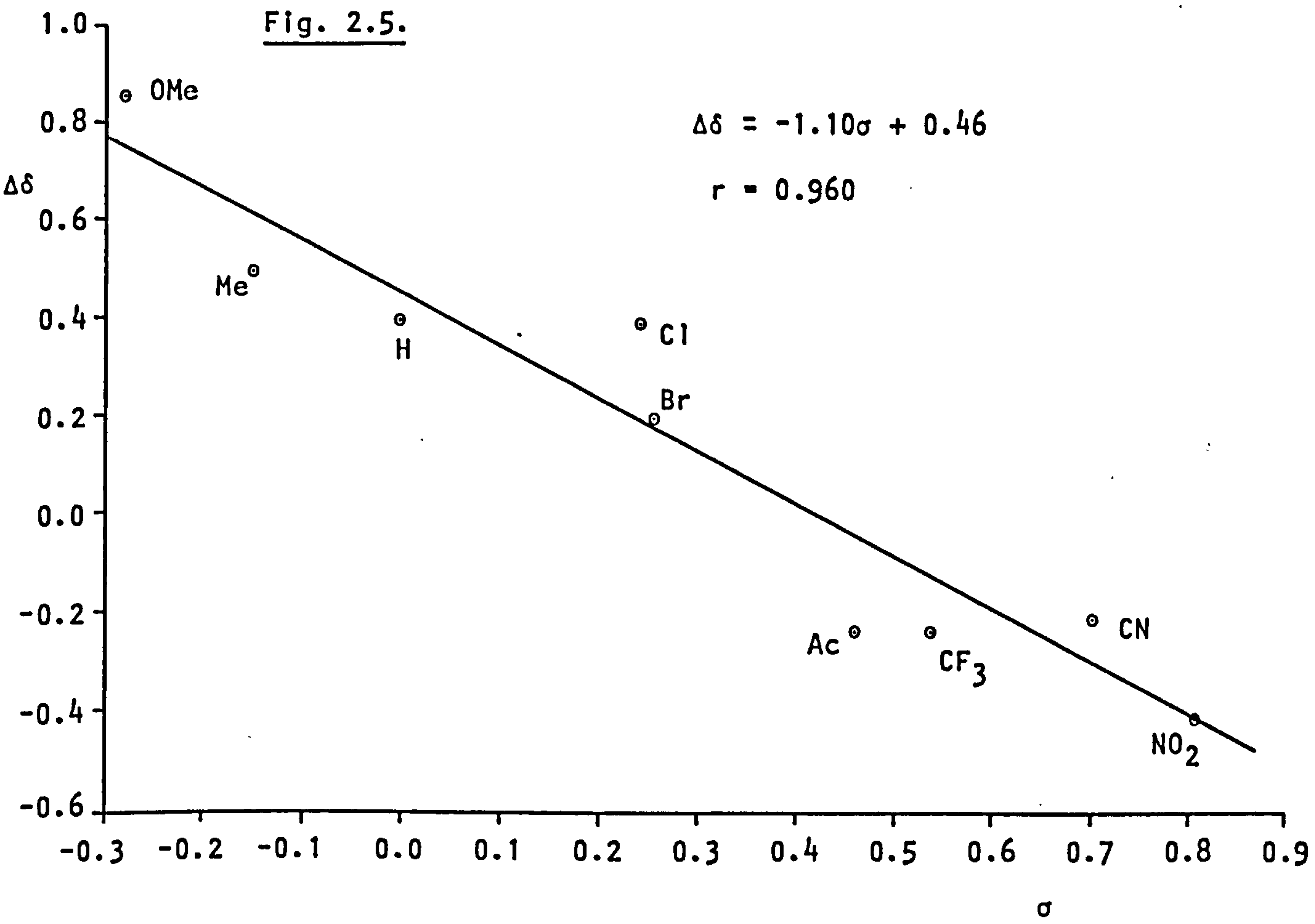
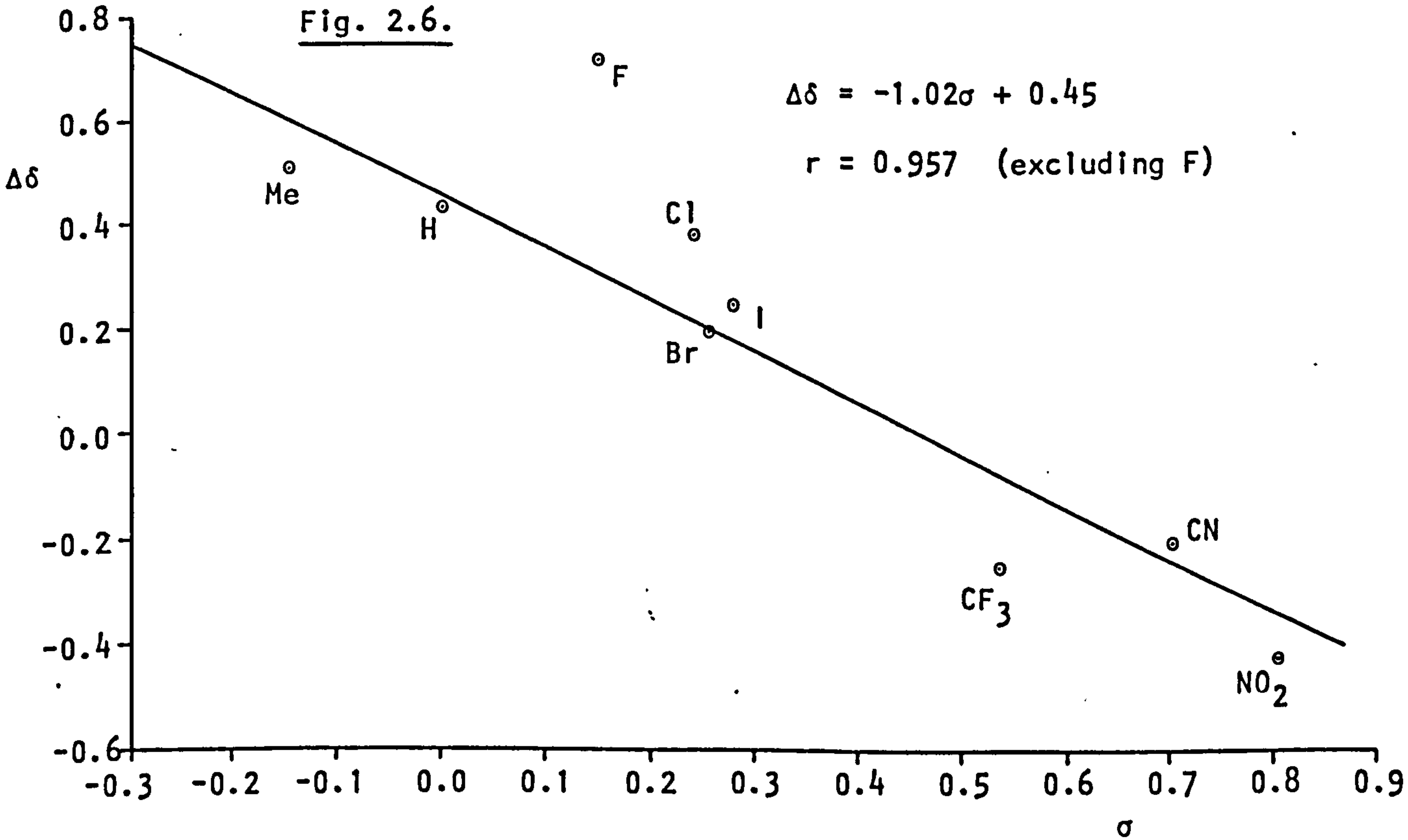
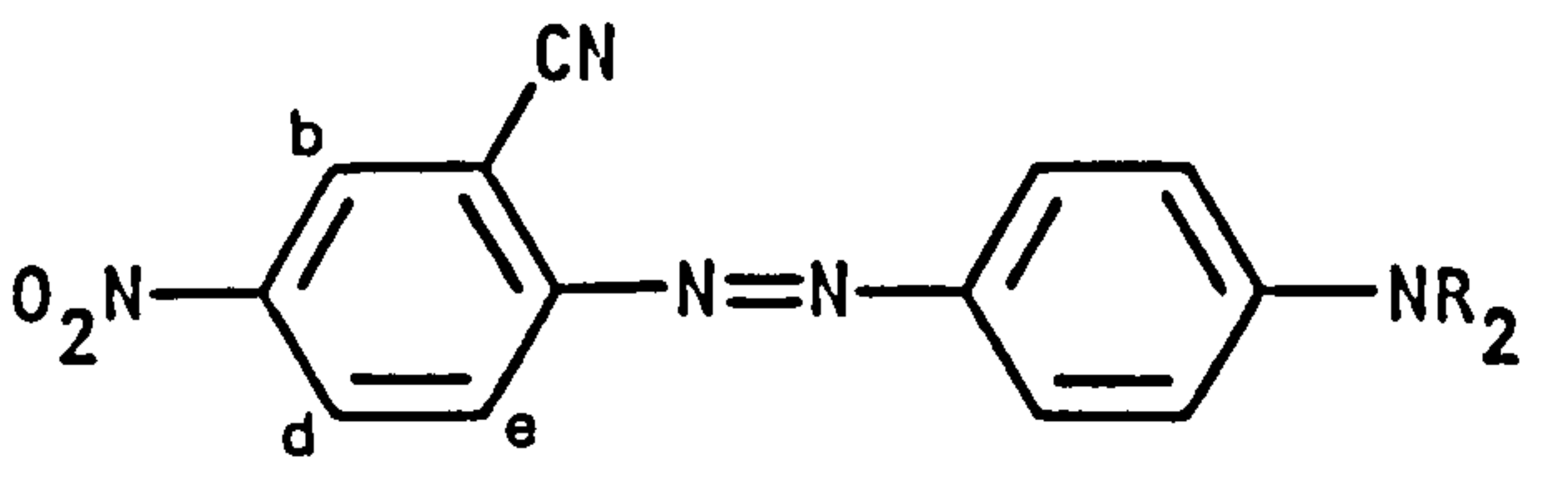


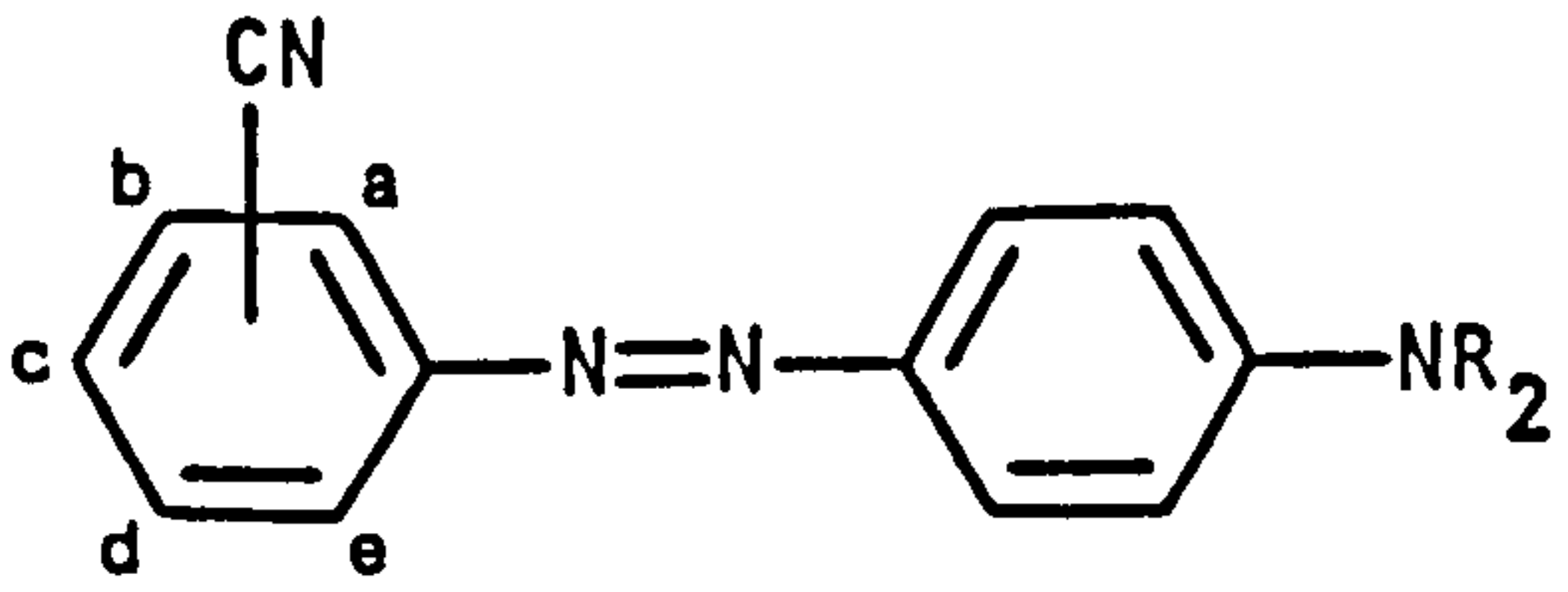
Fig. 2.6.



Relation between Hammett substituent constant (σ) and Δδ (a-b) for derivatives of 4-pyrrolidinoazobenzene (Fig. 2.15) and NN-diethylaminoazobenzene (Fig. 2.16) in deuteriochloroform (see Tables 2.20 and 2.25).



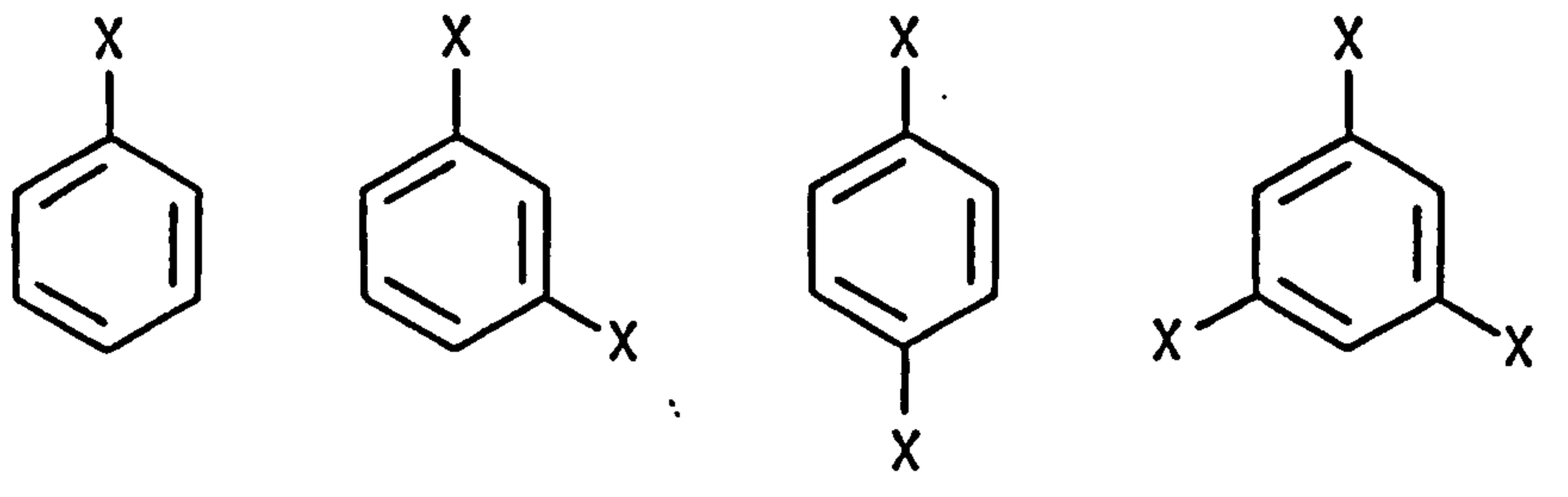
(103)



(104)

H_b and H_e irrespective of whether it is in the 2' - or the 4'-position; this is a reasonable assumption since the group will be positioned <u>ortho</u> to H_b, and <u>meta</u> to H_e, in each case.

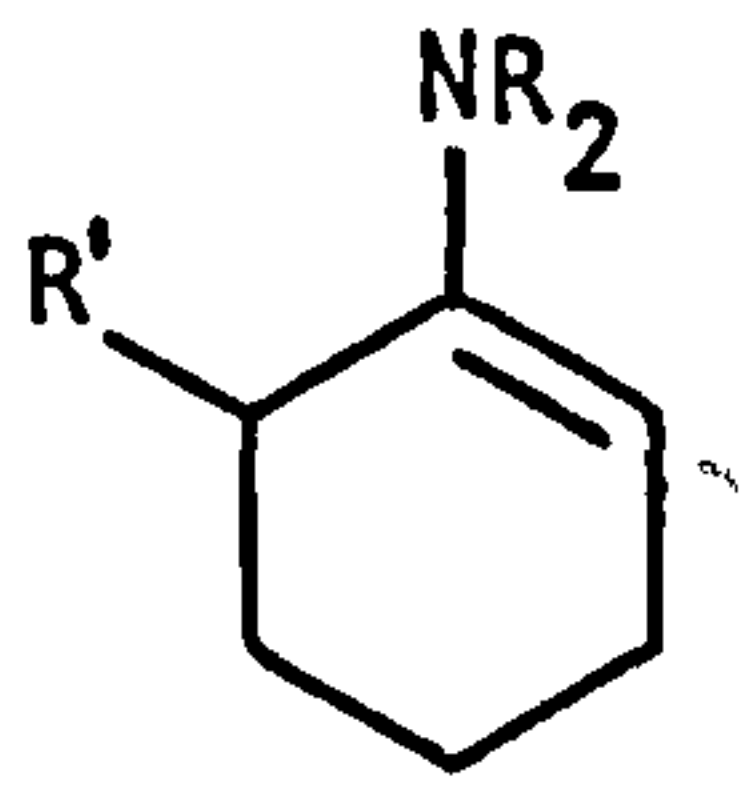
The chemical shifts of the H_g protons in the donor ring are essentially independent of the constitution of the diazo residue. Variations in the position of H_g with the donor group (Table 2.26) support previous indications that the order of decreasing donor power is pyrrolidino > <u>NN</u>-diethylamino > <u>NN</u>-dimethylamino > piperidino. Effenberger <u>et al</u>[126] have correlated the chemical shift of the <u>ortho</u>-amino protons with the π-electron density at the appropriate carbon atom, as calculated by Hückel MO theory, for the series of compounds (105) and obtained an order of mesomeric potential, as designated by the Hückel k values, of



X = <u>NN</u>-dimethylamino, pyrrolidino, piperidino, morpholino

(105)

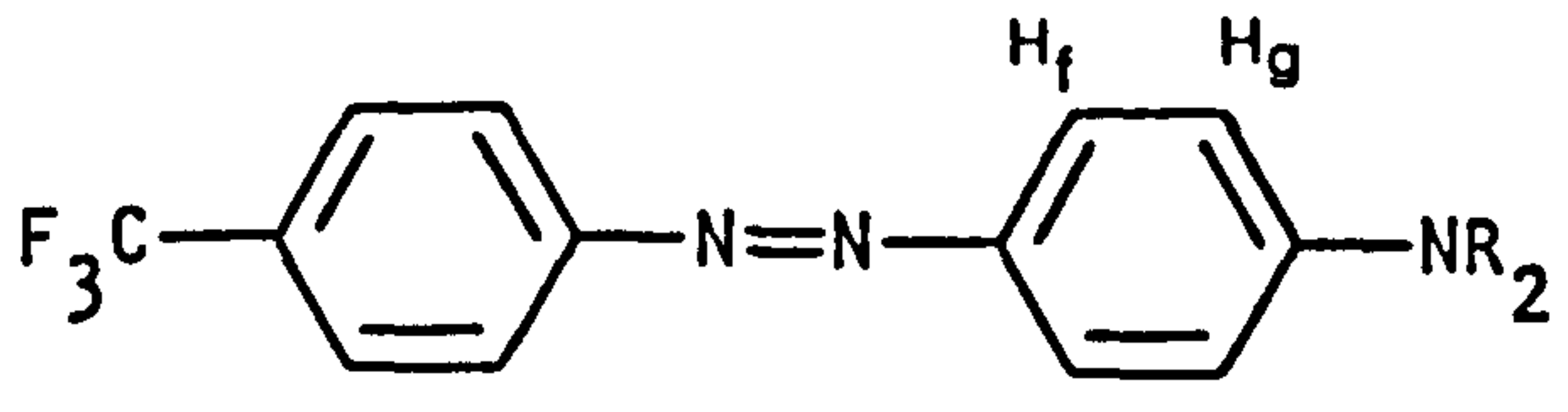
pyrrolidino > <u>NN</u>-dimethylamino > piperidino > morpholino. Incorporation of a γ-heteroatom into the six-membered ring system results in only minor changes in the chemical shift of H_g; this finding is confirmed by a series of analogues of Michler's ketone (Table 2.26), and by the similar vinyl proton chemical shifts of the enamines (106).[128]

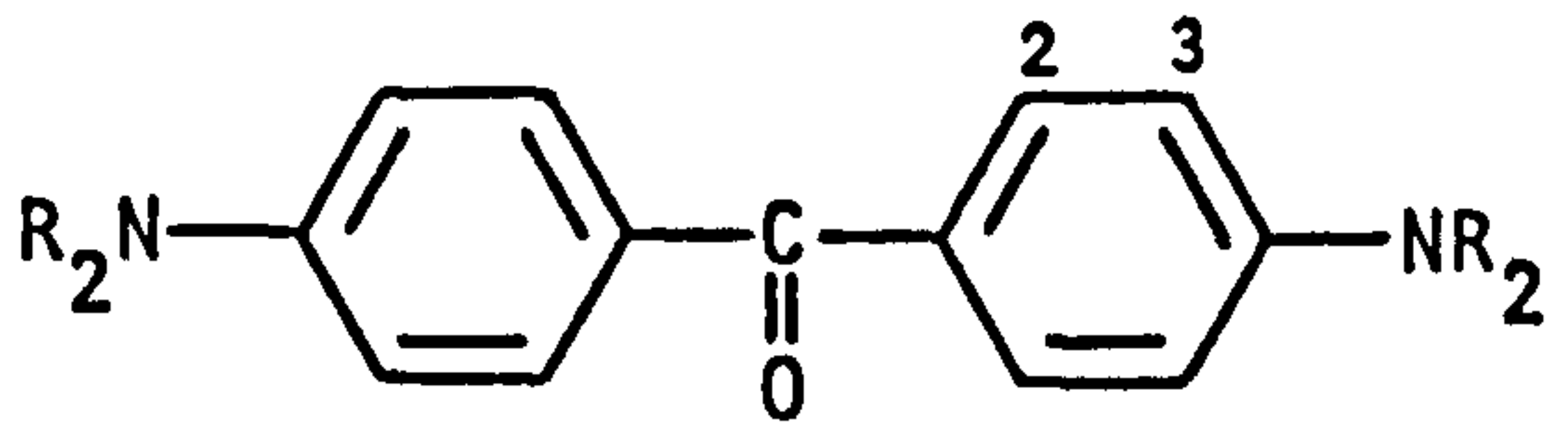


R_2 = piperidino, morpholino

(106)

Table 2.26. The Effect of Terminal Amino Groups on the Chemical Shift (δ) of Aromatic Protons.





decreasing donor power ↓

NR_2	H_f	H_g	2-position[a]	3-position[a]
$\overline{N(CH_2)_4}$	7.92	6.64	7.78	6.57
NEt_2	7.92	6.74	7.74	6.63
NMe_2	7.92	6.78	7.74	6.67
$\overline{N(CH_2)_5}$	7.90	6.97	7.78	6.92
$\overline{N(CH_2)_2S(CH_2)_2}$	7.91	6.93	7.79	6.89
$\overline{N(CH_2)_2N(Et)(CH_2)_2}$	7.92	6.98	7.81[b]	6.96[b]
$\overline{N(CH_2)_2O(CH_2)_2}$	7.94	6.98	7.79	6.93
$\overline{N(CH_2)_2N(Ac)CH_2)_2}$	7.97	6.97	-	-
$\overline{N(CH_2)_2SO_2(CH_2)_2}$	7.97	7.02	-	-

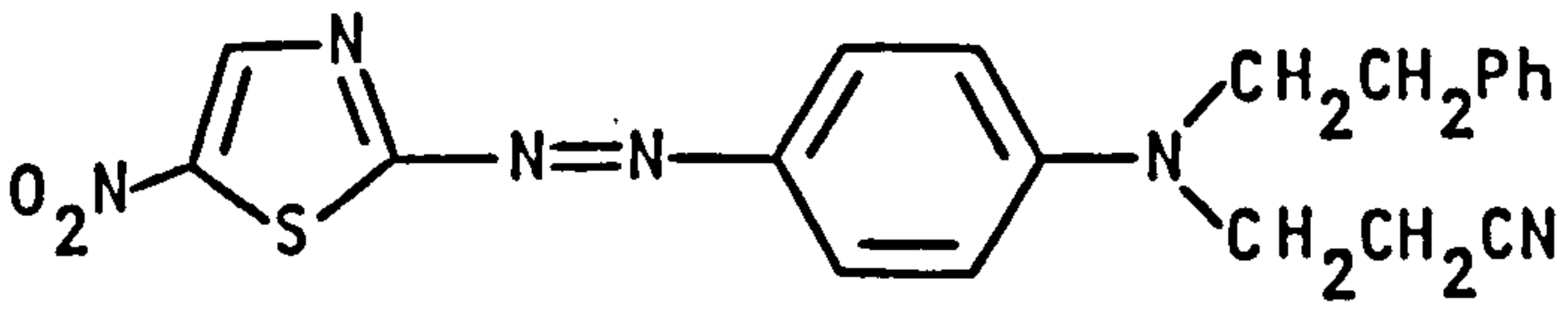
[a] Ref. 158

[b] $NR_2 = \overline{N(CH_2)_2N(Me)(CH_2)_2}$

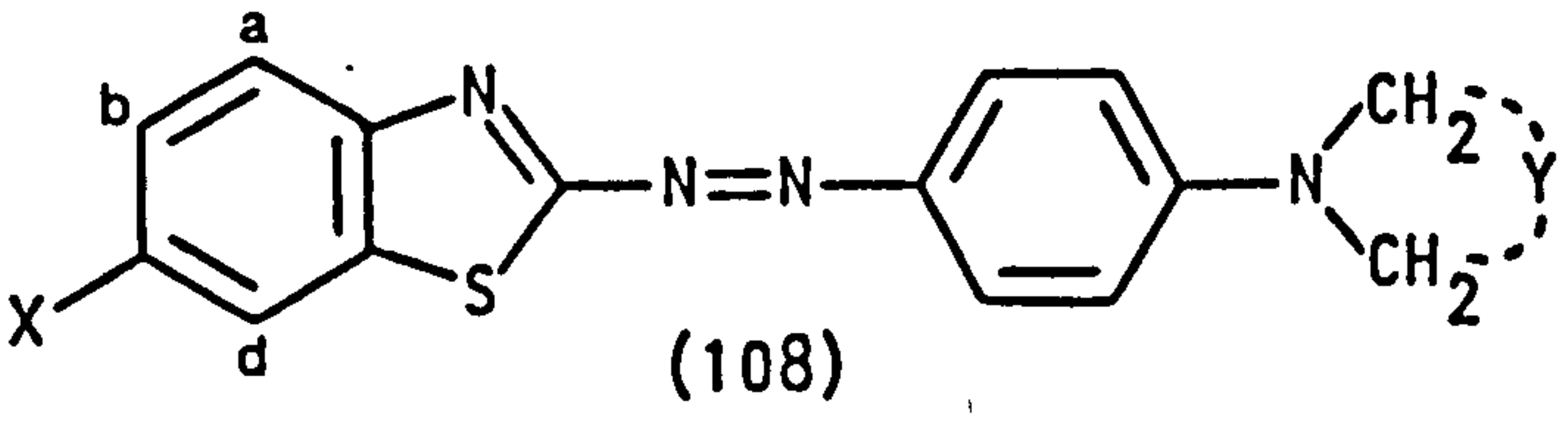
These results suggest that the ground state hybridisation of the terminal nitrogen atom is minimally affected by the heteroatom. Thus, the heteroatom must play a more important role in the excited state of the dye, where it will destabilise the charge-separated structure, thereby producing a hypsochromic shift of the visible absorption band.

The invariance of the chemical shifts of the H_f protons as the terminal amino group is changed, suggests that the conjugation of the nitrogen lone pair with the phenyl ring is rather localised, and is not transmitted beyond the ortho carbon atoms, although it can be argued that the position which is meta to the amino group will be affected much less than the ortho and para positions.

Protons situated in a heterocyclic aromatic ring tend to show greater downfield shifts than their phenyl counterparts, as exemplified by the proton ortho to a nitro group in a thiazole ring which absorbs at δ ca. 8.6 (Venkataraman[159] quotes δ 8.57 for the related dye (107) measured in CD_2Cl_2), compared with ca. δ 8.35 for the phenyl analogue. This difference is due to the presence of atoms of high electronegativity in the ring and also to the enhanced electron withdrawing power of the nitro group. The proton H_d of the 6'-nitrobenzthiazole derivative (108;$X=NO_2$) is even more deshielded, at ca. δ 8.75. The relative positions of H_a, H_b and H_d protons in dyes of the latter type are also in agreement with the data of Venkataraman.[159] When the electron withdrawing group is less powerful, as in (108;$X=SO_2Me$), the protons ortho to the acceptor group (H_b, H_d) absorb at higher field, whilst the proton H_a, in a position



(107)



(108)

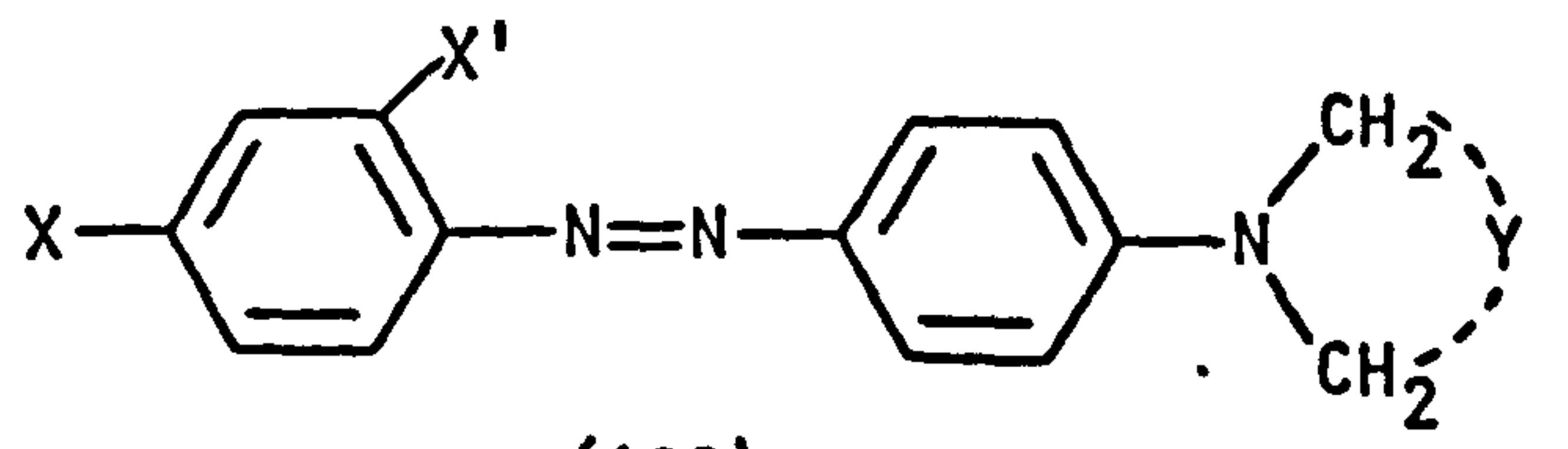
of non-conjugation in terms of resonance theory, shows only a small change. The n.m.r. spectrum of dye (108; X=OEt) is poorly resolved so that assignments are somewhat difficult, although the ortho protons (H_b, H_d) may in this case be expected to be shielded due to mesomeric donation by the methoxy group. The two protons of the thiazole nucleus of dyes (66) absorb at significantly different frequencies; H_a is assigned at lower field by comparison with the n.m.r. spectrum of thiazole,[152b] a conclusion supported by PPP-MO electron density calculations (see Appendix 1). Similar considerations were invoked in the assignment of protons H_a and H_b for dye (5;2'-CO_2Me, Table 2.20). The low field absorption of protons H_a of the dye (6;3'-Ph, Table 2.20) is probably due to the combined effects of the diamagnetic ring currents of two aromatic rings.

The terminal ring protons H_h and H_i are, in most cases, seen as two distinct signals, usually multiplets. Comparison with the appropriate coupler indicates that these protons are largely unaffected by the presence of the arylazo residue, as might be expected. At ambient temperature (∿40 °C), it was not possible to derive constants for the geminal and vicinal couplings. Protons attached to the same carbon atom tend towards equivalence due to rapid changes in the conformation of the rings; indeed, some evidence of triplet splitting is observed in certain dyes. Protons H_h absorb at the same frequency in both pyrrolidine and piperidine rings (slightly upfield from their NN-diethylamino counterpart), whereas the H_i protons of the pyrrolidine ring are shifted downfield by δ ca. 0.35 relative to those of the piperidine ring. This may be a consequence of the differing proximities of these protons, with respect to the nitrogen lone pair, brought about by the change in ring size. H_h and H_i protons in rings where a heteroatom is present have been assigned after reference to related systems.[152c] The heteroatom causes rather irregular shifts in H_h within the region δ 3.3-4.1. The effect of oxygen appears to be anomalous, but the proton assignment agrees with the literature values measured on N-phenylmorpholine itself,[152c] and it has been previously observed in open chain aliphatic compounds that the deshielding effect of a β-sulphur atom can be greater than that of a β-oxygen.[152d] Nevertheless, the upfield shift of H_h in the morpholine ring, relative to the value in the piperidine ring, is rather surprising. H_i protons are in every case shifted to lower field by the presence of a heteroatom, but correlations with the -I effects of the heteroatoms (as defined by electronegativity or by neutral dye λ_{max}) are not apparent.

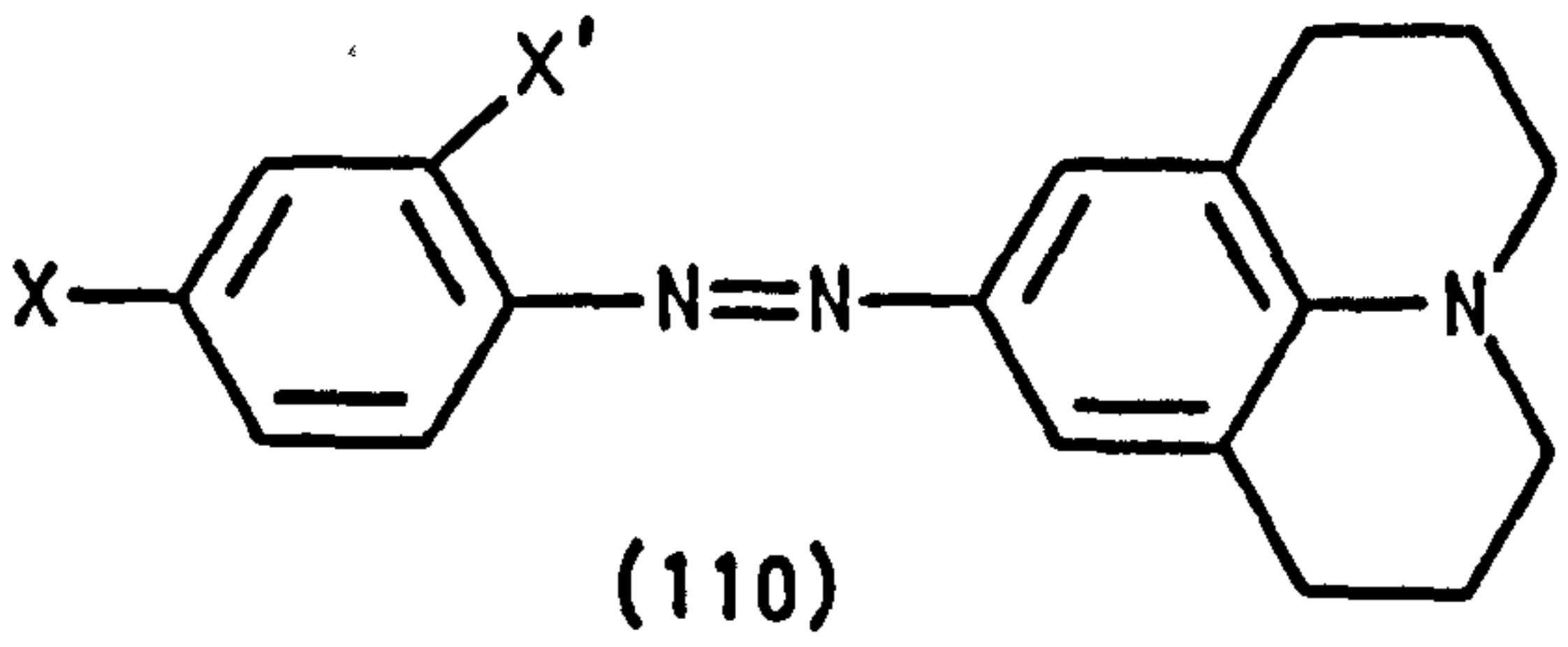
2.6. Basicity Measurements of the Azo Dyes

The basicities of a selection of azo dyes synthesised in this study are given in Table 2.27. It is clear from the 4'-cyano series (109;X=CN, X'=H) that the pK_a' values vary considerably with changes in the terminal amino grouping. The pyrrolidino and piperidino dyes have similar pK_a' values (1.98 and 2.31, respectively) although the latter compound is slightly more basic. As stated previously (Section 1.8), the pK_a' value measures the overall basicity of the azo molecule, and does not distinguish between the two sites of protonation, namely at the β-azo and the terminal nitrogen atoms. As a consequence of the difference in ring sizes, the pyrrolidino derivative exists mainly (∿95%) as the azonium cation in acid solution (Table 2.4), whereas the piperidino analogue forms mainly (∿85%) the ammonium tautomer (Table 2.5). Consequently, in these cases, the pK_a' value can be approximately related to protonation at a specific site, and it can be concluded that protonation occurs most readily at the terminal nitrogen atom. This finding is not a general rule, of course, and the general situation will depend largely upon the relative conjugation (or deconjugation) of the terminal nitrogen

Table 2.27. pK_a' Values of Some 4-Aminoazobenzene Derivatives in 50% Aqueous Ethanol at 25 °C.



(109)



(110)

X	X'	Y	pK_a'	$\sigma_p (\sigma_p^+)$
109;CN	H	$-CH_2CH_2-$	1.98 ± 0.01	
109;CN	H	$-CH_2CH_2CH_2-$	2.31 ± 0.01	0.70
109;CN	H	$-CH_2SCH_2-$	0.66 ± 0.01	
109;CN	H	$-CH_2N(Et)CH_2-$	-0.679 ± 0.003	
109;CN	H	$-CH_2N(Me)CH_2-$	-0.717 ± 0.009	
109;CN	H	$-CH_2OCH_2-$	0.29 ± 0.01	
109;CN	H	$-CH_2N(Ac)CH_2-$	0.29 ± 0.02	
109;CN	H	$-CH_2SO_2CH_2-$	-0.92 ± 0.01	
110;CN	H	-	3.55 ± 0.06	
109;OMe	H	$-CH_2CH_2-$	1.94 ± 0.02	
109;Me	H	$-CH_2CH_2-$	2.18 ± 0.01[a]	
109;H	H	$-CH_2CH_2-$	2.16 ± 0.02[b]	
109;Cl	H	$-CH_2CH_2-$	1.84 ± 0.01[c]	
109;Br	H	$-CH_2CH_2-$	1.85 ± 0.01	
109;CF_3	H	$-CH_2CH_2-$	1.95 ± 0.01	
109;Ac	H	$-CH_2CH_2-$	2.13 ± 0.01	
109;NO_2	H	$-CH_2CH_2-$	1.96 ± 0.01	
109;H	CN	$-CH_2CH_2-$	0.41 ± 0.06	
109;NO_2	CN	$-CH_2CH_2-$	0.21 ± 0.02	
109;OMe	H	$-CH_2CH_2CH_2-$	3.15 ± 0.01	-0.28(-0.76)
109;H	H	$-CH_2CH_2CH_2-$	2.68 ± 0.02	0.00
109;NO_2	H	$-CH_2CH_2CH_2-$	2.27 ± 0.02	0.81

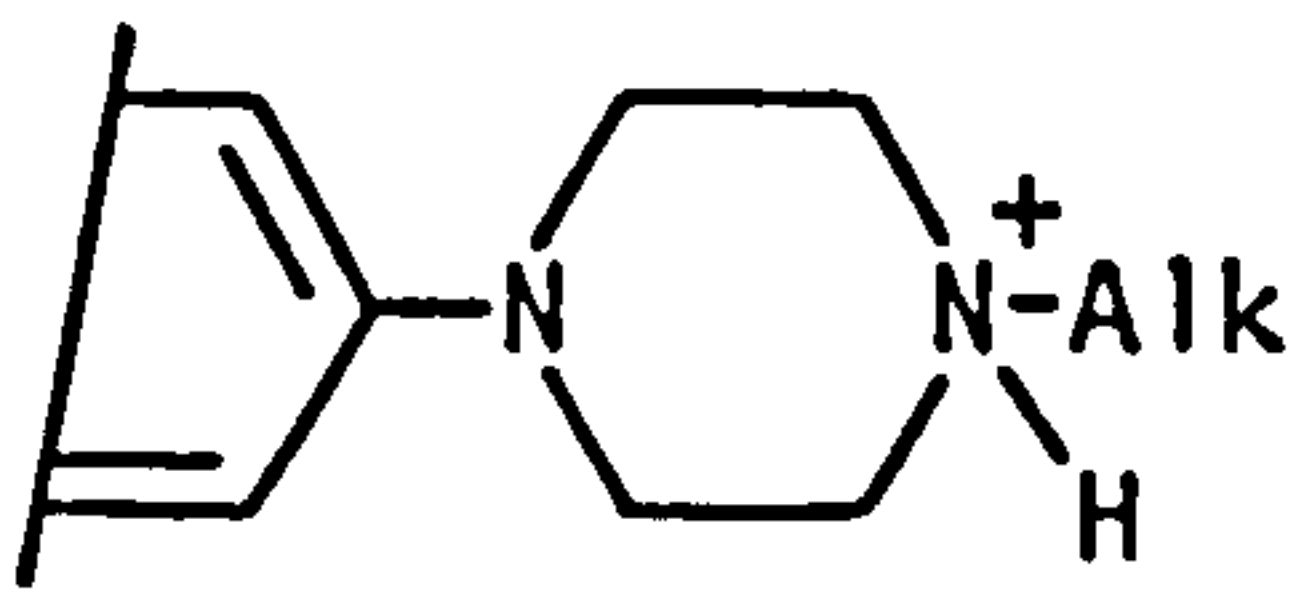
[a] Ref. 89 gives 2.43

[b] Ref. 89 gives 2.38

[c] Ref. 89 gives 2.15

lone pair. Thus, for example, the cyanoazojulolidine dye (110), which forms the azonium cation almost exclusively in acid solution, is considerably more basic ($pK_a' = 3.55$) than the piperidino analogue. Since the julolidine and the pyrrolidine dyes both protonate almost quantitatively at the same site, their basicities can be compared directly; the higher pK_a' value of the former species supports the view that π-interaction of the lone pair is optimal in this case.

Each of the remaining p-cyano derivatives contains a six-membered cyclic terminal amino grouping with a heteroatom in the γ-position; the -I effect of the latter atom results in a decrease in the overall electron density at the two protonation sites of the dyes, leading to decreases in their basicities, relative to that of the corresponding piperidino dye. The relative basicities (with two exceptions) follow the same order as the relative λ_{max} values (in ethanol) of the neutral dyes, decreasing as the strength of the -I effect of the γ-heteroatom increases. The deviation from this order occurs with the N-alkylpiperazinyl types, where the basicities are much lower than expected, reinforcing the view that in these systems the initial protonation site is the tertiary aliphatic nitrogen atom:



This situation results in a large -I effect (as discussed in Section 2.3.2). The higher basicity of the N'-acetylpiperazinyl compound suggests that the equivalent protonation reaction does not occur in this system.

In the pyrrolidinoazo series pK_a' values appear to be largely independent of the substituent X, all values falling in the range 2.0±0.16. This is a rather unexpected result, since a related series of dyes derived from NN-diethylaminoazobenzene shows a drop in basicity as the electron withdrawing strength of X increases (Table 1.13). Also, similar work on three pyrrolidinoazo dyes likewise showed this decrease in basicity,[89] although the difference in pK_a' values was small; the same trend is in fact observed in the present work for these dyes. This situation may be linked with the fact that each dye of the series protonates almost exclusively at the β-azo nitrogen (in this respect it would be of interest to examine the trend in pK_a' values for the azo-julolidines) if the availability of the β-azo nitrogen lone pair (presumably governed by the electron density at this site) is essentially constant. It can be envisaged that, relative to the parent dye, any loss of electron density caused by the electron-withdrawing substituent X is offset by the increased conjugation of the terminal nitrogen lone pair produced by this same substituent. Thus, in such circumstances, the electron density at the β-azo nitrogen atom would remain essentially constant, but a decrease would be evident at the terminal nitrogen atom. Since protonation occurs almost exclusively at the azo group, however, the basicity of the dye should be largely independent of substituent X, as appears to be the case.

Application of this scenario to the piperidinoazo dyes in which the ammonium tautomer is dominant in acid solution (a situation where the electron density at the terminal nitrogen atom should directly influence pK_a') would suggest a decrease in pK_a' as X becomes more electron withdrawing. In the small group of dyes examined, this trend is observed and, indeed, a good linear correlation is found between pK_a' and the appropriate Hammett σ constant (Fig. 2.17), especially when

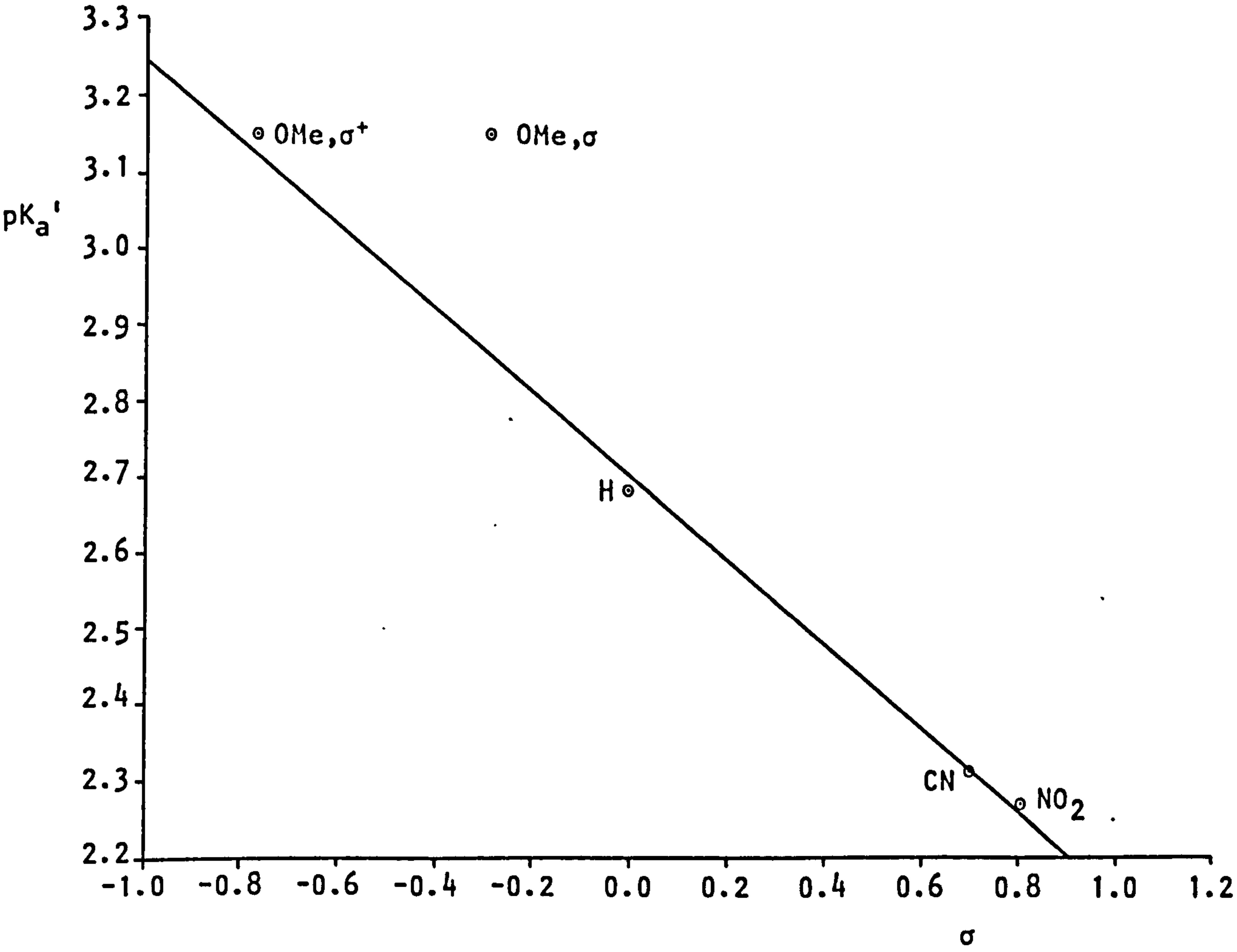


Fig. 2.17. Relationship between pK_a' value and Hammett σ constant for some derivatives of 4-piperidinoazobenzene (see Table 2.27).

an enhanced σ constant (σ^+) is employed for the methoxy substituent This usage can be justified on the grounds that the donor group can conjugate directly with the positively charged site and will thus encourage protonation since it can stabilise the cation. It is of interest, therefore, to obtain pK_a' values for the remaining dyes of this series, in order to confirm this correlation.

Relatively low basicities are observed for the two pyrrolidinoazo dyes containing an o-cyano group; this result can be attributed to a shielding of the β-azo nitrogen lone pair by the substituent, thus hindering attack by the proton. It is interesting to note, that, although relatively high acidities are needed to effect protonation in these cases, there is no sign of any ammonium ion formation. Clearly, small electron density changes at the terminal nitrogen atom can appreciably affect rates of protonation at this site. It is anticipated that the corresponding piperidinoazo dyes containing an o-cyano group in the acceptor ring will have pK_a' values more in line with the para-substituted analogues, since protonation here is mainly at the terminal amino group and should therefore be little affected by the presence of an ortho-substituent.

3. DISCUSSION OF EXPERIMENTAL

3.1. Preparation of Intermediates

3.1.1. Coupling Components

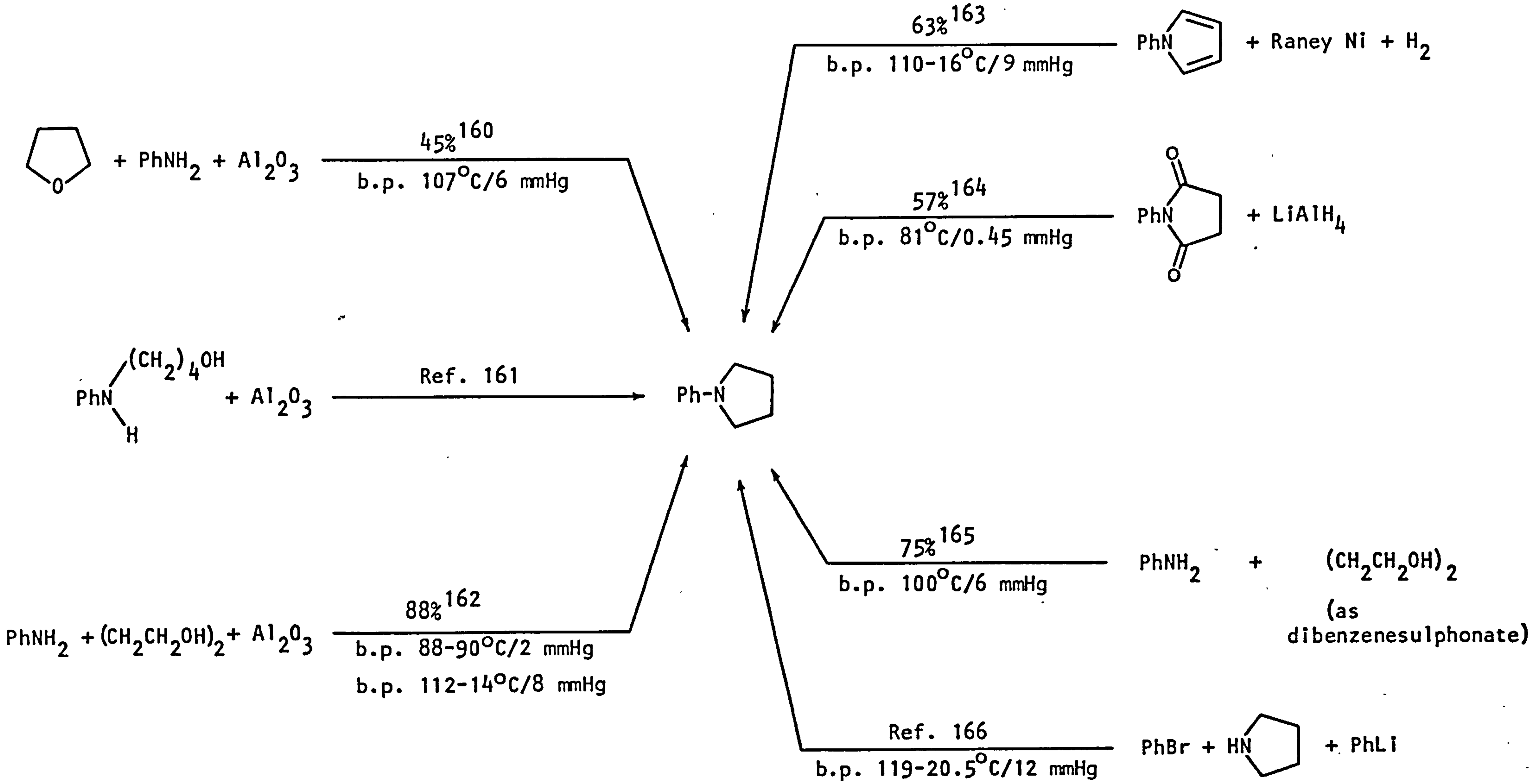
Methods for the preparation of the coupling components were chosen to combine synthetic ease with a high yield of product. Literature methods were used in all cases with the exception of *N*'-ethyl-*N*-phenylpiperazine. A selection of alternative procedures from the literature is shown in Schemes 3.1-3.7; percentage yields and melting points of product are given (where available) for comparison purposes.

3.1.2. Diazo Components

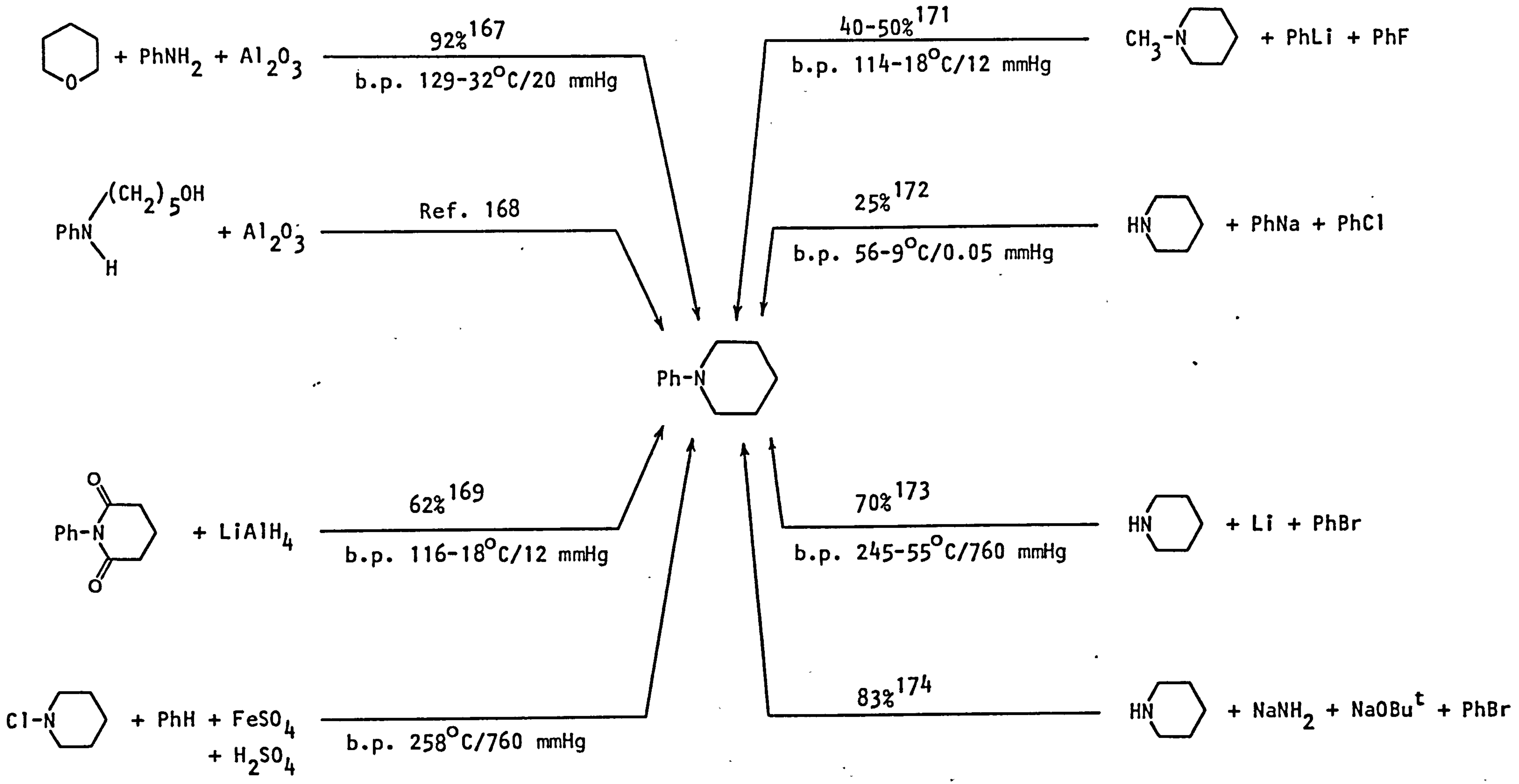
Most of the amines used in the diazotisation reaction were commercial samples, used without further purification unless otherwise stated. However, three heterocyclic amines were synthesised, using literature methods: 2-amino-3-nitro-5-acetylthiophene, 5-amino-3-methylthio-1,2,4-thiadiazole and 2-amino-5-ethylthio-1,3,4-thiadiazole. In the case of the first heterocycle, the nitration step used by Dickey *et al.*[19] gave rise to 2-chloro-3,5-dinitrothiophene, m.p. 119-20 °C (lit.,[186] 120-21 °C), i.r. showed no $\rangle$C=O stretch. The mono-nitro derivative was prepared, however, by the method of Hurd and Kreuz,[187] in which the nitrating mixture is added to the 2-chloro-5-acetylthiophene, rather than *vice-versa*. The two thiadiazoles were isolated in somewhat lower yields than claimed in the literature, owing in the case of the 1,3,4-thiadiazole possibly to an inferior sample of diethyl sulphate.

3.1.3. Miscellaneous Preparations

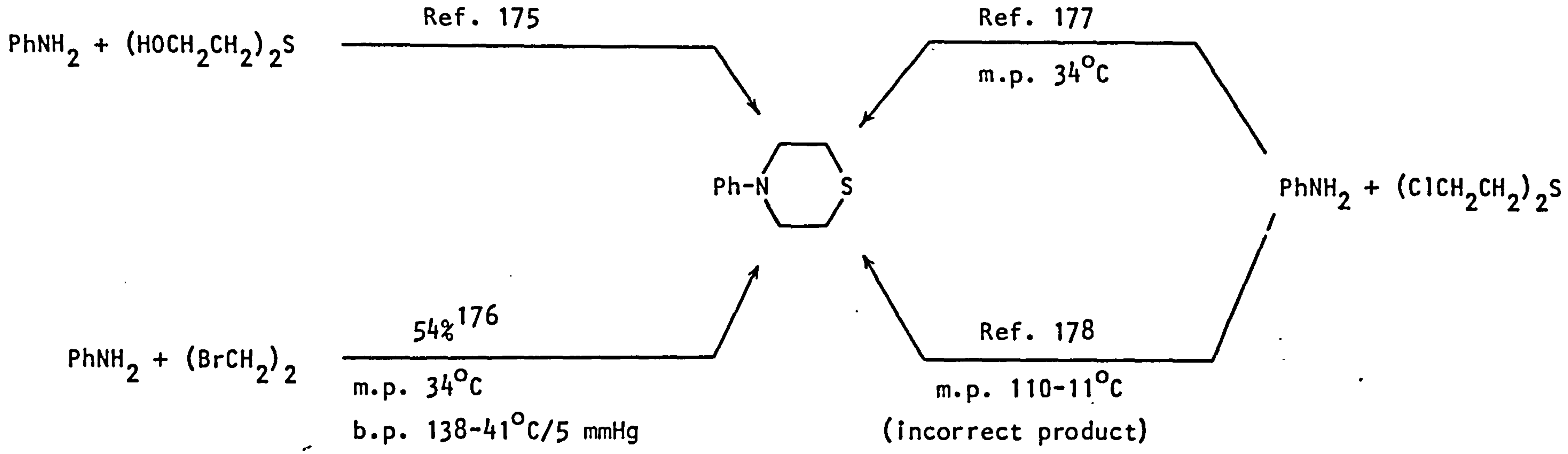
Several 4-substituted-*N*-phenylthiomorpholines were prepared for use in dipole moment studies. The 4-nitro and 4-cyano derivatives were made



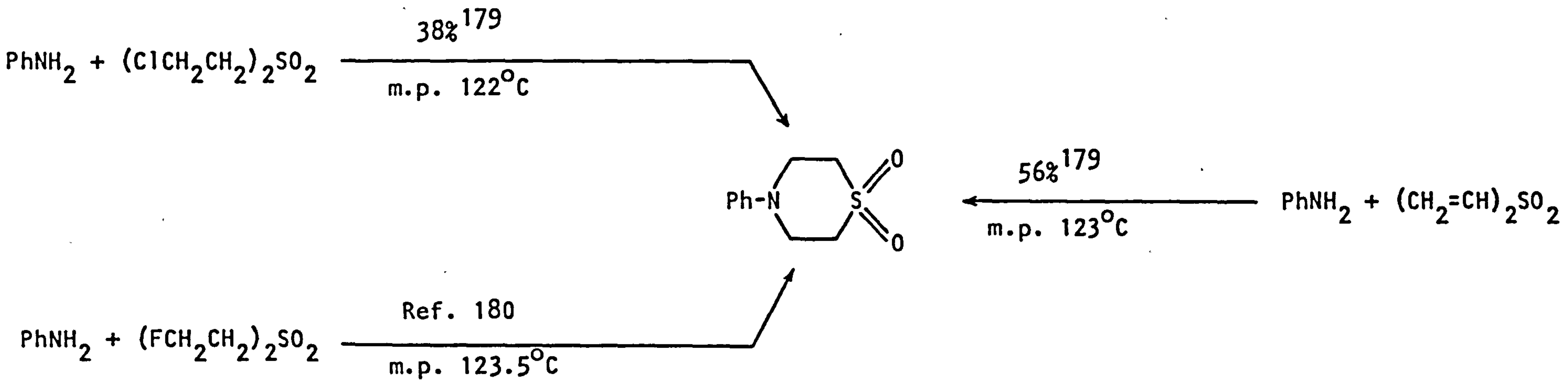
Scheme 3.1. Alternative literature syntheses of N-phenylpyrrolidine.



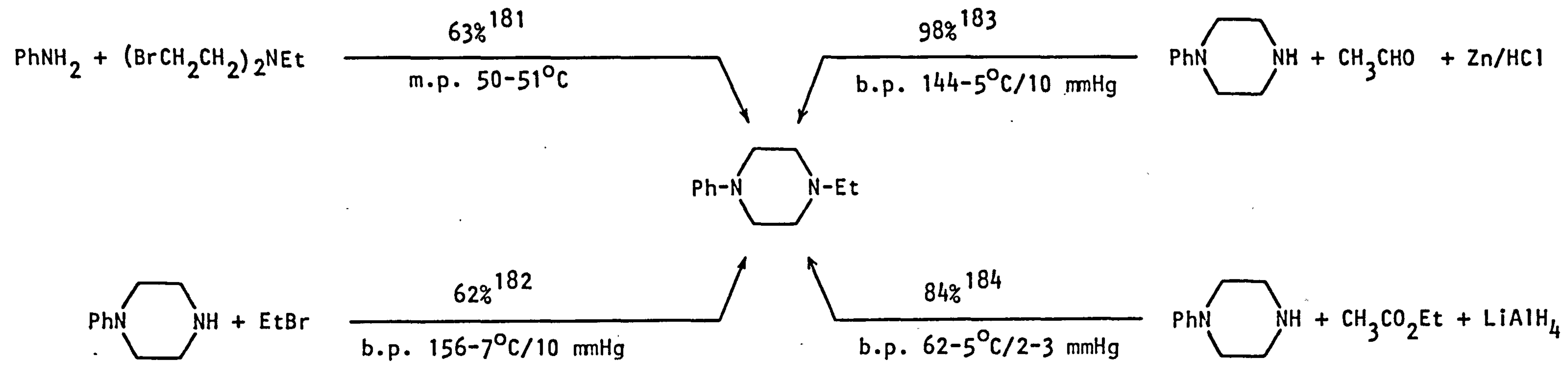
Scheme 3.2. Alternative literature syntheses of N-phenylpiperidine.



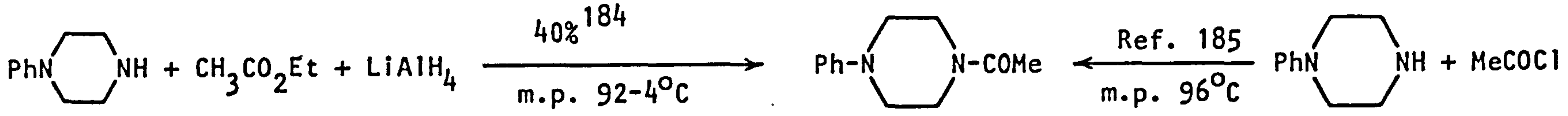
Scheme 3.3. Alternative literature syntheses of N-phenylthiomorpholine.



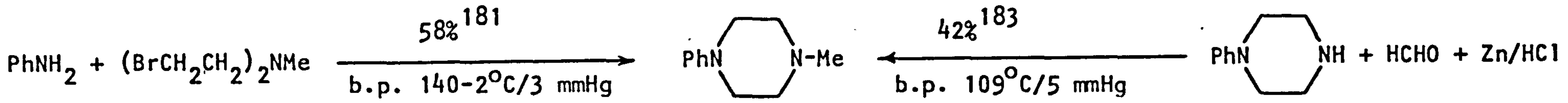
Scheme 3.4. Alternative literature syntheses of N-phenylthiomorpholine-1,1-dioxide.



Scheme 3.5. Alternative literature syntheses of N'-ethyl-N-phenylpiperazine.



Scheme 3.6. Alternative literature syntheses of N'-acetyl-N-phenylpiperazine.



Scheme 3.7. Alternative literature syntheses of N'-methyl-N-phenylpiperazine.

by the appropriate nucleophilic displacement of halogen with thiomorpholine, using 4-nitrochlorobenzene and 4-fluorobenzonitrile respectively; in both cases, butanol (b.p. 110 °C) was used as solvent, ethanol affording little product.

Bromination of *N*-phenylthiomorpholine gave the 4-bromo derivative in high yield. Methylation of the latter compound (via metallation with butyl-lithium) gave crude 4-methyl-*N*-phenylthiomorpholine shown to be reasonably pure by n.m.r. However, column chromatography, vacuum distillation and several recrystallisations from cyclohexane and ethanol were required to obtain a sample which remained crystalline (m.p. 30-31 °C) at room temperature.

In order to compare the p.m.r. spectrum of 4,4'-thiomorpholinobenzophenone with analogous benzophenone derivatives, this compound was synthesised from 4,4'-difluorobenzophenone. Use of butanol as solvent gave only the mono-amino derivative after prolonged heating under reflux; dimethylsulfoxide (b.p. 189-92 °C) was therefore used as a high-boiling solvent. Although some mono-amino compound was again produced, the majority of the crude product was found to be the required ketone.

3.2. Synthesis of Azo Dyes

The dyes were prepared by standard methods of diazotisation[188] (in particular the direct method and that involving nitrosylsulphuric acid) and coupling.[188]

3.2.1. Diazotisation

The diazotisation of aromatic primary amines, followed by a coupling reaction, is the method by which practically all technical azo dyes are produced. In diazotisation, the amine in aqueous solution is converted into the diazonium ion at 0 °C by the action of sodium nitrite in the presence of mineral acid (3.1). Normally the use of 2.5-3 equivalents

$$ArNH_2 + 2HX + NaNO_2 \longrightarrow Ar\overset{+}{N}_2\overset{-}{X} + NaX + 2H_2O \qquad (3.1)$$

$$(X = Cl,\ Br,\ NO_3,\ HSO_4,\ etc.)$$

of acid is essential for smooth reaction, for the following reasons:

(i) To maintain the equilibrium (3.2) in favour of the amine salt which

$$ArNH_2 + H^+ \rightleftharpoons ArNH_3^+ \qquad (3.2)$$

prevents the combination of unreacted free base with newly formed diazonium ions, resulting in the formation of diazoamino compounds. Although the concentration of neutral amine is consequently low, the equilibrium is maintained during reaction so that more neutral amine becomes available.

(ii) To maintain the nitrosating agent in an active form.

(iii) To stabilise the resulting diazonium ion in solution (i.e. to obviate formation of diazoamino compounds).

A slight excess of nitrous acid should be present at the end of the reaction, and this can be detected by the instantaneous blue-black coloration with starch-iodide paper. A large excess of nitrous acid is detrimental to the stability of the diazonium ion, and can be destroyed by the addition of urea or sulphamic acid (3.3).

$$Z\text{-}NH_2 + HNO_2 \longrightarrow Z\text{-}OH + N_2 + H_2O \qquad (3.3)$$

Urea: $Z = H_2NCO\text{-}$

Sulphamic acid: $Z = HO_3S\text{-}$

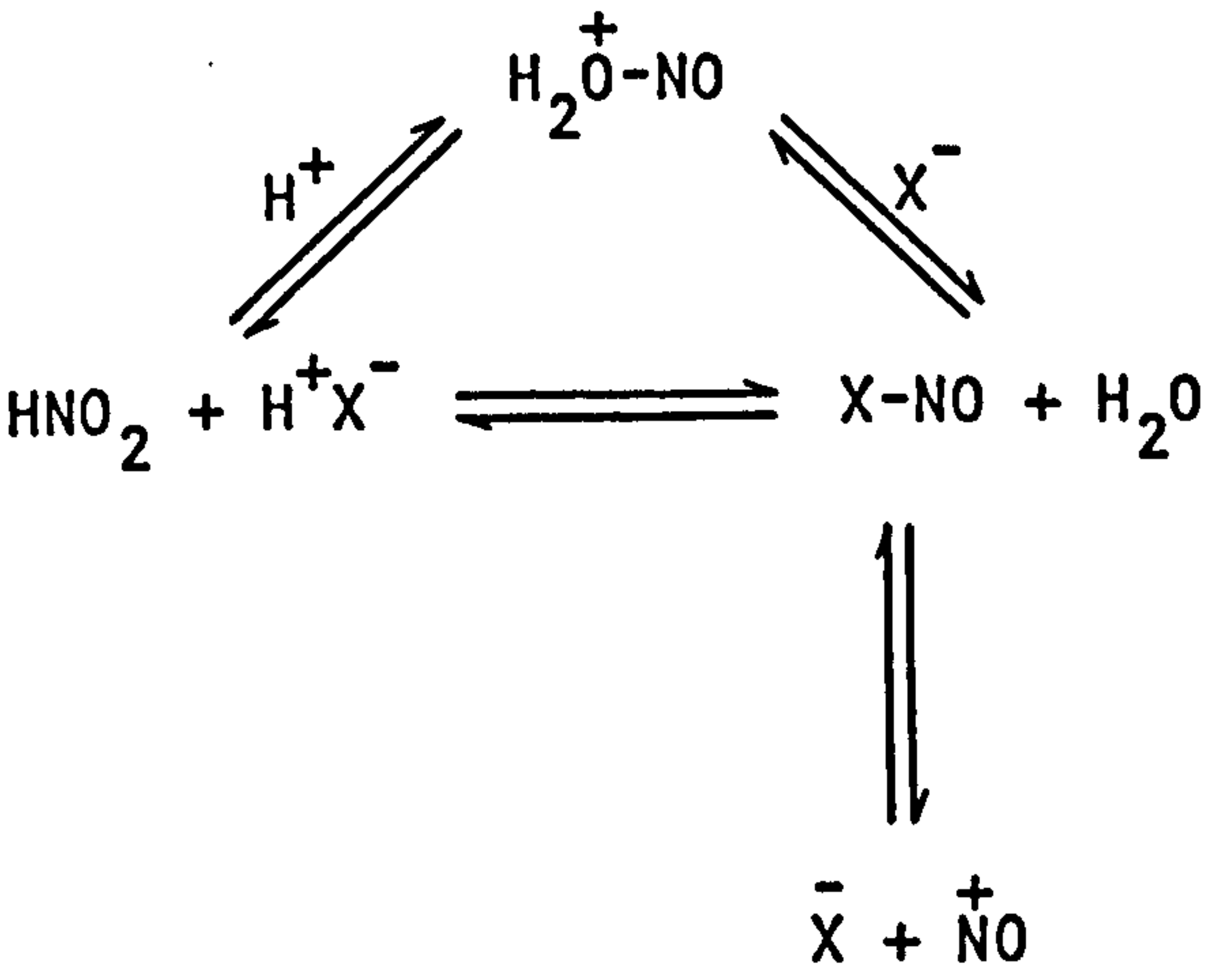
The low temperature of diazotisation is a prerequisite demanded by the moderate stability of most diazo compounds. An advantage of a low reaction temperature is the higher stability of nitrous acid at $0^{\circ}C$, which ensures that there is less danger of nitrous gases escaping from the acid medium than at a higher temperature. These two factors outweigh the lower rate of reaction and inferior solubility of the starting material at this temperature.

More strongly acidic conditions than those suggested by eqn. (3.1) are required in the diazotisation of more weakly basic amines, in order to shift the equilibrium (3.2) in favour of the amine salt and to encourage the formation of more electrophilic nitrosating moeities. This is the case with aniline derivatives in which the total electron withdrawing power of the substituents is sufficiently strong, such as 2-cyano-4-nitroaniline, and with many heterocyclic amines (in which the heterocycle is an inherent electron acceptor) such as the thiazole, thiadiazole and thiophene types. Concentrated sulphuric acid is used as the diazotising medium for these amines and the active species is nitrosylsulphuric acid ($NO^{+}\ HSO_4^{-}$).

Formation of the attacking species involved in the diazotisation reaction[189] can be summarised by equations (3.4) and (3.5). It is clear that the nitrous acidium ion ($H_2\overset{+}{O}\text{-}NO$) does not simply lose water to form the electrophilic nitrosonium ion ($\overset{+}{N}O$) as the attacking species, but is often associated with a base X^{-} in the system either as an unsymmetrical molecular nitrous anhydride or (more likely) as an ion pair ($\bar{X}\ \overset{+}{N}O$).

The general mechanism of diazotisation was mainly elucidated by Hughes, Ingold and Ridd,[190,191] and is shown in Scheme 3.8.

$$2HNO_2 \rightleftharpoons O_2N\text{-}NO + H_2O \qquad \text{Low acidity (dil. } HClO_4 \text{ or} < 85\%\ H_2SO_4) \qquad (3.4)$$

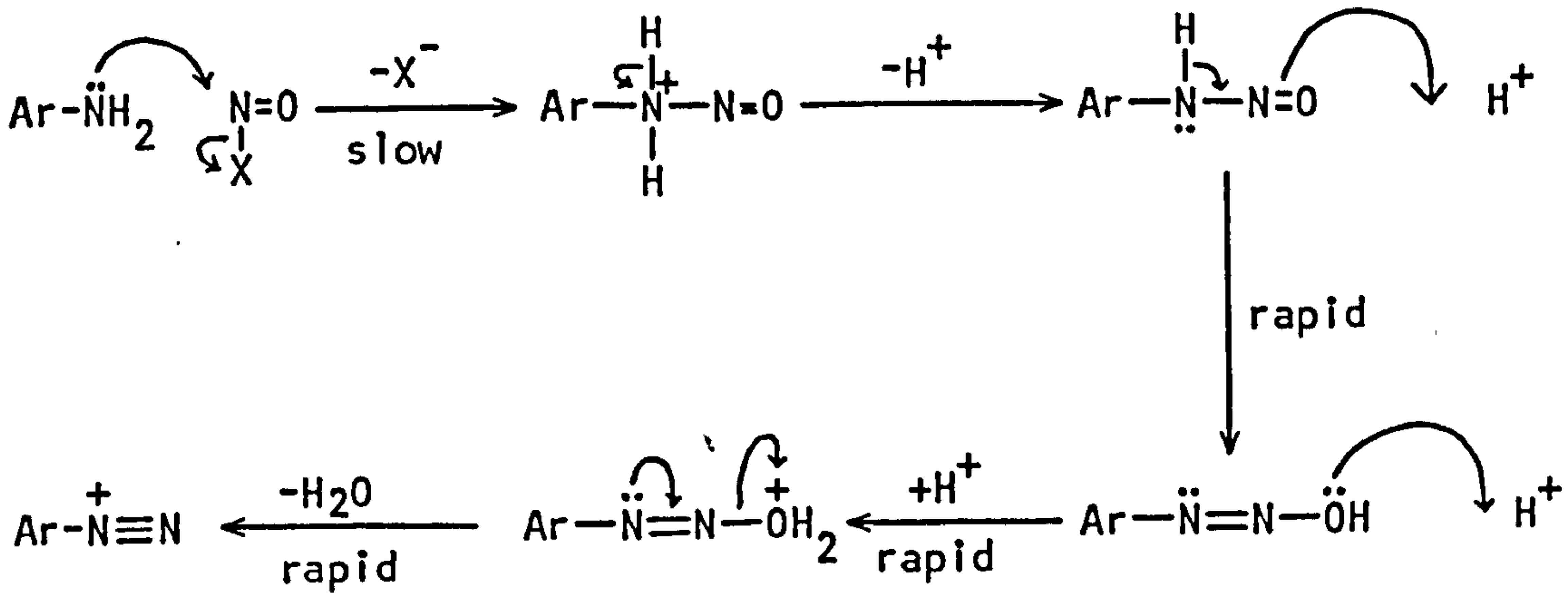


Moderate acidity: X = Cl, Br (in dil. HCl or HBr)

High acidity: X = OSO_3H (in > 85% H_2SO_4)

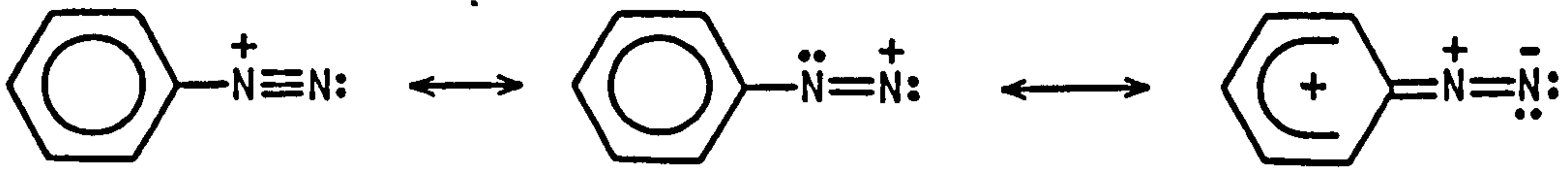
(3.5)

Order of reactivity: $O_2N\text{-}NO < X\text{-}NO \leq H_2\overset{+}{O}\text{-}NO < \overset{+}{N}O$



Scheme 3.8. General mechanism for diazotisation.

Although the aliphatic analogues readily lose N_2 (g) to form alcohols, aryl diazo compounds are relatively stable due to delocalisation of the positive charge into the aromatic ring:

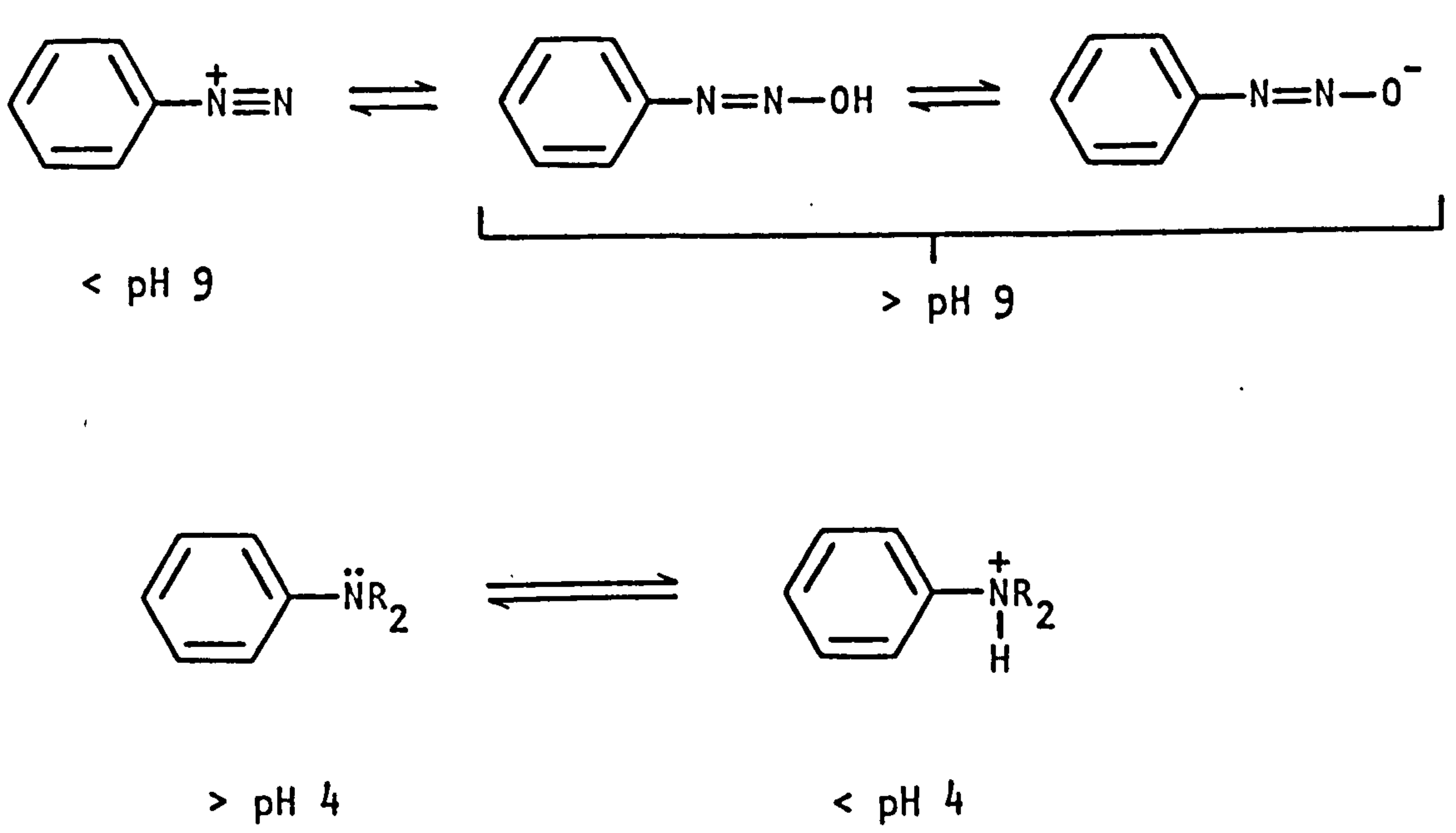


Of the amines used, the monosubstituted anilines were diazotised smoothly by the direct method. The lower basicity of 2-cyano-4-nitroaniline required the use of nitrosylsulphuric acid, as did 3,5-bistrifluoromethylaniline which, by the direct method, gave significant amounts of a water insoluble solid after diazotisation and a low yield (44%) when coupled to N-phenylmorpholine (cf., 77% using nitrosylsulphuric acid). In the diazotisation of 2,3,4,5,6-pentafluoroaniline by this method, some loss of the original purple colour was observed when the freshly prepared diazonium solution was heated to a maximum of 60°C. It may be that this heating stage should be omitted, in view of the moderate yields obtained in the present work. The nitrosylsulphuric method was also utilised for the heterocyclic amines.

Owing to the more extreme reaction conditions, the nitrosylsulphuric method may be expected to give rise to more side reactions leading to impurities, thereby lowering the yield of dye and making purification more difficult. This behaviour was indeed found to be the case.

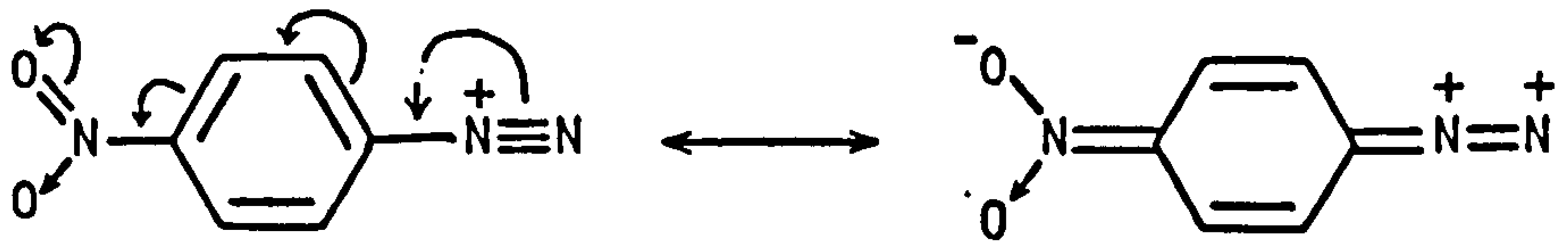
3.2.2. Azo Coupling

Coupling reactions (to amines) are carried out in a medium in which the equilibria associated with the diazo and coupling components lie as far as possible towards the diazonium ion and neutral amine, respectively. This situation obtains with an acidity of pH 4-9 (see Scheme 3.9). Consequently, coupling is carried out under buffered acidic conditions (using acetic acid and sodium acetate) and at 0 °C to reduce the decomposition of the diazonium ion. Reaction times vary and are dependent on the reactivities of the diazonium and the coupler species. Although the diazonium group is one of the strongest electrophiles known, aromatic diazonium ions are relatively weak electrophiles due to charge delocalisation into the aromatic ring, as previously mentioned. The electrophilicity is sensitive to substituent effects; electron withdrawing groups in the aromatic ring accentuate the positive charge associated with the diazo group (and hence increase the reactivity) either by mesomeric interaction [at *ortho* and/or *para*

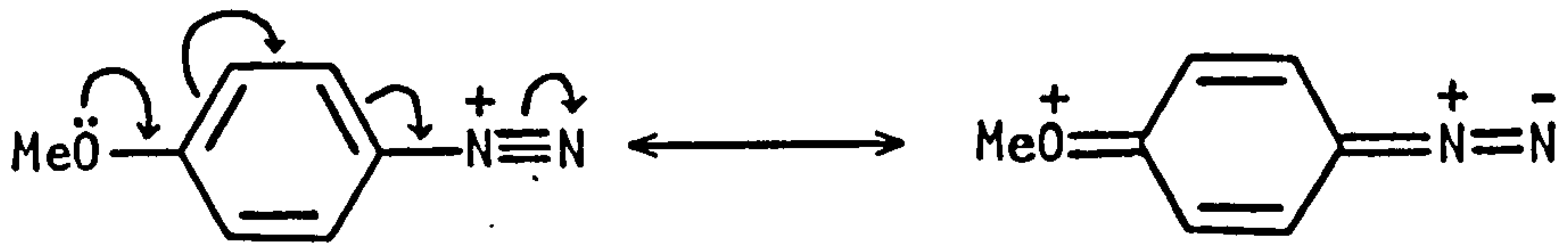


Scheme 3.9. Species involved in azo coupling reactions.

positions; large effects (111)] or by inductive interaction(at meta positions; smaller effect). Electron donating groups in ortho and/or para positions decrease the reactivity by lowering the positive charge on the diazo group (112) but meta substituents generally behave similarly



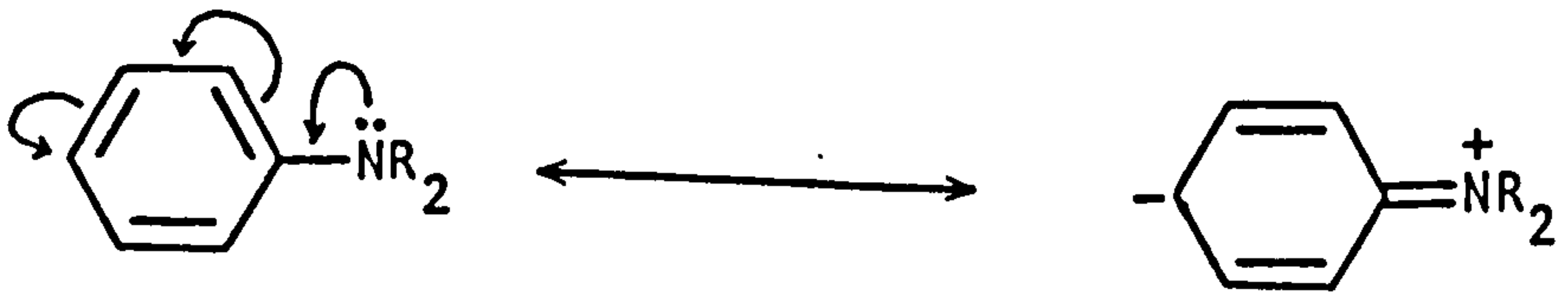
(111)



(112)

to electron withdrawing groups due to the inductive effect. Each of the above substituents increases the stability of the ion, relative to that of the parent species by increasing the double bond character of the C-N bond.

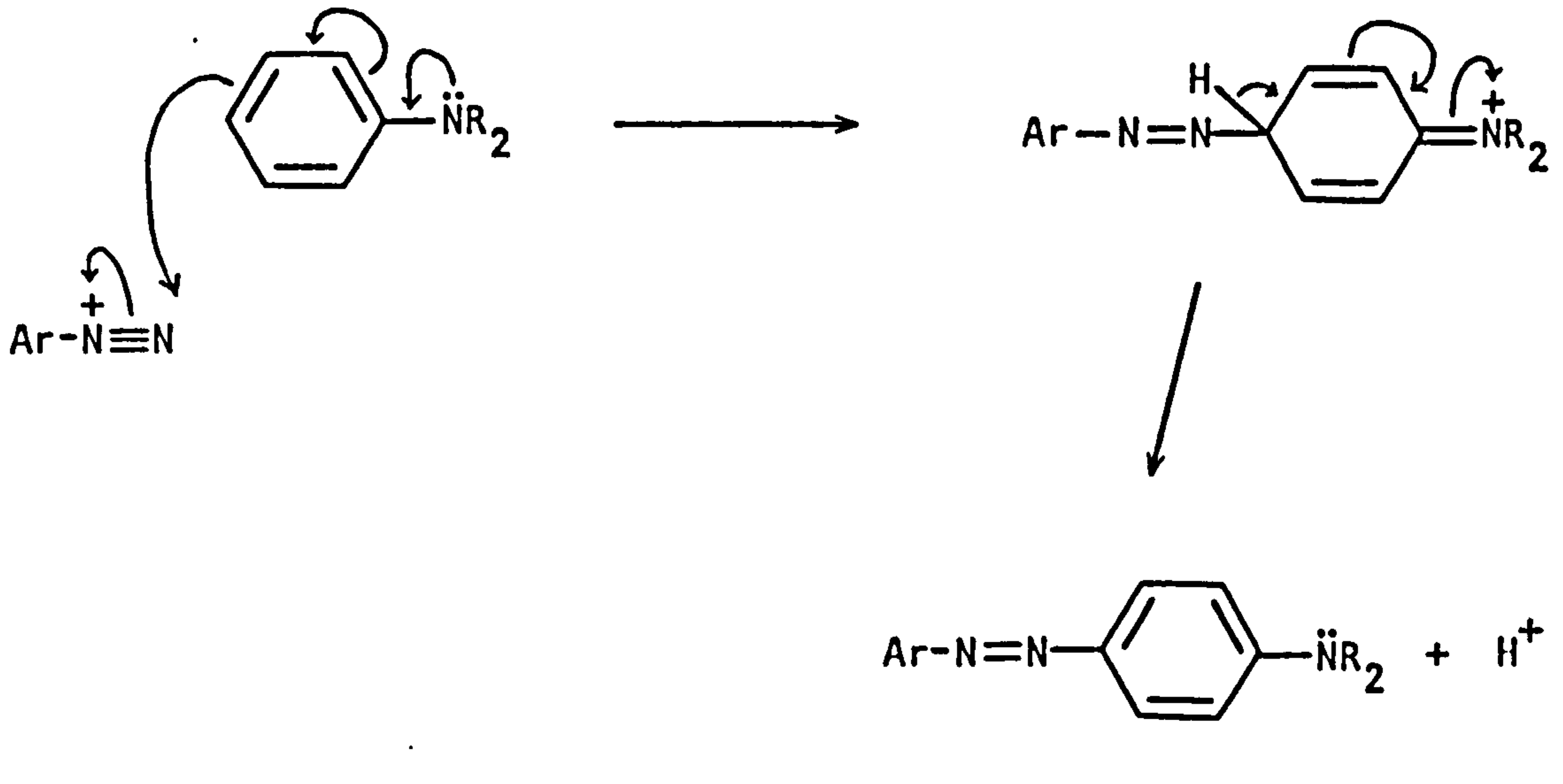
The weak electrophilic character of the diazonium ion ensures that a centre of high electron density is required for any coupling reaction to occur. This requirement is provided in the coupling component by mesomeric donation by the terminal nitrogen lone pair (113), and coupling



(113)

generally occurs at the para position. ortho-Coupling is normally prevented by the steric crowding caused by the R substituent groups.

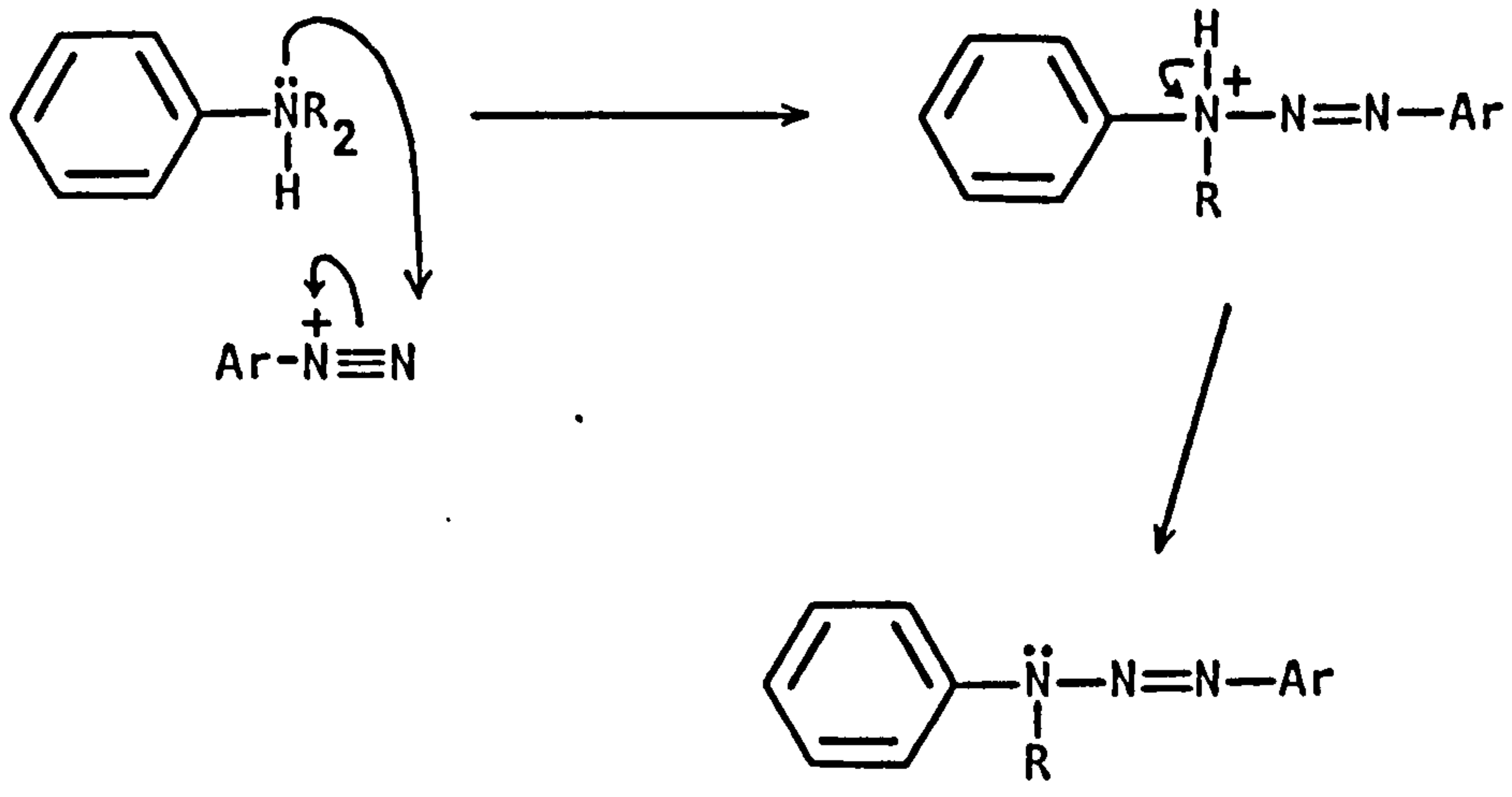
The C-coupling mechanism with tertiary amines is shown in Scheme 3.10. Primary and secondary aromatic amines can also couple at the nitrogen atom (N-coupling) to give diazoamino compounds (Scheme 3.11). Rearrangement of (115) to the azo dye (114) is achieved by heating the compound in acid conditions with the addition of an excess of the coupling component.



(114)

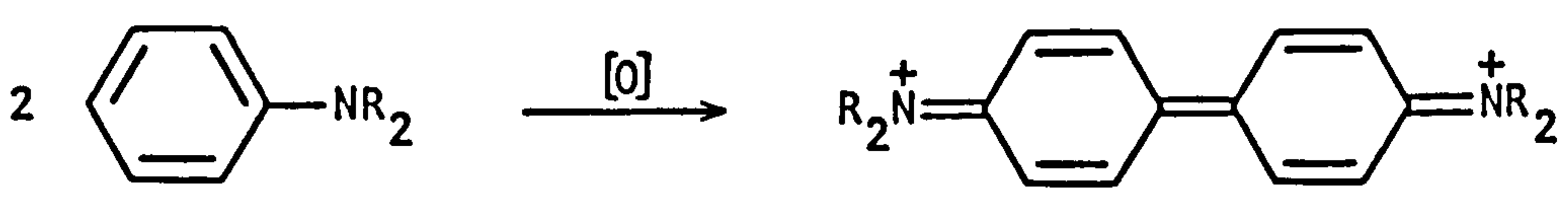
Scheme 3.10. General coupling reaction involving t-amines.

It should be noted that aromatic amines generally deteriorate on standing, probably due in part in the case of t-amines to the formation of quinonoid species (116) by oxidative self-coupling.[192] Such coloured impurities can usually be removed by distillation (or recrystallisation) and prevented by storage under a nitrogen atmosphere.



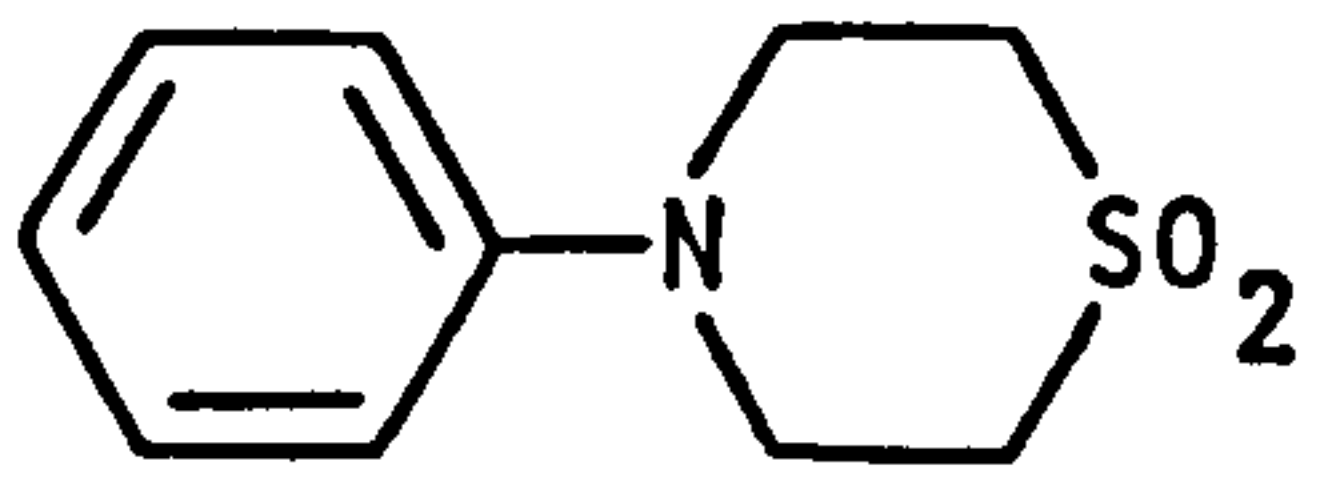
(115)

Scheme 3.11. N-Coupling reaction involving p- and s-amines.



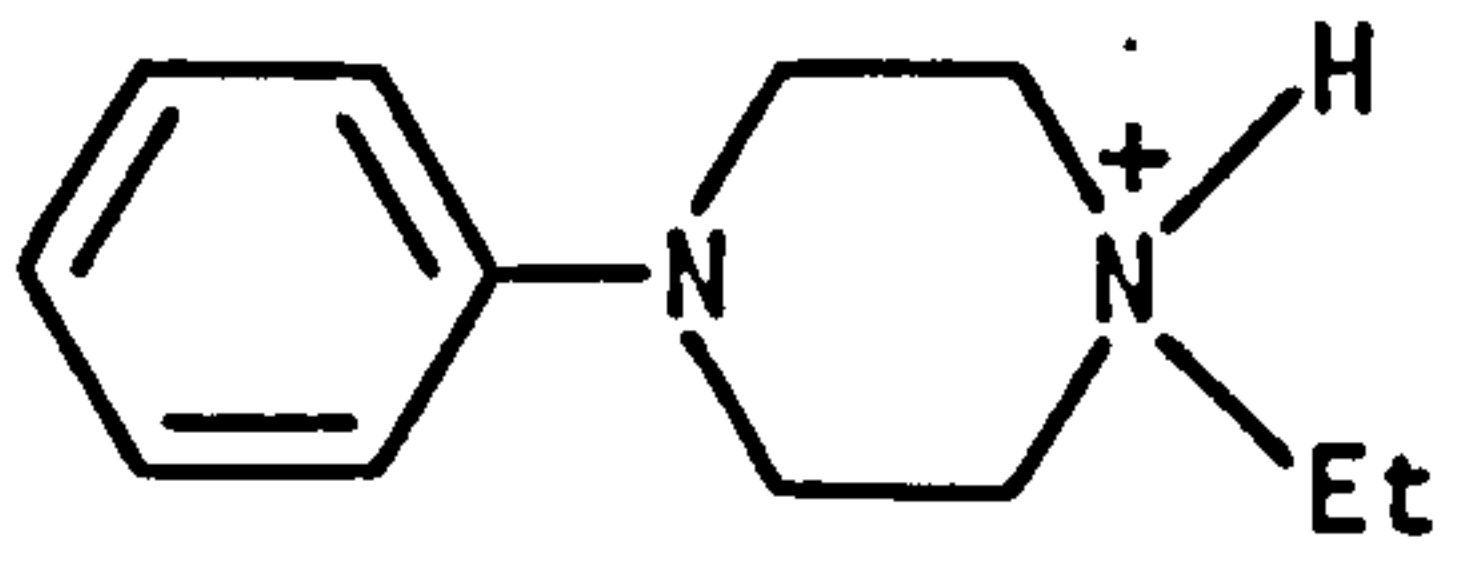
(116)

Of the coupling components used, *N*-phenylthiomorpholine-1,1-dioxide (117) proved to be very unreactive with diazotised aniline and *p*-anisidine, due to the large -I effect of the $\rangle SO_2$ group, so that dyes from these diazo components were difficult to isolate in the pure state. Reaction



(117)

between coupler and diazonium ion was continued until a test for diazonium ion (an alkaline solution of β-naphthol gives a red coloration on treatment with a drop of the test solution) proved negative; in the case of 4-methoxyphenyldiazonium chloride, the ion could be detected after several weeks at room temperature, an indication of the relative stability of this species. This procedure, however, did not lead to improved yields. The method of Ellwood and Griffiths[193] involving phase-transfer coupling was also used in an attempt to improve the yields of these dyes; this procedure proved largely unsuccessful, although a small sample of pure dye was obtained from the reaction with 4-methoxyphenyldiazonium chloride. Very low yields with the less reactive diazo components were also obtained in the case of N'-ethyl- and N'-methyl-N-phenylpiperazine, probably owing to protonation of the aliphatic amino group (see 118) during coupling which reduces the



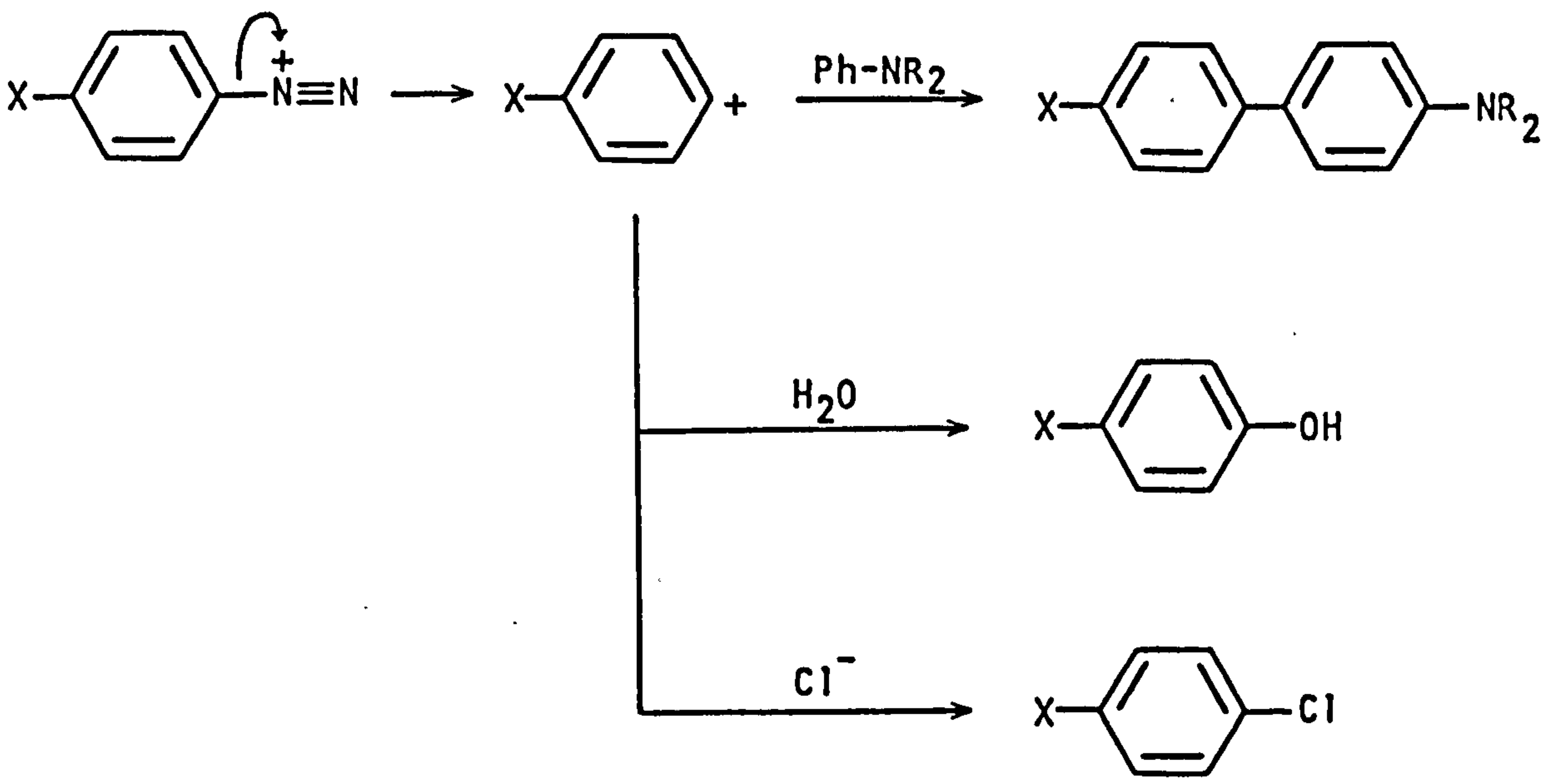
(118)

reactivity of the coupler by providing a large -I effect. The fact that N'-acetyl-N-phenylpiperazine gives much higher yields of dye supports this view, since the amide nitrogen atom is unlikely to protonate during coupling.

The other coupling components gave rise to satisfactory yields of dye.

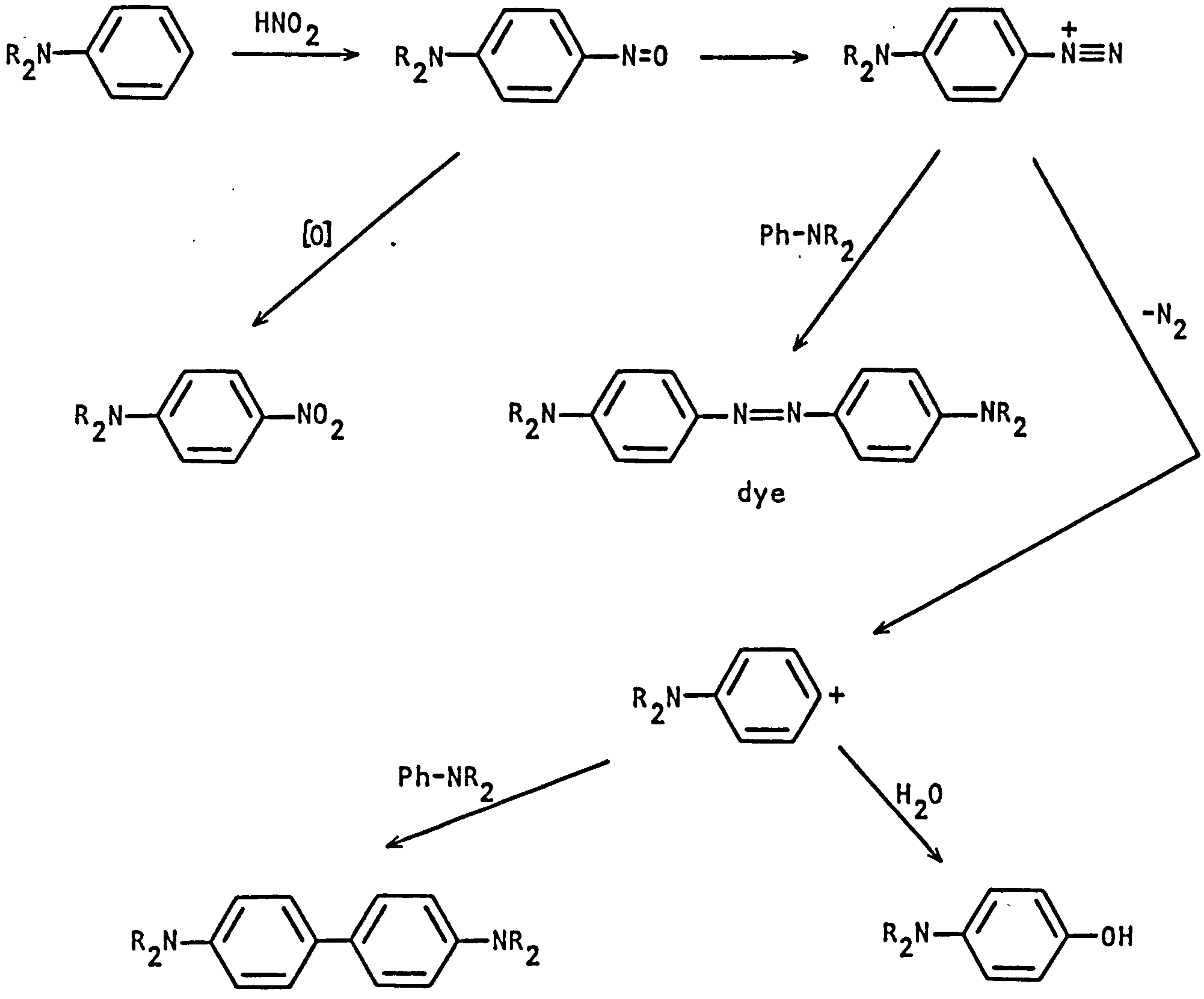
3.3. Side Reactions

Although the formation of impurities during diazotisation and coupling reactions has not been well studied, it is known that the diazonium ion is subject to loss of nitrogen by the action of light and heat. Although this decomposition is minimised by reaction at low temperature, it will still occur to some extent to give cations and radicals which may react, for instance, as shown in Scheme 3.12.



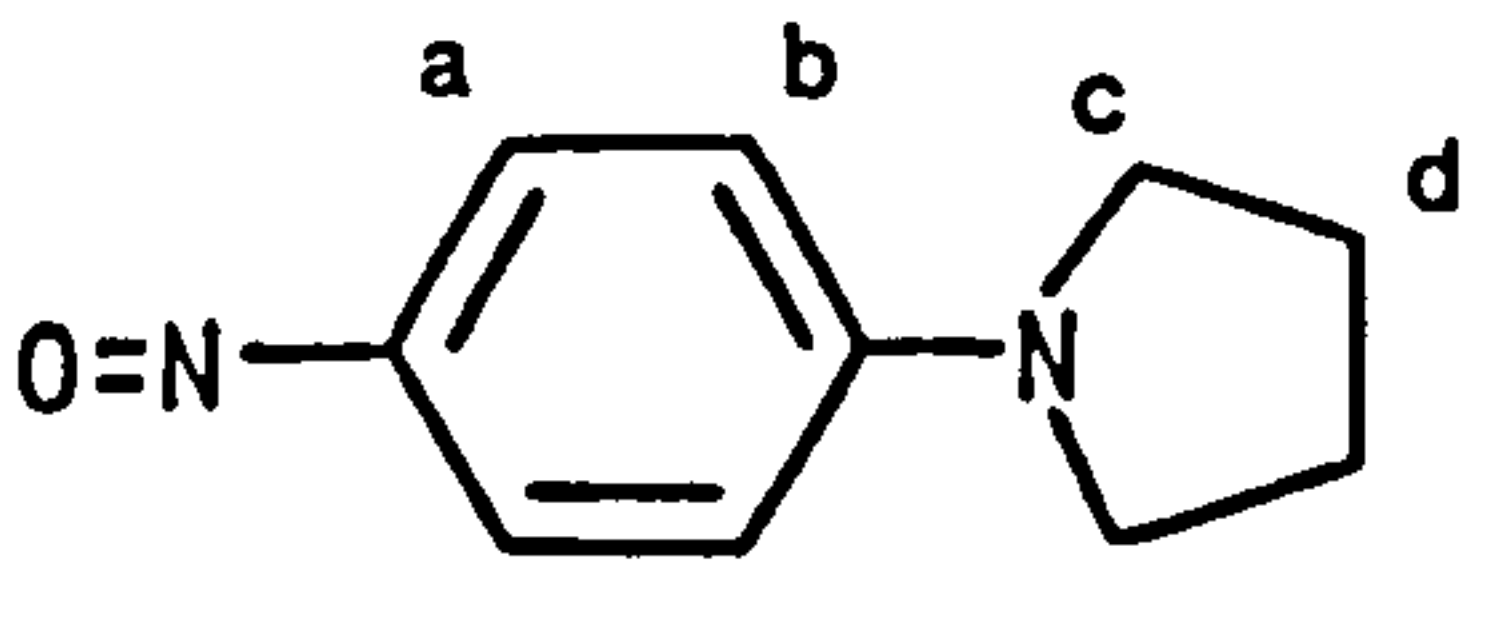
Scheme 3.12. Side reactions of diazonium ions.

Incomplete diazotisation, particularly in the case of heterocyclic amines, results in the amine being present in the end product, and the unused nitrous acid may react with coupler to give several by-products (Scheme 3.13). Thus, a small amount of N-(4-nitrosophenyl)pyrrolidine (119) was isolated and characterised by elemental analysis and n.m.r. [δ ($CDCl_3$), 7.6-8.1 (2H, broad, H_a), 6.55 (2H, d, J 9.0 Hz, H_b), 3.35-3.6 (4H, m, H_c), 1.95-2.25 (4H, m, H_d)] from the attempted coupling of diazotised (nitrosylsulphuric acid method) 5-amino-3-methylthio-1,2,4-thiadiazole with N-phenylpyrrolidine. No dye was obtained from this reaction since the diazotisation step was unsuccessful (a nitrosation process gave better results), so that appreciable amounts of nitrous acid

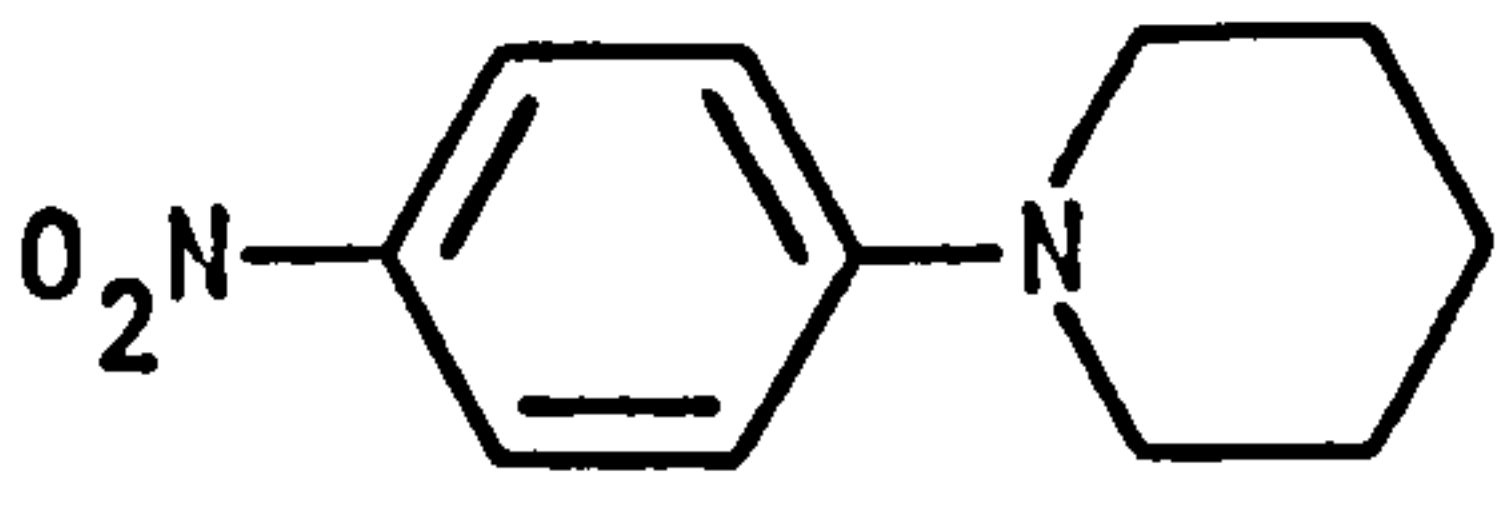


Scheme 3.13. By-products associated with incomplete diazotisation.

would have been present during the coupling stage. From the reaction of diazotised 2-amino-5-nitrothiazole with N-phenylpiperidine, a sample of N-(4-nitrophenyl)piperidine (120) was isolated (Found: C, 63.9;



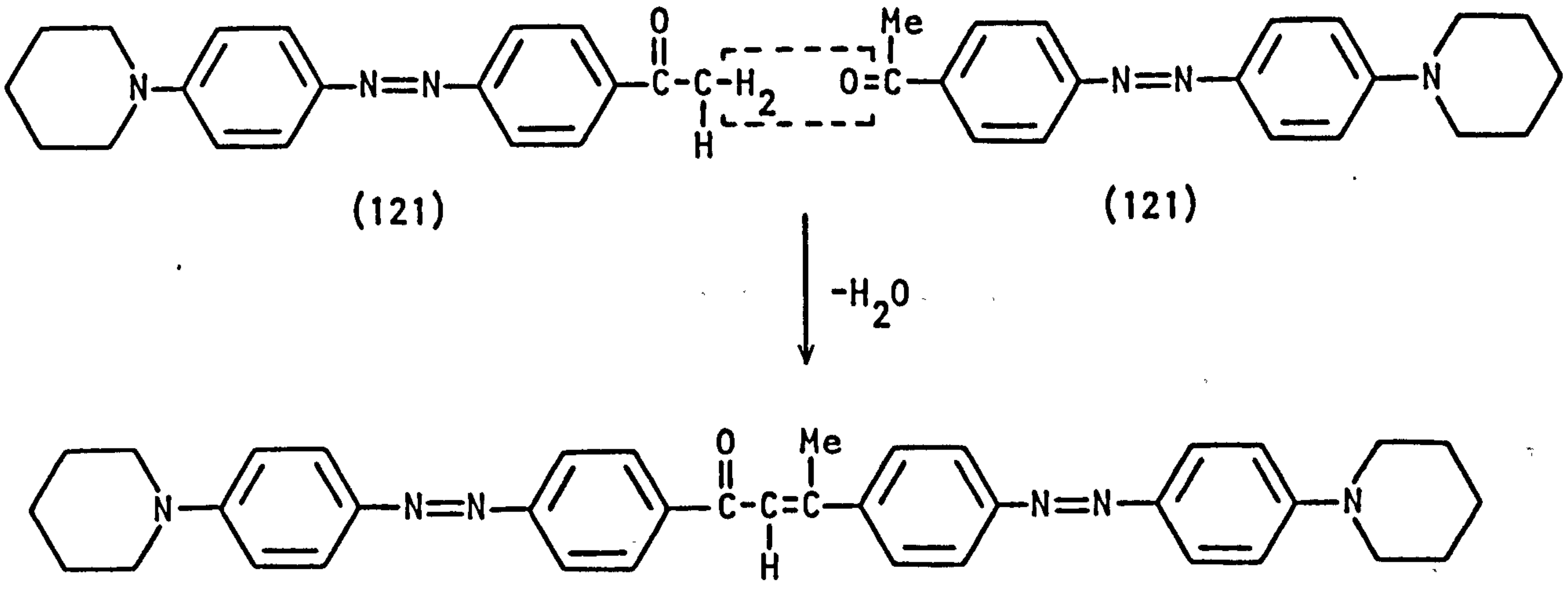
(119)



(120)

H, 6.45; N, 13.9%; M^+, 206. $C_{11}H_{14}N_2O_2$ requires C, 64.1; H, 6.8; N, 13.6% M, 206). This compound must be formed via oxidation of the corresponding intermediate nitroso derivative.

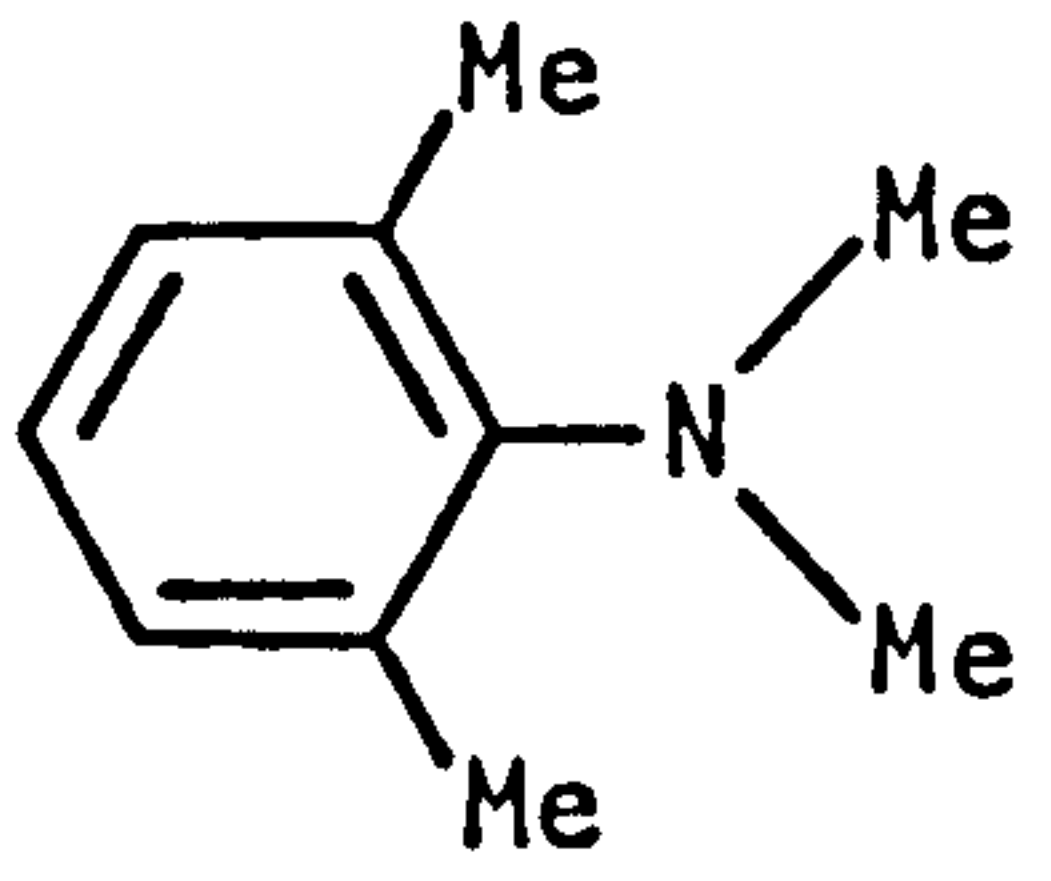
An impurity which occurred not from the coupling reaction but during purification by column chromatography (alumina, dichloromethane) was observed in the case of dye (121). Thus, condensation between two molecules of dye, involving loss of water, gave compound (122) (Found: M^+, 596; $C_{38}H_{40}N_6O$ requires M , 596) of similar colour but of slightly lower R_F value than the parent species.



(121) (121)

(122)

The coupling component (123) has been observed to undergo dealkylation of the terminal nitrogen atom during the coupling stage.[194]



(123)

Analogous reactions by the couplers in the present study would involve ring opening to give impurities of similar colour to the original dye. Such products, however, would be expected only in small amounts under normal conditions.

The nature of the diazotisation reaction is such that impurities can be expected in the final product, especially in the case of heterocyclic amines where the reaction conditions are more severe. A detailed study of these impurities would be of interest.

3.4. Purification Techniques

Most of the crude dyes were obtained as solids by filtration of the basified reaction mixture. Exceptions include many of the dyes derived from N'-ethyl- and N'-methyl-N-phenylpiperazine where unreacted coupler was removed by steam distillation and the residue was then extracted with dichloromethane; evaporation of the solvent gave the crude dye as a solid.

Purification of a crude dye was generally effected by column chromatography followed by recrystallisation. In some cases preparative layer chromatography was necessary. In the case of N-[4-(4-acetylphenylazo)phenyl]piperidine, two recrystallisations were sufficient.

Dyes obtained from heterocyclic diazo components were found to be less soluble in a given amount of solvent than their benzenoid counterparts; the dyes have lower R_F values and also contain more impurities. In practice, with these dyes, a large solution of dye was made up and added to the top of the column until it became clear that impurities of higher R_F values would not all have time to be eluted before the dye came off the column. Addition was then stopped and the dye was eluted in the normal manner. The combination of low solubility and additional impurities made purification of these dyes much more difficult.

Dye purity was confirmed by t.l.c., elemental analysis and, where solubility permitted, by n.m.r. Solubility problems were again evident in the latter case with several of the heterocyclic dyes; n.m.r. spectra for these dyes were obtained using the CAT technique.

3.5. Examination of the Dyes

In the preparation of solutions for visible spectral measurements, solubility problems were encountered with certain dyes, especially with cyclohexane as solvent and in the case of heterocyclic dyes and dyes derived from N-phenylthiomorpholine-1,1-dioxide. In these cases, λ_{max} values were measured, where possible, but ε_{max} values could not be obtained.

It has been stated[195] that the formation of cis isomers on irradiation of azo dyes is favoured by hydrocarbon solvents, such as cyclohexane, whereas ethanol inhibits this isomerisation to the greatest extent. Nevertheless, dye solutions kept overnight in the dark contain negligible amounts of cis isomer.

In the spectral measurement of acidified dyes, those species containing o-cyano groups behaved anomalously; certain dyes faded rapidly on acidification and only rough estimates of ε_{max} could be obtained.

3.6. Calculation of pK_a Values

Ionisation constants can be calculated by using the equation:[196,197]

$$pK = pH - \log\left[\frac{\varepsilon - \varepsilon_{BH^+}}{\varepsilon_B - \varepsilon}\right] - \log\left[\frac{f_B}{f_{BH^+}}\right]$$

where ε_B and ε_{BH^+} are the molar extinction coefficients of the non-protonated (base) form and the mono-protonated form of the dye, respectively, and ε is the apparent molar extinction at a given pH. All measurements are taken at one wavelength when using the equation. Rogers et al.,[198] when measuring the pK values of some 4'-substituted-4-NN-dimethylaminoazobenzenes, took the activity coefficient ratio f_B/f_{BH^+} to be unity because their dye concentrations were always small ($\sim 10^{-4}$ mol dm^{-3}). However, activity coefficients depend on the total ionic strength of the solution; in the present work the range of acidities is such that the activity coefficient ratio is not necessarily unity. As this term is to be omitted, and also since the calculations are based on acidity function (H_o) values, the basicities obtained are referred to as pK_a' values. The solubility of some of the dyes was such that their stock solutions had to be filtered before the protonated dye solutions could be produced. The unknown dye concentrations of these solutions necessitated the use of absorbance readings instead of extinction coefficients, leading to an overall modified equation:

$$pK_a' = H_o - \log\left[\frac{A - A_{BH^+}}{A_B - A}\right]$$

where A_B and A_{BH^+} are the absorbances of the solutions containing 100% non-protonated dye and 100% mono-protonated dye, respectively, and A is the absorbance of the solution at the appropriate acid concentration and at the same wavelength (usually at the λ_{max} value for BH^+, unless the extinction coefficient of the latter species is low, in which case the λ_{max} value for B was used).

The determination of A_{BH^+} (at a given acid concentration) was not straightforward for each dye. It has been stated[102] that a solution containing 100% BH^+ cannot be obtained for 4-aminoazobenzene because the pK values for mono- and di-protonation are too similar. For each dye in the present examination, the diprotonated form (BH_2^{2+}) of the dye can be obtained in concentrated sulphuric acid. However, the procedure of Carpentier and Dominique[102] could not be used because 100% BH_2^{2+} could not be obtained for most of the dyes in 50% ethanol. For the azopyrrolidine and the azojulolidine dyes it was deduced, from the constancy of the absorbance values over an appreciable range of acidities (~1-5N), together with the excellent isosbestic obtained, that the pK values for mono- and di-protonation were sufficiently separated for 100% mono-protonated dye to be obtained over this range, and this absorbance value, at the chosen wavelength, was taken as A_{BH^+}. The azopiperidine dyes showed similar behaviour, but measurements were at the λ_{max} of the neutral dye, and would therefore be insensitive to any changes in A_{BH^+} due to shifts in the tautomeric equilibrium, with increasing acid concentration, towards the azonium form. Thus, A_{BH^+} was erroneously taken as constant in this case, leading to a slight discrepancy in the calculated pK_a' value. The error involved, however, will be much smaller than if measurements had been taken at λ_{max} for BH^+, since at this wavelength the spread of absorbance values is small, thereby making the basicity calculation prone to large errors.

No such range of acidities was found for the other dyes and, in addition, a slight lateral displacement of the isosbestic point was observed at higher acidities. For these dyes, "titration plots" of absorbance, adjusted laterally[199] where necessary, against H_o, revealed a significant "medium effect", i.e. the absorbance value did not level off to some constant value, but instead showed a gradual increase as the amount of azonium species increased. The procedure adopted, based on the work of Reeves,[199] Safta and Ostrogovich,[200] Haldna[201] and Katritzky et al.[202] was to extrapolate the linear part of the "titration plot" at high acidities backwards to cover the region $pK_a' \pm 1$. An approximate value of pK_a' was estimated from the "titration plot". Adjusted values of A_{BH^+}, corresponding to the appropriate H_o value, were then read off the graph (Fig. 3.1). Each pK_a' value was determined from

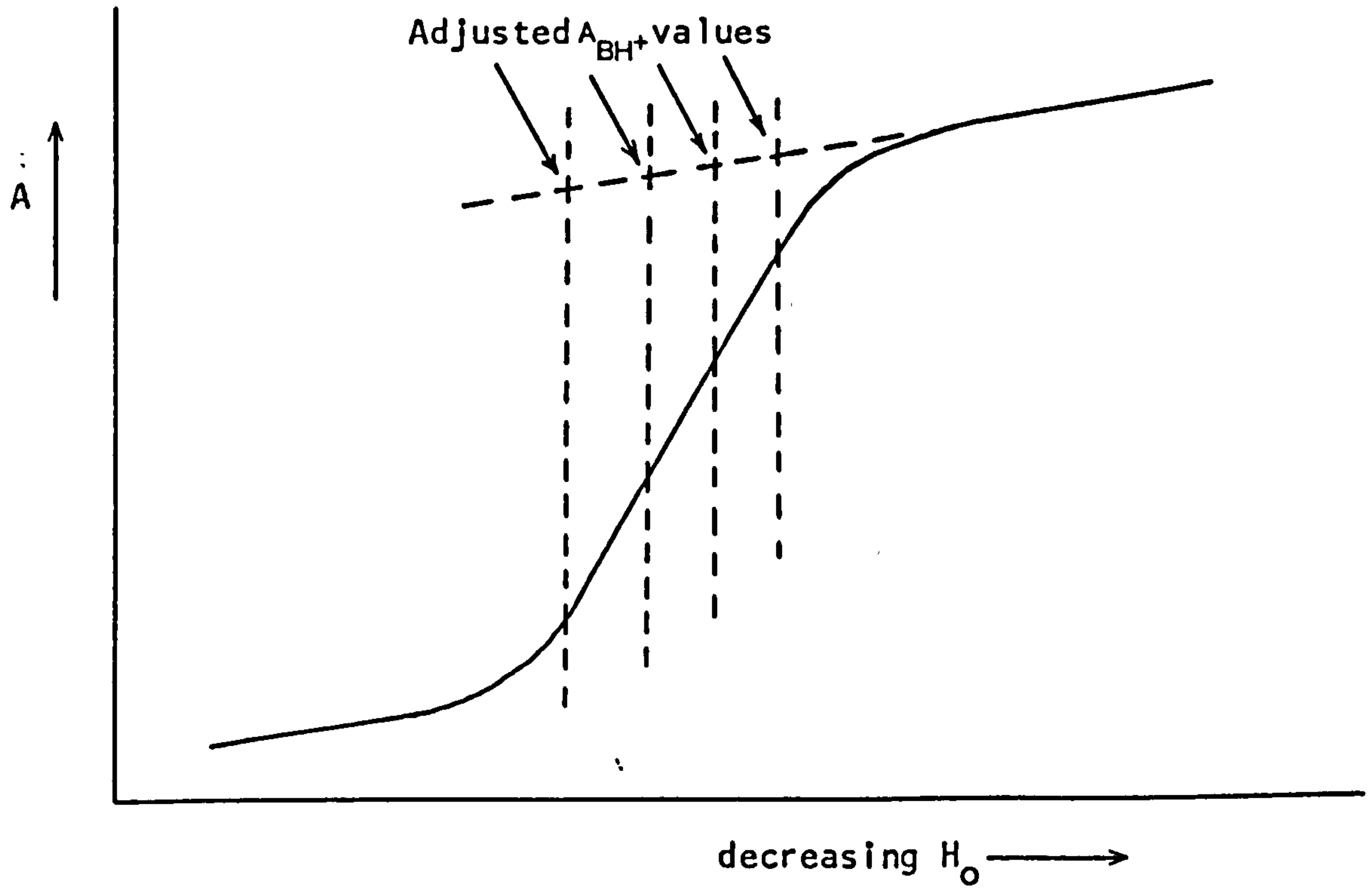


Fig. 3.1. A typical "titration plot".

the linear plot of H_o against log $(\frac{A-A_{BH^+}}{A_B-A})$. Manual plots enabled "suspect points", which were remote from the straight line, to be identified. These points were found to arise when the H_o values were outside the range $pK_a' \pm 1$, and were not used thereafter. The best values of pK_a' were then calculated by least squares analysis.

The H_o values used in this work are those obtained by White et al.[203] using nitro- and chloro- substituted anilines as indicators. Yamamoto et al.[91] state that the protonation behaviour of azobenzenes, primary anilines and diphenylamines are sufficiently different to invalidate an acidity function based upon a mixture of different kinds of indicators. However, Safta[200] compared H_o values obtained for sulphuric acid in 50% ethanol based on E-1,3-dimethyl-6-(p-X-β-styryl)2,4-dioxo-1H,3H-1,3,5-triazines with those obtained for perchloric acid in 50% ethanol by Vetesnik et al.[204] using 2-hydroxyazobenzenes (the acid powers of sulphuric and perchloric acids are practically identical up to a high limit of acidity[205]). The two scales coincided excellently and were practically identical with that of the nitroaniline indicators in the same medium and in all regions studied. The H_o values of Safta[200] differ from those of White et al.[203] The latter values were chosen in the present study because of the larger range of acidities covered. It should be noted, however, that these values are quoted at 30 °C whereas a temperature of 25 °C was used in this work. However, it appears from tables of H_o values at varying temperatures[206-208] that a change from 30 °C to 25 °C will have only a negligible effect on the H_o values.

4. EXPERIMENTAL DETAILS

4.1. General Information

Melting points were determined in a Gallenkamp apparatus and are uncorrected.

Visible absorption spectra were measured in a Unicam SP800 recording spectrophotometer.

Infra-red absorption spectra were measured in a Unicam SP200 recording spectrophotometer, employing a disc made up from 1 mg of the substance in 200 mg of AnalaR potassium bromide.

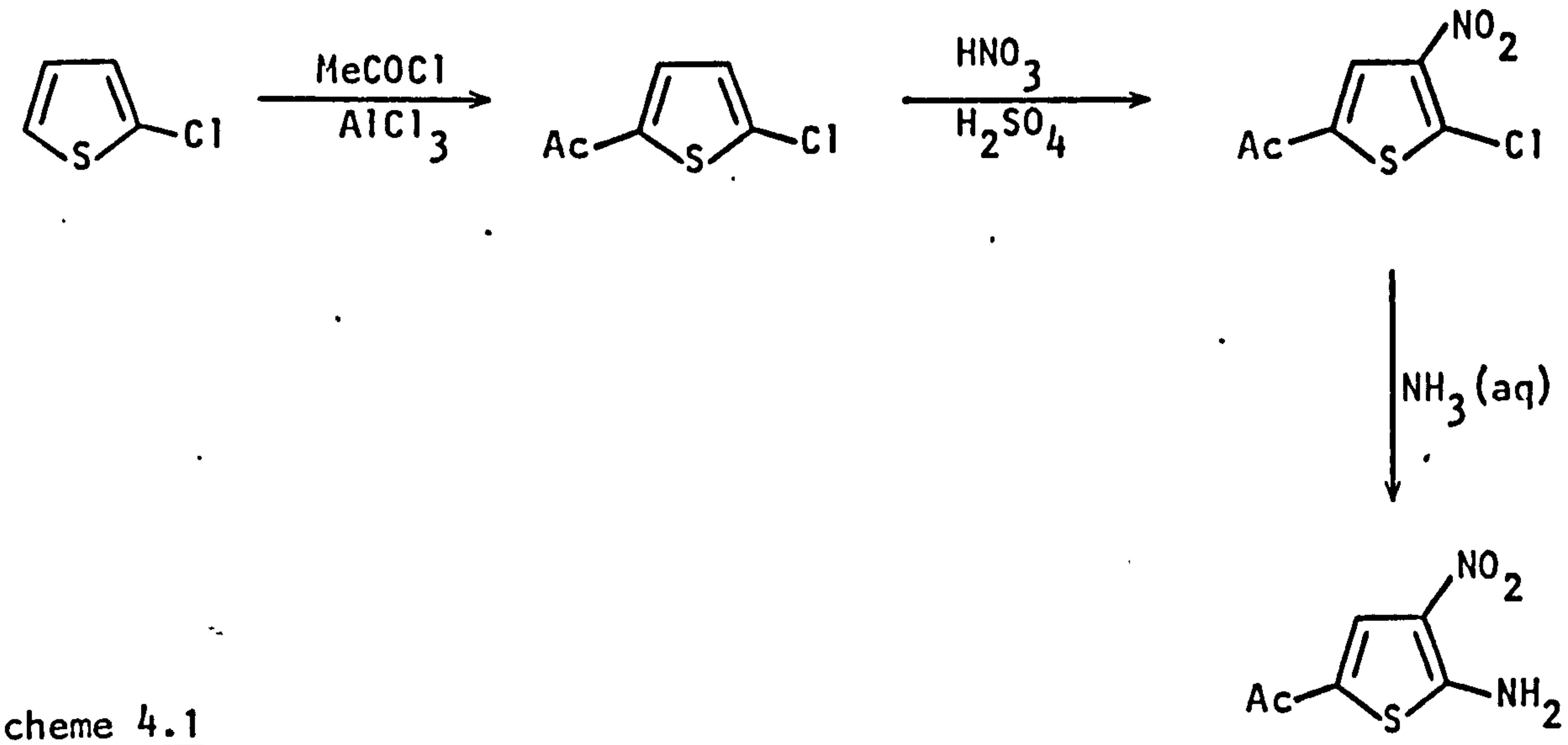
Nuclear magnetic resonance spectra were obtained with a Perkin-Elmer 12B spectrometer at 60 MHz for solutions in deuteriochloroform, unless otherwise stated.

Mass spectra were determined at the Physico-Chemical Measurements Unit, Harwell.

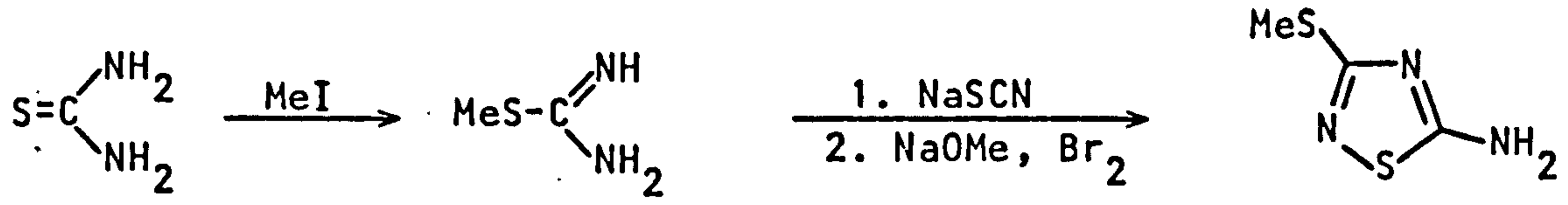
Microanalyses were carried out in the Department of Organic Chemistry, University of Leeds.

Column chromatography was carried out using active neutral alumina (Brockmann grade 1) or silica gel 100 (70-230 mesh); for preparative-layer chromatography (p.l.c.), silica gel 60H (layer thickness 0.75 mm) was used, and in the case of thin-layer chromatography (t.l.c.), silica gel 60 pre-coated aluminium sheets (without fluorescent indicator, layer thickness 0.2 mm), and alumina 60 F_{254} neutral (type E) pre-coated aluminium sheets (layer thickness 0.2 mm) were employed.

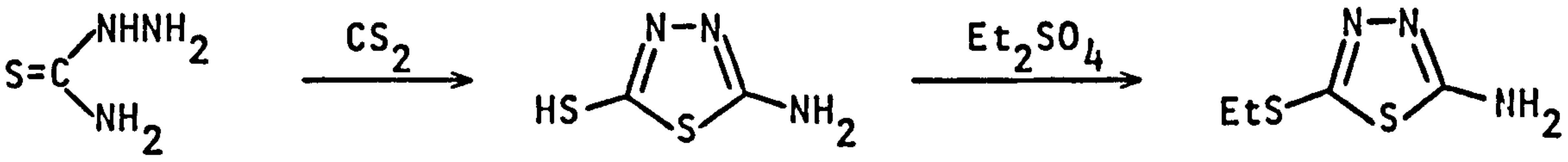
4.2. Reaction Schemes



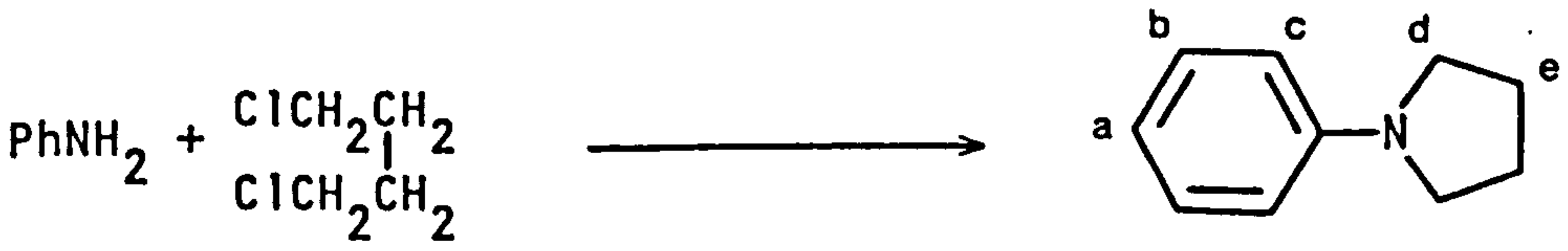
Scheme 4.1



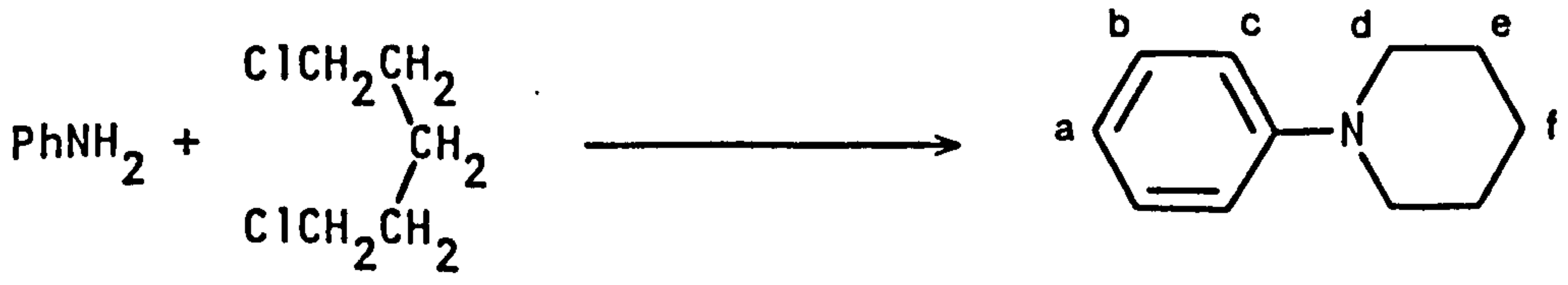
Scheme 4.2



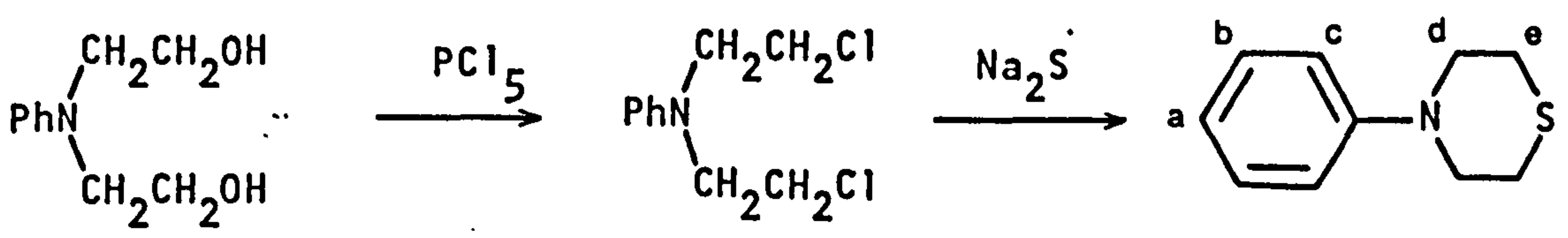
Scheme 4.3



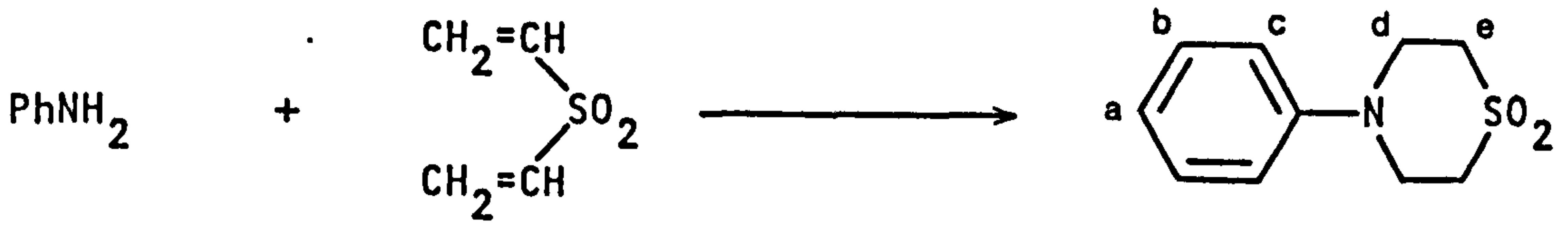
Scheme 4.4



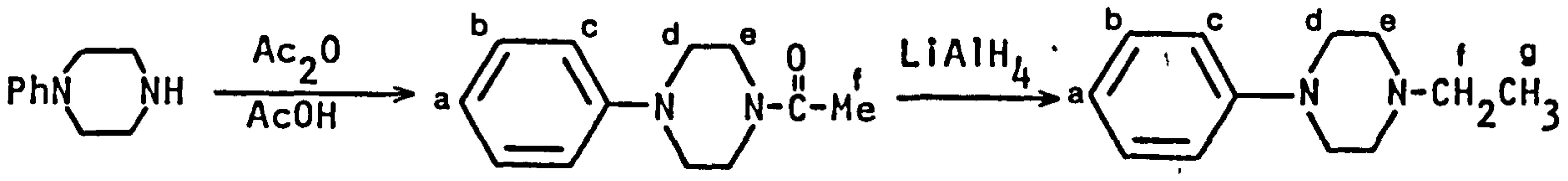
Scheme 4.5



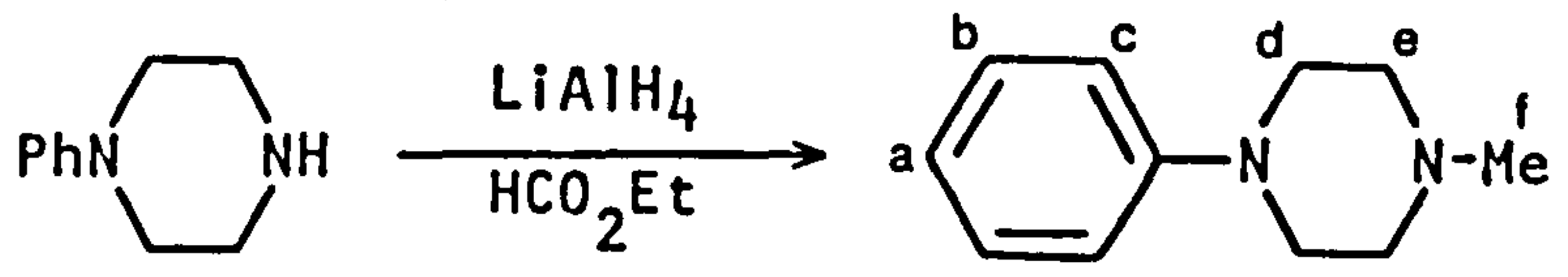
Scheme 4.6



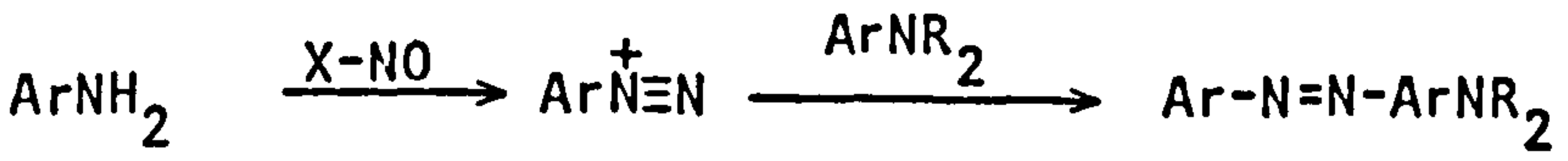
Scheme 4.7



Scheme 4.8

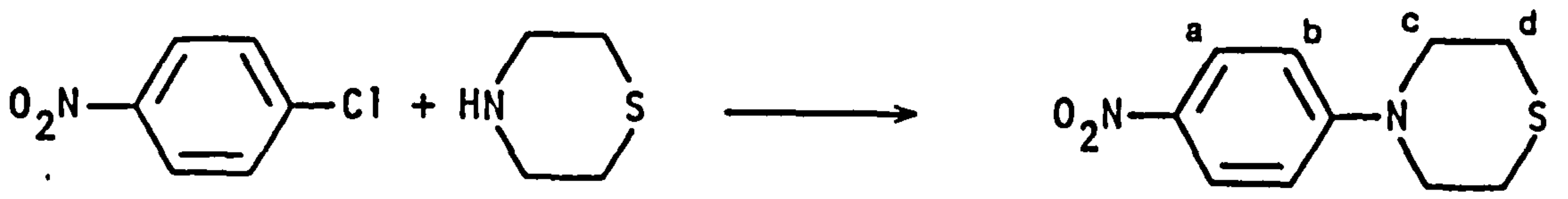


Scheme 4.9



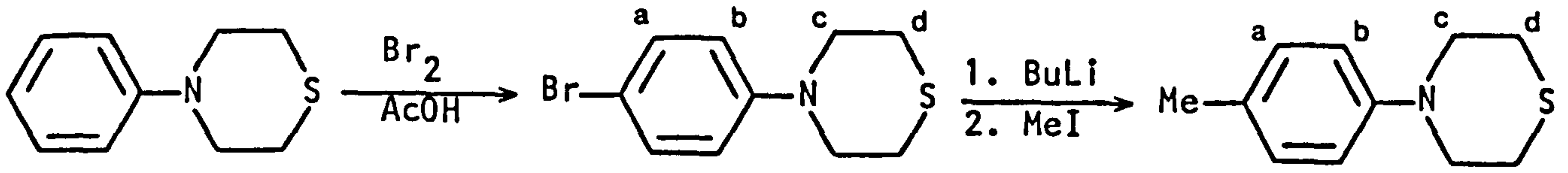
$$ArNH_2 \xrightarrow{X-NO} Ar\overset{+}{N}\equiv N \xrightarrow{ArNR_2} Ar-N=N-ArNR_2$$

Scheme 4.10

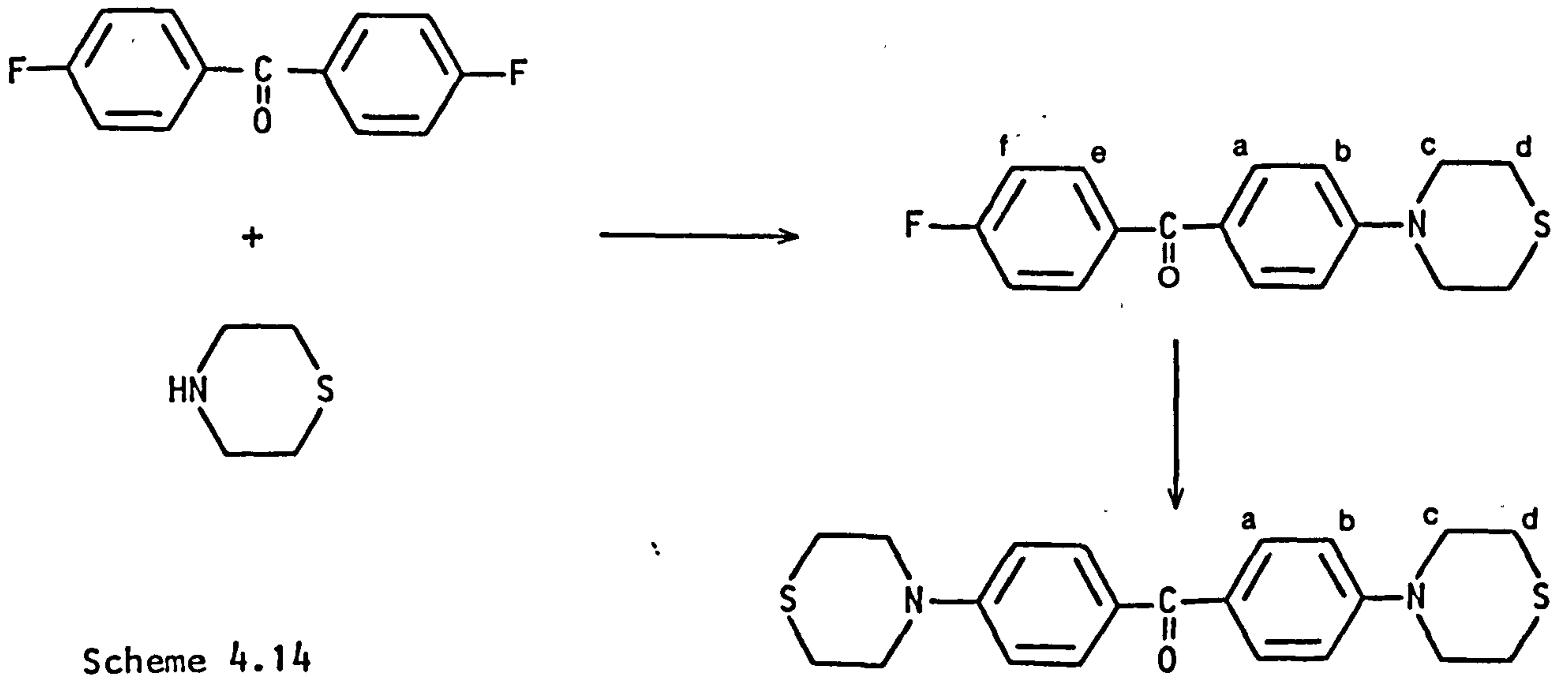


Scheme 4.11

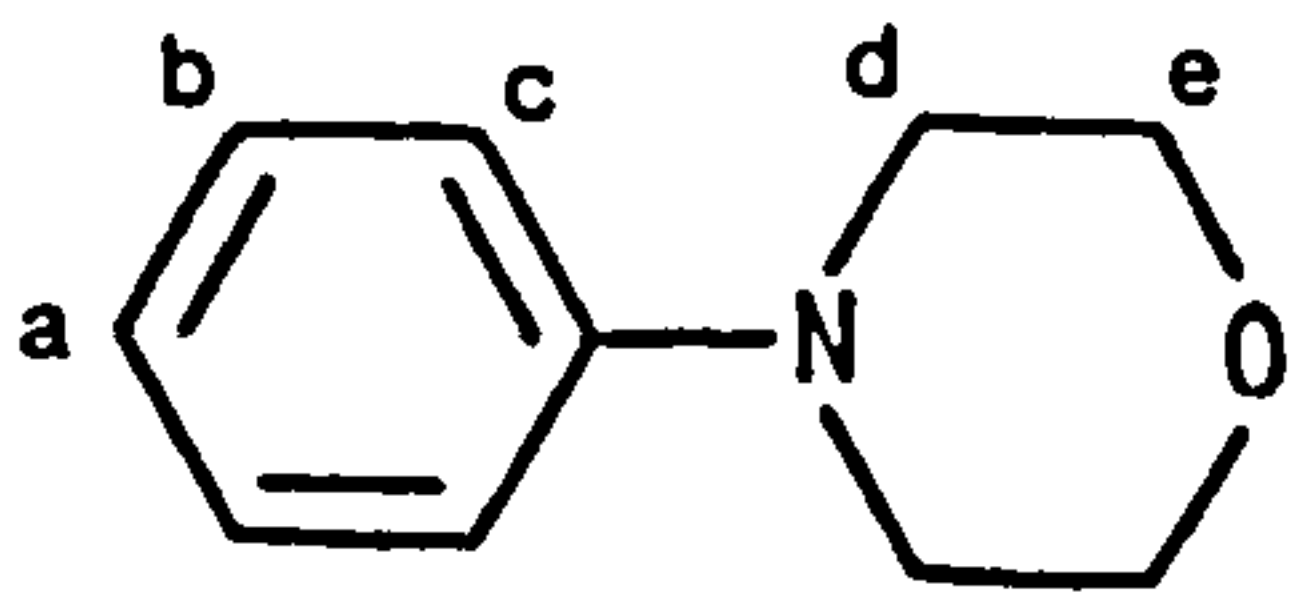
Scheme 4.12



Scheme 4.13



Scheme 4.14



(59c)

4.3. Preparation of Diazo Components.

(i) 5-Acetyl-2-amino-3-nitrothiophene (Scheme 4.1)

A solution of 2-chlorothiophene (50 g, 0.42 mole) and acetyl chloride (33 g, 0.42 mole) in hexane (300 cm^3) was treated portionwise with anhydrous aluminium chloride (56 g, 0.42 mole) at 40 °C over 40 min; a mild reaction ensued and a purple complex separated. After stirring the mixture for 1 h, the hexane was decanted off and the dark residue was decomposed by adding ice. Distillation in steam yielded a white, low melting solid (41.3 g) which was washed with a small amount of ice-cold pentane to give 5-acetyl-2-chlorothiophene (31.4 g, 48.8%), m.p. 42-4 °C (lit.,[19] 44-6 °C), $\nu_{C=O}$ 1665 cm^{-1}.

To a solution of 5-acetyl-2-chlorothiophene (24 g, 0.15 mole) in concentrated sulphuric acid (25 cm^3) was added the nitrating mixture (13 g of nitric acid and 15 g of sulphuric acid) at 0-5 °C during 30 min. The reaction mixture was poured on to ice and the resulting solid was filtered, washed with water and crystallised from ethanol, giving brown needles of 5-acetyl-2-chloro-3-nitrothiophene (21.5 g, 69.8%), m.p. 81-3 °C. Further recrystallisation from cyclohexane followed by ethanol/charcoal gave pale yellow needles, m.p. 84-6 °C (lit.,[187] 85-7 °C), $\nu_{C=O}$ 1670 cm^{-1}, ν_{NO_2} 1515 cm^{-1}.

A solution of 5-acetyl-2-chloro-3-nitrothiophene (14.5 g, 0.07 mole) and aqueous ammonia (32-33%, 50 cm^3) in methanol (300 cm^3) was heated under reflux for 1 h. On cooling, brown crystals separated and were collected. Concentration of the mother liquor produced additional solid to give a combined yield of 9.85 g (73.5%), m.p. 222-5 °C. Crystallisation from methanol/charcoal afforded 5-acetyl-2-amino-3-nitrothiophene as dark yellow needles(8.93 g, 66.6%), m.p. 224-6 °C (lit.,[19] 227-8 °C, $\nu_{C=O}$ 1645 cm^{-1},

ν_{NH_2} 3410, 3290 cm^{-1}, δ ($CDCl_3$/DMSO-d_6) 8.76 (2H, s, NH_2), 7.88 (H, s, H_{ring}), 2.46 (3H, s, Ac); signal at 8.76 disappears upon addition of D_2O.

(ii) 5-Amino-3-methylthio-1,2,4-thiadiazole (Scheme 4.2)

Methyl iodide (71 g, 0.5 mole) and thiourea (38 g, 0.5 mole) were heated together under reflux in methanol (150 cm^3) for 1 h. The solution was distilled until 30 cm^3 of distillate had been collected thereby removing the excess of methyl iodide. Sodium thiocyanate (50 g, 0.63 mole) in dry methanol (300 cm^3) was then added and the solution was stirred and cooled to -15 °C. Simultaneously, solutions of sodium (23 g, 1 mole) in methanol (300 cm^3) and of bromine (80 g, 1 mole) in methanol (215 cm^3) were added dropwise over 90 min at less than -5 °C, a proportion (1/7th) of the sodium methoxide solution being added before the addition of bromine was commenced. The mixture was then stirred for 2 h without cooling and the resulting faintly alkaline solution was neutralised with a little concentrated hydrochloric acid. The reaction mixture was evaporated to dryness and the residue was crystallised from toluene/light petroleum (b.p. 80-100 °C) to yield pale yellow needles of 5-amino-3-methylthio-1,2,4,-thiadiazole (28 g, 38.5%), m.p. 141-2 °C (softens at 134 °C) (lit.,[209] 138-39 °C), ν_{NH_2} 3325(3270 sh), 3105(3070 sh)cm^{-1}.

(iii) 2-Amino-5-ethylthio-1,3,4,-thiadiazole (Scheme 4.3)

Thiosemicarbazide (45.5 g, 0.5 mole), carbon disulphide (38 g, 0.5 mole) and sodium carbonate (29.2 g, 0.28 mole) were stirred and heated under reflux in ethanol (250 cm^3) for 15 h. The ethanol was removed by rotary evaporation and warm water (250 cm^3) was added to the residue. Diethyl sulphate (77 g, 0.5 mole) was then added dropwise at less than 70 °C and the whole was heated at 80 °C for 1 h. The cooled solution was filtered and the precipitated product was washed with cold water and crystallised from methanol to give 2-amino-5-ethylthio-1,3,4-thiadiazole as a pale yellow solid (37.5 g, 46.6%), m.p. 129-32 °C (lit.,[209] 132-5 °C), ν_{NH_2} 3260,3100 cm^{-1}.

4.4. Preparation of Coupling Components

(i) N-Phenylmorpholine (59c - p.161)

A commercial sample was used (m.p. 50-54 °C), δ ($CDCl_3$) 7.2-7.5(2H, m, H_b); 6.8-7.1(3H, m, $H_{a,c}$), 3.8-4.05 (4H, m, H_e), 3.1-3.3 (4H, m, H_d).

(ii) N-Phenylpyrrolidine (Scheme 4.4)

1,4-Dichlorobutane (63.5g, 0.5 mole) and redistilled aniline (172g, 1.85 mole) were heated together under reflux for 30 min, the mixture was cooled and poured into water (300 cm^3). Evaporation of the dried ($MgSO_4$) dichloromethane extracts (2 x 150 cm^3) gave a dark red oil which was boiled with acetic anhydride (100 cm^3) for 1 h and then distilled under reduced pressure. The fraction collected at 90-100 °C/0.6 mm Hg was redistilled to give N-phenylpyrrolidine as a colourless liquid (57.1g, 77.7%), b.p. 91-2 °C/0.6 mm Hg (lit.,[210] 124 °C/14 mm Hg, see also Scheme 3.1) (Found: C, 80.0; H, 8.6; N, 9.45%. $C_{10}H_{13}N$ requires C,81.6; H, 8.85; N, 9.5%), δ ($CDCl_3$) 7.0-7.6 (2H, m, H_b), 6.55-6.85 (3H, m, $H_{a,c}$) 3.2-3.45 (4H, m, h_d), 1.9-2.15 (4H, m, H_e).

(iii) N-Phenylpiperidine (Scheme 4.5)

1,5-Dichloropentane (70.5g, 0.5 mole) and redistilled aniline (172g, 1.85 mole) were heated together under reflux for 30 min, the mixture was cooled and worked up as in (ii) to give N-phenylpiperidine as a colourless liquid (56.4g, 70.1%), b.p. 100 °C/0.7 mm Hg (lit.,[211] 257-8 °C/752 mm Hg, see also Scheme 3.2)(Found: C, 80.3; H, 9.0; N, 9.05%. $C_{11}H_{15}N$ requires C, 82.0; H, 9.3; N, 8.7%), $\delta(CDCl_3)$ 7.2-7.5 (2H, m, H_b), 6.7-7.1 (3H, m, $H_{a,c}$), 3.1-3.3 (4H, m, H_d), 1.6-1.9 (6H, m, $H_{e,f}$).

(iv) N-Phenylthiomorpholine (Scheme 4.6)

Phosphorous pentachloride (30 g, 0.14 mole) was carefully added portionwise to a solution of NN-bis-(β-hydroxyethyl)aniline (25 g, 0.14 mole) in chloroform (100 cm^3) and the mixture was heated on a steam bath for about 6 h until the evolution of hydrogen chloride had ceased. Evaporation of the solvent gave a red gelatinous solid which, after crystallisation from methanol, gave NN-bis-(β-chloroethyl)aniline as a white solid (23.0 g, 76.4%), m.p. 42-4 °C (lit.,[212] 36-8 °C), i.r. shows absence of ν_{OH} in 3500-3000 cm^{-1} region.

A mixture of NN-bis-(β-chloroethyl)aniline (30 g, 0.14 mole) and sodium sulphide hydrate (equivalent to 31% Na_2S, 45 g, 0.18 mole Na_2S) in ethanol (200 cm^3) was heated under reflux for 18 h. The solvent was evaporated, water (200 cm^3) was added and the dried ($MgSO_4$) dichloromethane extracts (3 x 100 cm^3) were evaporated to give white needles of N-phenylthiomorpholine (11.1g, 79%), m.p. 31-2 °C (lit.,[212] 32.3-32.6 °C, see also Scheme 3.3), $\delta(CDCl_3)$ 7.15-7.45 (2H, m, H_b), 6.75-7.05 (3H, m, $H_{a,c}$), 3.45-3.7 (4H, m, H_d), 2.65-2.85 (4H, m, H_e).

(v) N-Phenylthiomorpholine-1,1-dioxide (Scheme 4.7)

Divinylsulphone (59g, 0.5 mole) and redistilled aniline (46.5 g, 0.5 mole) were stirred together on a steam bath for 3h, the mixture was then cooled and poured into water (700 cm^3). Concentrated hydrochloric acid was added dropwise at the boil until the organic layer had completely dissolved; cooling yielded white needles of N-phenylthiomorpholine-1,1-dioxide (32g, 30.3%), m.p. 118-21 °C (lit.,[213] 118-20 °C, see also Scheme 3.4),

ν_{SO2} 1310,1120 cm^{-1}, δ(CDCl$_3$) 7.2-7.5 (2H, m, H_b), 6.8-7.1 (3H, m, $H_{a,c}$), 3.75-4.0 (4H, m, H_d), 3.0-3.2 (4H, m, H_e).

(vi) N'-Acetyl-N-phenylpiperazine (Scheme 4.8)

A mixture of *N*-phenylpiperazine (20g, 0.12 mole), acetic anhydride (150g, 1.5 mole) and acetic acid (75g, 1.25 mole) was heated under reflux for 1h. The excess solvents were removed by rotary evaporation, the residual red oil was quenched with water (200 cm^3) and the organic material was extracted with dichloromethane (3 x 100 cm^3) and dried ($MgSO_4$). The dichloromethane was gradually exchanged for light petroleum (b.p. 80-100 °C) at the boil and a small amount of insoluble residue was removed by decantation. The solution was concentrated and cooled to give *N*'-acetyl-*N*-phenylpiperazine as a white crystalline solid (22.0g, 87.4%), m.p. 96 °C (lit.,[185] 96 °C, see also Scheme 3.6), $\nu_{C=O}$ 1625 cm^{-1}, δ(CDCl$_3$) 7.2-7.5 (2H, m, H_b), 6.75-7.05 (3H, m, $H_{a,c}$), 3.5-3.9? (4H, m, H_d), 3.1-3.3? (4H, m, H_e), 2.14 (3H, s, H_f).

(vii) N'-Ethyl-N-phenylpiperazine (Scheme 4.8)

To a stirred suspension of lithium aluminium hydride (7.6 g, 0.2 mole) in dry ether (400 cm^3) was added a solution of *N*'-acetyl-*N*-phenylpiperazine (21g, 0.1 mole) in ether (200 cm^3) at such a rate that gentle refluxing occurred. The refluxing was continued for 6h, after which time the mixture was cooled in ice before ethyl acetate (17.6g, 0.2 mole) was carefully added to destroy the excess of lithium aluminium hydride. The resulting grey suspension was then poured carefully into chilled sulphuric acid (10% solution, 800 cm^3). Basification of the mixture gave a white precipitate in the aqueous layer which was filtered off; the filtrate was extracted with ether (3 x 100 cm^3). The filter cake was washed with ether and the combined extracts were dried (NaOH pellets).

Evaporation of the solvent and vacuum distillation of the residue gave N'-ethyl-N-phenylpiperazine as a viscous oil which solidified in the receiver flask to give a white solid (17.0 g,89.5%), 95-8 °C/ 0.7 mm Hg, m.p. 40-43 °C. Two recrystallisations from ethanol raised the melting point to 47-49 °C (lit.,[181] 50-51 °C, see also Scheme 3.5), $\delta(CDCl_3)$ 7.1-7.4 (2H, m, H_b), 6.7-7.0 (3H, m, $H_{a,c}$), 3.15-3.35 (4H, m, H_d), 2.5-2.7 (4H, m, H_e), 2.52 (2H, q, J7.0Hz, H_f), 1.14 (3H, t, J7.0Hz, H_g).

(viii) N'-Methyl-N-phenylpiperazine (Scheme 4.9)

A solution of N-phenylpiperazine (purified via the acetyl derivative) (8.1 g, 0.05 mole) in dry THF (150 cm^3) was added dropwise to a suspension of lithium aluminium hydride (7.6 g, 0.2 mole) in dry THF at room temperature. After 10 min, ethyl formate (11.35 g, 0.15 mole) was added with stirring and cooling in ice. After 1h, the reaction mixture was decomposed by the careful addition of aqueous sodium hydroxide (3M, 400 cm^3). The white inorganic salts were filtered off and the filtrate was extracted with ether (3 x 100 cm^3). These extracts were combined with the ether washings of the filter cake and dried (NaOH pellets). Evaporation of solvent and vacuum distillation of the residue gave N'-methyl-N-phenylpiperazine as a viscous yellow oil (6.5 g, 74.3%) b.p. 120-24 °C/1.5 mm Hg (lit.,[184] 145 °C/2-3 mm Hg, see also Scheme 3.7) (Found: C, 74.9; H, 9.35; N, 16.05%. $C_{11}H_{16}N_2$ requires C, 75.0; H, 9.1; N, 15.9%), $\delta(CDCl_3)$ 7.1-7.4 (2H, m, H_b), 6.7-7.1 (3H, m, $H_{a,c}$), 3.1-3.3 (4H, m, H_d), 2.4-2.7 (4H, m, H_e), 2.33 (3H, s, H_f).

4.5. Preparation of Dyes (Scheme 4.10)

4.5.1. Diazotisation Procedures

(i) Monosubstituted Anilines[188]

The amine (A g,[a] B mole)[b] was dissolved in concentrated hydrochloric acid (C cm^3, 3B mole)[b] and water (20 cm^3), using heat if necessary. The clear solution was then cooled to 0 °C with efficient stirring to give a solution/suspension of the amine hydrochloride, which was treated with a solution of sodium nitrite (Dg,[a]B mole) in water (10 cm^3) at such a rate that no brown fumes were evolved. The reaction temperature was maintained at 0 °C by the addition of ice. Stirring was continued for about 15 min. The presence of a slight excess of nitrous acid in solution was tested for by using starch/iodide paper (blue-black coloration develops immediately); similarly, excess acid was detected with Congo Red paper. Any residual undissolved material was removed by filtration. The resultant clear diazonium solution was used immediately in the coupling reaction.

[a] For weights of the various amines, see Table 4.1

[b] e.g. B=0.02 mole; C=5 cm^3; D=1.4 g.

Table 4.1. Diazotisation of Monosubstituted Anilines - Amounts of Amine Used.*

Substituent	Amount of Amine		Substituent	Amount of Amine	
	A/g	B/mole		A/g	B/mole
4'-OMe	2.46	0.02	4'-CF_3	0.64	0.004
4'-Me	2.14	0.02	4'-Ac	2.70	0.02
4'-H	1.86	0.02	2'-CN	2.36	0.02
4'-Br	3.44	0.02	4'-CN	2.36	0.02
4'-Cl	2.55	0.02	4'-NO_2	2.76	0.02

*Refers to reactions with N-phenyl-piperidine, -pyrrolidine and -morpholine; for other couplers, the amounts are modified to the same number of moles as coupler (see Table 4.2).

(ii) 2,3,4,5,6-Pentafluoroaniline[56]

Finely ground sodium nitrite (0.276 g, 0.004 mole) was added portion-wise with stirring at below 20 °C to sulphuric acid (3 cm^3) at a rate such that no brown fumes were evolved. After stirring for 10 min, the suspension was heated to a maximum of 65 °C to give a clear solution which was cooled to 0 °C to give a solution/suspension of nitrosyl-sulphuric acid. This reagent was added slowly with stirring at 0 °C (external cooling) to a solution of 2,3,4,5,6-pentafluoroaniline (0.73 g, 0.004 mole) in sulphuric acid (3 cm^3) and the resulting purple solution was warmed to a maximum of 60 °C, then cooled to 0 °C to give the diazonium solution ready for coupling.

(iii) 2-Cyano-4-nitroaniline

The amine was twice recrystallised from ethanol/charcoal to give yellow needles, m.p. 203-4 °C.

Finely ground 2-cyano-4-nitroaniline (3.26 g, 0.02 mole) was added portionwise to a solution of nitrosyl-sulphuric acid (0.02 mole, made as in (ii)) at 0-5 °C. The mixture was stirred for 1h (until a test sample diluted by ice gave only a faint test for nitrite) and was ready to be used in the coupling reaction.

This method was also used for 3,5-bis-trifluoromethylaniline (4.6g, 0.02 mole).

(iv) 2-Aminothiazole[213]

A solution of nitrosyl-sulphuric acid (0.02 mole) was prepared as in (ii). At a temperature below 15 °C, 1:5 acid (propionic : acetic, 10 cm^3) was added dropwise; the resulting cloudy mixture was cooled to 0 °C and 2-aminothiazole (2g, 0.02 mole) was added portionwise. The mixture was stirred for 2h at 0 °C to give the diazonium ion as a dark orange-brown viscous solution.

This method was also used for 2-amino-5-nitrothiazole (2.03 g, 0.014 mole), all the aminothiophenes and 2-amino-5-ethylthio-1,3,4-thiadiazole (0.48 g, 0.003 mole).

(v) 2-Aminobenzthiazole[213]

2-Aminobenzthiazole (2.7 g, 0.018 mole) was dissolved in a mixture of concentrated sulphuric acid (28 cm^3) and water (50 cm^3) and cooled to 0 °C. A solution of sodium nitrite (1.3 g, 0.018 mole) in concentrated sulphuric acid (5 cm^3) was added dropwise at 0 °C and the mixture was stirred for 2h to give a viscous orange solution of the diazonium ion.

This method was also used for 2-amino-6-ethoxybenzthiazole (3.5 g, 0.018 mole).

(vi) 2-Amino-6-methylsulphonylbenzthiazole[214]

2-Amino-6-methylsulphonylbenzthiazole (4.24 g, 0.02 mole) was added to a mixture of concentrated sulphuric acid (38 cm^3) and water (30 cm^3); the mixture was heated to 90-95 °C to effect solution. The solution was cooled to 0 °C with stirring to give a fine suspension of the amine, which was treated dropwise with a solution of sodium nitrite (1.55 g, 0.0225 mole) in water (20 cm^3). The mixture was stirred for 1h to give a clear brown solution of the diazonium salt.

(vii) 2-Amino-6-nitrobenzthiazole

Nitrosyl-sulphuric acid [0.02 mole, made as in (ii)] was added to a solution of 2-amino-6-nitrobenzthiazole (3.5 g, 0.018 mole) in a mixture of orthophosphoric acid (30 cm^3) and acetic acid (9 cm^3) at 0 °C. Stirring for 4h gave a viscous dark brown diazonium solution.

4.5.2. Coupling Procedure

The general procedure used was the same for all the coupling components. A typical example is given below.

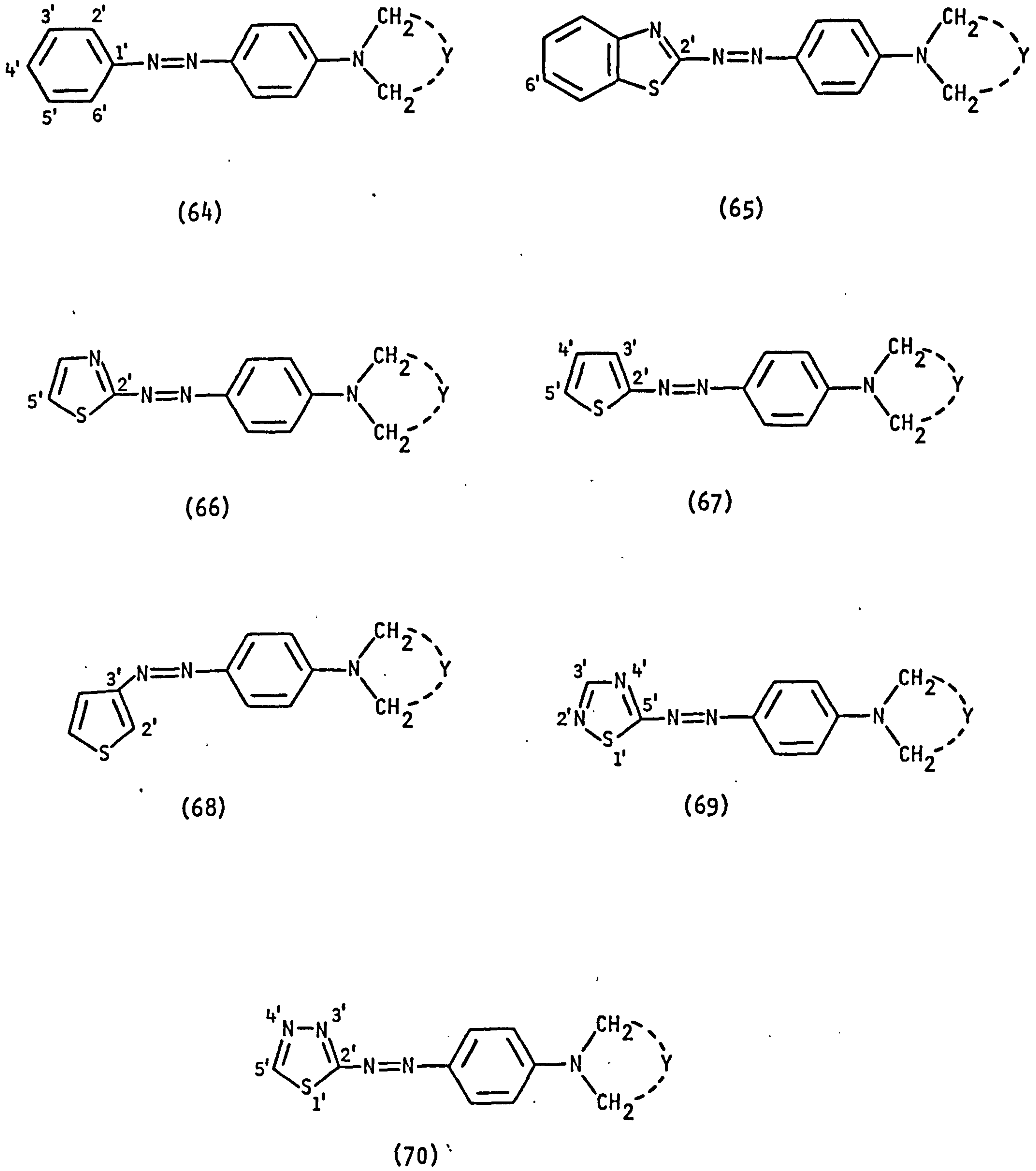
Powdered *N*-phenylpyrrolidine (2.94 g, 0.02 mole) was dispersed in a solution of acetic acid (5 cm^3) and sodium acetate (10 g) in water (10 cm^3) and cooled to 0 °C. The diazonium component was added dropwise over 15 min and the whole was stirred for 3h with internal cooling (ice) at 0 °C, then overnight at room temperature to complete the coupling reaction [in cases where an unreactive diazonium ion was added to an unreactive coupling component, the mixture was stirred for several days, often until a test for the diazonium ion (addition of a sample to a solution of alkaline β-naphthol on filter paper gives a red coloration) proved negative]. After basification with sodium hydroxide solution, the product was filtered off, washed with water and dried (or, if after basification the product remained oily, distillation in steam was carried out and the product was then filtered off or extracted with dichloromethane and isolated).

Unless otherwise stated,the crude dyes were isolated as solids.

4.5.3. Nitrosation of 5-Amino-3-phenyl-1,2,4-thiadiazole and Coupling to N-Phenylpyrrolidine[214]

5-Amino-3-phenyl-1,2,4-thiadiazole (3.55 g, 0.02 mole) was added to formic acid (90%, 20 cm^3) and the mixture was stirred for 15 min at room temperature. The milky suspension was cooled to 0 °C and finely powdered sodium nitrite (1.4 g, 0.02 mole) was added portionwise at 0-5 °C. Stirring was continued at this temperature for 1h., after which the mixture was checked for excess nitrite.

To the nitrosamine slurry was added a solution of N-phenylpyrrolidine (2.94 g, 0.02 mole) in formic acid (90%, 30 cm^3) at 0°C. After stirring for 30 min, the mixture was heated to 70 °C and maintained at 70-75 °C for 3h, producing an intense dark red solution. Water (200 cm^3) was added and the mixture was cooled to room temperature and neutralised with sodium hydroxide solution to pH 6-8; the product was filtered off and dried.



Scheme 4.1. Types of dye prepared.

Table 4.2. Physical Data of Some Azo Dyes Derived from N-Phenylpyrrolidine (59a).

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(i) N-(4-Phenylazo)phenylpyrrolidine dyes (64;Y=$-CH_2CH_2-$)							
4'-OMe	0.02	5.0	89.0	A	3.55	63.2	Orange feathery crystals
4'-Me	0.02	4.55	85.8	A	2.85	53.9	Orange feathery crystals
4'-H	0.02	3.7	73.7	A	1.9	37.8	Dark orange leaflets
4'-Br	0.02	4.9	74.2	A	3.8	57.6	Orange crystalline powder
4'-Cl	0.02	3.5	61.3	A	2.75	48.2	Orange crystalline powder
4'-CF_3	0.004	1.15	90.1	A	0.75	58.8	Orange crystalline powder
4'-Ac	0.02	4.6	78.5	A	3.0	51.2	Maroon leaflets
2'-CN	0.02	3.2	58.0	A	1.35	24.5	Dark red leaflets
4'-CN	0.02	4.3	77.9	A	3.75	67.9	Red plates
4'-NO_2	0.02	4.35	73.5	A	1.25	29.5	Purple needles
2'-CN,4'-NO_2	0.02	4.6	71.7	A	1.9	29.6	Blue-black feathery crystals
3',5'-$(CF_3)_2$	0.02	6.7	86.6	A	2.85	42.5	Orange crystalline powder
F_5	0.004	0.8	58.7	A	0.4	29.3	Orange-red plates
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]pyrrolidine dyes (65;Y=$-CH_2CH_2-$)							
6'-OEt	0.018	4.95	78.1	A	2.15	34.0	Shiny maroon leaflets
6'-H	0.018	4.0	72.2	A	2.1	38.5	Maroon needles
6'-SO_2Me	0.02	2.8	36.3	A	0.8	10.4	Fluffy maroon solid
6'-NO_2	0.018	2.6	40.9	A	1.2	18.9	Dark blue crystalline powder

continued/ ....

Table 4.2., continued/ ....

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]pyrrolidine dyes (66;Y=-CH$_2$CH$_2$-)							
5'-H	0.02	3.55	68.8	B	1.4	27.1	Dark red needles
5'-NO$_2$	0.014	1.8	29.7	A	0.5	8.3	Blue-black crystalline powder
(iv) N-[4-(Thienyl-2'-azo)phenyl]pyrrolidine dyes (67;Y=-CH$_2$CH$_2$-)							
3',5'-(CN)$_2$, 4'-Me	0.01	3.1	96.6	C	1.2	37.4	Shiny green needles
3'-NO$_2$,5'-Ac	0.015	4.65	90.1	D	1.4	27.2	Shiny green needles
3',5'-(NO$_2$)$_2$	0.01	3.2	92.0	E	0.45	12.9	Dull green-black solid
(v) N-[4-(Thienyl-3'-azo)phenyl]pyrrolidine dyes (68)							
2'-CO$_2$Me	0.01	-	-^{b}	C	0.045	1.43	Red crystalline powder
2'-COMe	0.01	-	-^{b}	F	0.12	4.0	Dark red crystalline powder
(vi) N-[4-(1',2',4'-Thiadiazolyl-5'-azo)phenyl]pyrrolidine dyes (69)							
3'-Ph	0.02	5.65	84.3	A	0.9	13.4	Violet leaflets
3'-SMe	0.01	1.3^b	42.6	A	0.4	13.1	Violet leaflets
(vii) N-[4-(1',3',4'-Thiadiazolyl-2'-azo)phenyl]pyrrolidine dye (70)							
5'-SEt	0.003	0.45	47.0	G	0.25	26.1	Purple leaflets

Table 4.3. Physical Data of Some Azo Dyes Derived from N-Phenylpiperidine (59b).

Substituent	Molarity of Reaction	Crude /%	Yield /%	Purification Technique	Pure /%	Yield /%	Appearance
(i) N-(4-Phenylazo)phenylpiperidine dyes (64; Y = $-CH_2CH_2CH_2-$)							
4'-OMe	0.02	2.75	46.6	A	1.2	20.3	Yellow leaflets
4'-Me	0.02	3.2	57.3	A	2.2	39.4	Yellow-orange leaflets
4'-H	0.02	3.4	64.3	A	2.4	45.3	Orange leaflets
4'-Br	0.02	6.2	90.1	A	3.5	50.9	Orange leaflets
4'-Cl	0.02	5.1	73.0	A	2.2	36.7	Orange leaflets
4'-CF_3	0.004	1.1	82.6	A	0.35	26.3	Dull orange solid
4'-Ac	0.02	5.5	89.6	H	3.1	50.5	Red leaflets
2'-CN	0.02	2.5	43.1	A	1.6	27.6	Dark red plates
4'-CN	0.02	4.6	79.3	A	4.0	69.0	Red leaflets
4'-NO_2	0.02	5.2	83.9	A	3.15	50.8	Maroon leaflets
2'-CN,4'-NO_2	0.02	5.15	76.7	A	4.1	61.2	Blue-black crystalline powder
3',5'-$(CF_3)_2$	0.02	4.0	49.9	I	3.1	38.7	Orange-brown feathery needles
F_5	0.004	0.3	21.2	A	0.1	7.0	Orange plates

Continued/ ....

Table 4.3.,(continued)/......

Substituent	Molarity of Reaction	Crude /%	Yield /%	Purification Technique	Pure /%	Yield /%	Appearance
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]piperidine dyes (65; Y=$-CH_2CH_2CH_2-$)							
6'-OEt	0.018	4.5	68.2	J	1.95	29.6	Red crystalline powder
6'-H	0.018	3.95	68.3	K	2.0	34.5	Violet crystalline powder
6'-SO_2Me	0.02	2.75	34.4	A	1.2	15.0	Dark blue crystalline powder
6'-NO_2	0.018	3.0	45.4	A	1.7	25.7	Black plates
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]piperidine dyes (66; Y=$-CH_2CH_2CH_2-$)							
5'-H	0.02	4.3	79.0	K	0.85	15.6	Maroon blocks
5'-NO_2	0.014	2.65	59.7	K	0.25	5.6	Blue-black needles
(iv) N-[4-(Thienyl-2'-azo)phenyl]piperidine dye (67; Y=$-CH_2CH_2CH_2-$)							
3'-NO_2,5'-Ac	0.01	1.5	41.9	K	0.65	18.2	Green needles

Table 4.4. Physical Data of Some Azo Dyes Derived from N-Phenylmorpholine (59c).

Substituent	Molarity of Reaction	Crude /%	Yield /%	Purification Technique	Pure /%	Yield /%	Appearance
(i) N-(4-Phenylazo)phenylmorpholine dyes (64; Y=$-CH_2OCH_2-$)							
4'-OMe	0.02	2.95	49.7	A	1.1	18.5	Orange leaflets
4'-Me	0.02	2.8	49.8	A	0.6	10.7	Yellow crystalline powder
4'-H	0.02	3.5	65.5	A	2.0	37.5	Yellow-orange leaflets
4'-Br	0.02	5.0	72.3	A	2.2	31.8	Yellow-orange crystalline powder
4'-Cl	0.02	4.15	68.9	A	1.3	21.6	Orange plates
4'-CF_3	0.004	1.2	89.6	A	0.7	52.2	Orange leaflets
4'-Ac	0.02	5.85	94.7	A	3.75	60.7	Orange leaflets
2'-CN	0.02	3.8	65.1	A	2.4	41.0	Red-brown feathery crystals
4'-CN	0.02	5.55	95.0	A	4.4	75.3	Red leaflets
4'-NO_2	0.02	5.1	81.7	A	3.75	60.1	Purple needles
2'-CN,4'-NO_2	0.02	5.7	84.6	A	3.6	53.5	Dull maroon powder
3',5'-$(CF_3)_2$	0.02	6.2	77.0	A	4.3	53.3	Orange plates
F_5	0.004	0.8	56.0	A	0.5	35.0	Dull orange powder

Continued/ ....

Table 4.4.,(Continued)/......

Substituent	Molarity of Reaction	Crude /%	Yield /%	Purification Technique	Pure /%	Yield /%	Appearance
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]morpholine dyes (65; Y=$-CH_2OCH_2-$)							
6'-OEt	0.018	4.0	60.4	A	2.3	34.7	Red leaflets
6'-H	0.018	3.8	65.2	A	2.1	36.2	Dull red powder
6'-SO_2Me	0.02	2.75	35.3	A	0.9	11.5	Fluffy maroon feathers
6'-NO_2	0.018	4.75	66.3	A	2.35	32.8	Violet plates
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]morpholine dyes (66; Y=$-CH_2OCH_2-$)							
5'-H	0.02	5.0	91.2	A	2.25	41.0	Red crystalline powder
5'-NO_2	0.014	2.8	78.4	A	0.25	7.0	Green-blue needles
(iv) N-[4-(Thienyl-2'-azo)phenyl]morpholine dye (67;Y=$-CH_2OCH_2-$)							
3'-NO_2,5'-Ac	0.01	2.7	75.0	L	0.55	15.3	Dull grey-green clumps

Table 4.5. Physical Data of Some Azo Dyes Derived from N-Phenylthiomorpholine (59d).

Substituent	Molarity of Reaction	Crude Yield /g	/%	Purification Technique	Pure Yield /g	/%	Appearance
(i) N-(4-Phenylazo)phenylthiomorpholine dyes (64;Y=$-CH_2SCH_2-$)							
4'-OMe	0.01	2.3	73.5	M	0.65	20.8	Orange blocks
4'-H	0.017	5.15	107.0	M	0.8	16.6	Yellow flakes
4'-Cl	0.005	1.0	63.0	M	0.7	44.1	Orange needles
4'-CF_3	0.004	1.35	96.2	M	0.85	60.6	Red leaflets
4'-CN	0.005	1.4	91.0	A	0.9	58.4	Red blocks
4'-NO_2	0.002	0.5	76.2	M	0.2	30.5	Red plates
2'-CN,4'-NO_2	0.015	5.3	99.1	A	1.8	33.7	Dark blue needles
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]thiomorpholine dye (65;Y=$-CH_2SCH_2-$)							
6'-NO_2	0.017	6.35	97.0	A	0.95	14.5	Dark blue needles
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]thiomorpholine dye (66;Y=$-CH_2SCH_2-$)							
5'-NO_2	0.005	1.25	74.6	N	0.4	23.9	Blue-green needles

Table 4.6. Physical Data of Some Azo Dyes Derived from N-Phenylthiomorpholine-1,1-dioxide (59e).

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(i) N-(4—Phenylazo)phenylthiomorpholine-1,1-dioxide dyes (64;Y=$-CH_2SO_2CH_2-$)							
4'-OMe	0.01	1.85^c	53.6	O	0.04	1.2	Yellow leaflets
4'-H		Pure dye not isolated					—
4'-Cl	0.015	2.55	48.6	A	0.8	15.2	Yellow leaflets
4'-CF_3	0.005	1.45	55.4	A	1.0	38.2	Orange crystalline powder
4'-CN	0.02	4.7	69.1	Q	1.8	26.5	Orange crystalline powder
4'-NO_2	0.02	5.7	79.2	P	2.55	44.8	Dark red crystalline powder
2'-CN,4'-NO_2	0.01	3.8	99.5	A	1.5	39.3	Purple needles
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]thiomorpholine-1,1-dioxide dye (65;Y=$-CH_2SO_2CH_2-$)							
6'-NO_2	0.01	3.5	83.9	A	0.8	19.1	Dull dark red powder
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]thiomorpholine-1,1-dioxide dye (66;Y=$-CH_2SO_2CH_2-$)							
5'-NO_2	0.014	3.85	74.9	R	0.5	9.7	Dark blue needles

Table 4.7. Physical Data of Some Azo Dyes Derived from N-Phenyl-N'-acetylpiperazine (59h).

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(i) N-(4-Phenylazo)phenyl-N'-acetylpiperazine dyes (64;Y=$-CH_2N(Ac)CH_2-$)							
4'-OMe	0.003	0.3	29.6	A	0.2	19.7	Yellow flakes
4'-H	0.003	0.5	48.7	A	0.15	12.8	Orange needles
4'-Cl	0.003	0.75	81.2	A	0.25	27.1	Orange leaflets
4'-CF_3	0.005	1.6	85.1	A	1.2	63.8	Orange crystalline powder
4'-CN	0.003	0.8	80.1	J	0.6	60.1	Orange leaflets
4'-NO_2	0.001	0.15	42.5	A	0.06	15.85	Dark red crystalline powder
2'-CN,4'-NO_2	0.003	1.05	92.6	A	0.55	48.5	Dark blue crystalline powder
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]-N'-acetylpiperazine dye (65;Y=$-CH_2N(Ac)CH_2-$)							
6'-NO_2	0.003	1.15	93.5	A	0.21	17.1	Dull maroon powder
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]-N'-acetylpiperazine dye (66;Y=$-CH_2N(Ac)CH_2-$)							
5'-NO_2	0.003	0.55	50.9	A	0.08	7.4	Dark blue crystalline powder

Table 4.8. Physical Data of Some Azo Dyes Derived from N-Phenyl-N'-ethylpiperazine (59f).

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(i) N-(4-Phenylazo)phenyl-N'-ethylpiperazine dyes (64;Y=$-CH_2N(Et)CH_2-$)							
4'-OMe	0.005	0.5^b	30.9	T	0.02	1.2	Dull yellow powder
4'-H	0.005	0.35^b	23.8	T	0.05	3.5	Dull yellow powder
4'-Cl	0.005	1.2^b	73.1	T	0.08	4.9	Dull yellow powder
4'-CF_3	0.005	1.15^b	63.5	U	0.75	41.4	Orange crystalline powder
4'-CN	0.005	1.3	81.0	A	0.9	56.1	Red blocks
4'-NO_2	0.005	1.3	77.0	S	0.4	23.7	Red leaflets
2'-CN,4'-NO_2	0.005	1.6^b	88.1	U	0.6	33.0	Dull purple powder
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]-N'-ethylpiperazine dye (65;Y=$-CH_2N(Et)CH_2-$)							
6'-NO_2	0.005	1.2	60.6	U	0.15	7.6	Dull black-red powder
(iii) N-[4-(Thiazolyl-2'-azo)phenyl]-N'-ethylpiperazine dye (66;Y=$-CH_2N(Et)CH_2-$)							
5'-NO_2	0.005	0.55	31.8	A	0.08	4.3	Blue-black plates

Table 4.9. Physical Data of Some Azo Dyes Derived from N-Phenyl-N'-methylpiperazine (59g).

Substituent	Molarity of Reaction	Crude Yield		Purification Technique	Pure Yield		Appearance
		/g	/%		/g	/%	
(i) N-(4-Phenylazo)phenyl-N'-methylpiperazine dyes (64;Y=$-CH_2N(Me)CH_2-$)							
4'-OMe	No Product Isolated						—
4'-H	No Product Isolated						—
4'-Cl	0.002	-	-	A	0.02	3.2	Dull orange blocks
4'-CF_3	0.002	0.65	93.4	V	0.06	8.6	Orange powder
4'-CN	0.002	-	-	K	0.06	10.1	Brick-red leaflets
4'-NO_2	0.003	0.7	71.8	W	0.08	7.7	Red plates
2'-CN,4'-NO_2	0.002	-	-	A	0.08	10.7	Dull purple powder
(ii) N-[4-(Benzthiazolyl-2'-azo)phenyl]-N'-methylpiperazine dyes (65;Y=$-CH_2N(Me)CH_2-$)							
6'-NO_2	0.003	1.1	96.0	A	0.16	14.0	Violet powder

[a] With many of the heterocyclic dyes, the solubility was such that several column chromatographic treatments would have been necessary to purify all the crude dye. Thus, only a portion of the dye was purified and the amount of pure product was extrapolated to obtain the total yield.

[b] Steam distillation treatment.

[c] Mainly coupler.

A : Column chromatography (alumina; dichloromethane) followed by crystallisation from toluene.

B : Column chromatography (silica; dichloromethane/toluene, 80/20 initially, then dichloromethane + 1% AR acetone to facilitate elution of dye from column) followed by crystallisation from toluene.

C : Column chromatography (silica; toluene) followed by crystallisation from toluene.

D : Column chromatography (alumina; dichloromethane) followed by two crystallisations from toluene.

E : Column chromatography (alumina; dichloromethane, repeat alumina; toluene) followed by crystallisation from toluene.

F : Column chromatography (silica; toluene) then p.l.c. (silica; toluene) followed by crystallisation from toluene. T.l.c. showed faint fluorescent impurity still present.

G : Column chromatography (alumina; dichloromethane/toluene, 50/50) followed by crystallisation from toluene.

H : Two crystallisations from toluene (chromatography promotes reaction on the column).

I : Column chromatography (alumina; dichloromethane) followed by crystallisation from ethanol/water.

J : Column chromatography (silica; dichloromethane) followed by crystallisation from toluene.

K : Column chromatography (alumina; toluene) followed by crystallisation from toluene.

L : Column chromatography (silica; toluene initially, then dichloromethane, followed by dichloromethane +0.5% ethanol) followed by crystallisation from toluene, then ethanol/light petroleum (b.p. 60-80 °C).

M : Column chromatography (alumina; toluene) followed by crystallisation from dichloromethane/light petroleum (b.p. 40-60 °C).

N : Column chromatography (silica; toluene initially, then gradually add dichloromethane up to 100%, to elute dye) followed by crystallisation from toluene.

O : Column chromatography (x2: alumina; toluene) then p.l.c. (silica; toluene) followed by crystallisation from toluene.

P : Column chromatography (alumina; dichloromethane) followed by crystallisation from acetic acid.

Q : Crystallisation from acetic acid, then butanol.

R : Column chromatography (alumina; dichloromethane initially, then add 5% AR acetone to remove dye from column) followed by crystallisation from toluene.

S : Column chromatography [(a) silica; dichloromethane initially, then gradually change to methanol; (b) alumina; dichloromethane] followed by crystallisation from ethanol.

T : Column chromatography (silica; AR acetone) then p.l.c. (silica; AR acetone) followed by crystallisation from toluene/light petroleum (b.p. 100-120 °C).

U : Column chromatography (silica; AR acetone) followed by crystallisation from toluene.

V : Column chromatography (alumina; toluene) then p.l.c. (silica; dichloromethane + 1% AR acetone) followed by crystallisation from toluene.

W : Column chromatography (silica; dichloromethane initially, then gradually add 10% AR acetone) followed by crystallisation from toluene).

Table 4.10. Melting Points and Elemental Analyses of Dyes Derived from N-Phenylpyrrolidine (59a).

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64; Y=$-CH_2CH_2-$)					
4'-OMe	168-70	72.6 73.0	6.8 6.85	14.95 15.0	
4'-Me	198-200	77.0 77.25	7.2 7.2	15.85 15.95	
4'-H	163-4	76.5 76.35	6.8 6.75	16.7 16.9	
4'-Cl	199-200	67.25 67.35	5.6 5.8	14.7 14.8	12.45(Cl) 12.3
4'-Br	202-3	58.2 58.35	4.85 4.85	12.75 12.5	24.25(Br) 24.7
4'-CF_3	206-8	63.95 64.2	5.0 4.95	13.2 13.4	17.9(F) 18.15
4'-Ac	213-15	73.7 73.8	6.5 6.35	14.3 14.45	
2'-CN	151-2	73.9 73.7	5.8 5.85	20.3 20.3	
4'-CN	222-4	73.9 74.1	5.8 5.8	20.3 20.5	
4'-NO_2	226-7	64.85 64.5	5.4 5.5	18.9 18.75	
2'-CN,4'-NO_2	210-11	63.55 63.45	4.7 4.65	21.8 21.7	
3',5'-$(CF_3)_2$	116-17	55.8 56.05	3.9 3.8	10.85 11.0	29.5(F) 29.65
F_5	146-8	56.3 56.4	3.5 3.85	12.3 12.5	27.9(F) 27.4

Continued/ ....

Table 4.10., continued/.......

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(ii) Heterocyclic Dyes (65-70; Y=$-CH_2CH_2-$)					
65; 6'-OEt	246-9	64.8 64.45	5.7 5.45	15.9 16.15	9.1(S) 9.35
65; 6'-H	252-4	66.2 66.3	5.2 5.2	18.2 18.2	10.4(S) 10.8
65; 6'-SO_2Me	260-2	56.0 56.1	4.7 4.5	14.5 14.4	16.6(S) 16.55
65;6'-NO_2	238-40	57.8 58.3	4.25 4.3	19.8 19.8	9.1(S) 8.9
66; 5'-H	195-7	60.5 60.75	5.4 5.2	21.7 21.5	12.4(S) 12.45
66;5'-NO_2	238-40dec.	51.5 51.6	4.3 4.35	23.1 22.65	10.6(S) 10.8
67;3',5'-$(CN)_2$, 4'-Me	221-2	63.55 63.85	4.7 4.85	21.8 21.6	10.0(S) 10.15
67,3'-NO_2,5'-Ac	201-2	55.8 56.3	4.65 4.65	16.3 16.15	9.3(S) 9.4
67;3',5'-$(NO_2)_2$	184-6dec.	48.4 48.95	3.75 3.95	20.2 19.9	9.2(S) 9.1
68;2'-CO_2Me	174-6	60.95 60.8	5.4 5.5	13.3 13.1	10.2(S) 10.1
68;2'-COMe[a]	155-7	–	–	–	–
69;3'-Ph	218-20	64.5 64.8	5.1 5.2	20.9 20.7	9.55(S) 9.6
69;3'-SMe	218-9	51.15 51.55	4.9 4.9	22.95 23.05	21.0(S) 21.0
70;5'-SEt	223-5	52.7 52.8	5.3 5.3	21.9 21.75	20.1(S) 19.95

---

[a] Mass spec. gives M^+, 299.1088; $C_{16}H_{17}N_3OS$ requires M, 299.1092

Table 4.11. Melting Points and Elemental Analyses of Dyes Derived from N-Phenylpiperidine (59b).

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64;Y=$-CH_2CH_2CH_2-$)					
4'-OMe	149-50	73.2 73.5	7.1 7.2	14.25 14.5	
4'-Me	166-7	77.4 77.4	7.55 7.4	15.05 15.05	
4'-H	151-2	77.0 76.8	7.15 7.35	15.85 15.95	
4'-Br	147-9	59.3 59.2	5.25 5.2	12.2 12.05	23.25(Br) 23.45
4'-Cl	133-5	68.1 68.25	6.0 5.85	14.0 14.1	11.85(Cl) 11.9
4'-CF_3	151-3	64.85 65.0	5.4 5.2	12.6 12.7	17.1(F) 17.0
4'-Ac	191-2	74.25 74.25	6.85 7.05	13.7 13.7	
2'-CN	108-10	74.5 74.35	6.2 6.5	19.3 19.4	
4'-CN	188-90	74.5 74.4	6.2 6.25	19.3 19.45	
4'-NO_2	202-3	65.8 65.65	5.8 5.75	18.05 18.0	
2'-CN,4'-NO_2	128-30	64.5 64.8	5.05 5.05	20.9 20.75	
3',5'-$(CF_3)_2$	89-91	56.85 56.95	4.25 4.2	10.45 10.7	28.45(F) 28.7
F_5	116-8	57.45 57.65	3.95 4.05	11.85 11.8	26.75(F) 26.45

continued/........

Table 4.11., continued/........

Dye	M.p./^{o}C	Elemental Analyses: Required/% Found/% C	H	N	Other
(ii) Heterocyclic Dyes (65-67;Y=-$CH_2CH_2CH_2$-)					
65;6'OEt	161-63	65.55 65.6	6.0 6.0	15.3 15.2	8.75(S) 8.8
65;6'-H	225-7	67.1 67.35	5.6 5.5	17.4 17.3	9.95(S) 9.85
65;6'-SO_2Me	228-30	57.0 57.35	5.0 4.8	14.0 13.85	16.0(S) 15.8
65;6'-NO_2	228-30	58.85 58.9	4.65 4.85	19.05 18.8	8.7(S) 8.5
66;5'-H	136-8	61.75 61.95	5.9 5.55	20.6 20.95	11.75(S) 11.55
66;5'-NO_2	239-40dec.	53.0 53.1	4.75 4.85	22.1 22.15	10.1(S) 9.9
67;3'-NO_2,5'-Ac	199-201	57.0 56.85	5.05 4.85	15.65 15.3	8.95(S) 8.75

Table 4.12. Melting Points and Elemental Analyses of Dyes Derived from N-Phenylmorpholine (59c).

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64;Y=-CH$_2$OCH$_2$-)					
4'-OMe	215-7	68.7	6.4	14.15	
		68.8	6.5	14.25	
4'-Me	219-21	72.6	6.75	14.95	
		72.7	6.85	14.8	
4'-H	194-6	71.9	6.35	15.75	
		71.8	6.35	15.95	
4'-Br	230-31	55.5	4.6	12.15	23.1(Br)
		55.45	4.65	12.2	23.6
4'-Cl	202-4	63.7	5.3	13.95	11.75(Cl)
		63.35	5.4	13.8	11.9
4'-CF$_3$	219-21	60.9	4.8	12.55	17.0(F)
		61.3	4.8	12.6	16.85
4'-Ac	235-7	69.9	6.15	13.6	
		69.9	6.15	13.85	
2'-CN	155-7	69.85	5.5	19.2	
		70.3	5.6	19.25	
4'-CN	209-11	69.85	5.5	19.2	
		69.9	5.6	19.35	
4'-NO$_2$	229-30	61.55	5.15	17.95	
		61.6	5.2	18.15	
2'-CN,4'-NO$_2$	183-5	60.55	4.45	20.75	
		60.65	4.45	21.05	
3',5'-(CF$_3$)$_2$	152-3	53.6	3.75	10.4	28.3(F)
		53.75	3.8	10.55	27.95
F$_5$	142-4	53.8	3.35	11.75	26.6(F)
		54.1	3.65	11.65	26.25

continued/........

Table 4.12., continued/.......

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(ii) Heterocyclic Dyes (65-67;Y=$-CH_2OCH_2-$)					
65;6'-OEt	217-9	61.95	5.45	15.2	8.7(S)
		61.9	5.3	15.3	8.55
65;6'-H	282-4	62.95	4.95	17.3	9.9(S)
		62.95	4.9	16.95	9.85
65;6'-SO_2Me	279-81	53.75	4.5	13.95	15.9(S)
		53.9	4.6	14.2	15.9
65;6'-NO_2	274-6	55.3	4.05	18.95	8.65(S)
		55.3	4.15	19.15	8.7
66;5'-H	211-12	56.9	5.1	20.45	11.7(S)
		56.65	5.0	20.8	11.6
66;5'-NO_2	261-3	48.9	4.1	21.95	10.05(S)
		49.0	4.35	22.25	10.2
67;3'-NO_2,5'-Ac	206-7	53.35	4.45	15.55	8.9(S)
		53.2	4.4	15.35	8.8

Table 4.13. Melting Points and Elemental Analyses of Dyes Derived from N-Phenylthiomorpholine (59d).

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64;Y=$-CH_2SCH_2-$)					
4'-OMe	156-9	65.2	6.05	13.4	10.2(S)
		65.2	5.95	13.6	10.25
4'-H	152-3	67.85	6.0	14.85	11.3(S)
		67.8	6.0	14.6	11.55
4'-Cl	179-81	60.45	5.05	13.25	11.2(Cl), 10.1(S)
		60.5	5.0	13.1	11.05 10.15
4'-CF_3	178-80	58.1	4.55	12.0	16.25(F), 9.1(S)
		57.9	4.25	11.95	16.35 9.05
4'-CN	182-4	66.25	5.2	18.2	10.4(S)
		66.2	5.1	18.1	10.05
4'-NO_2	220-22	58.55	4.9	17.05	9.75(S)
		58.65	4.6	17.05	9.4
2'-CN,4'-NO_2	143-4	57.8	4.25	19.85	9.05(S)
		57.8	4.5	19.7	9.15
(ii) Heterocyclic Dyes (65-66;Y=$-CH_2SCH_2-$)					
65;6'-NO_2	231-3	53.0	3.9	18.2	16.6(S)
		52.8	4.0	18.55	16.75
66;5'-NO_2	248-50	46.6	3.9	20.9	19.1(S)
		46.9	4.1	21.2	18.9

Table 4.14. Melting Points and Elemental Analyses of Dyes Derived from *N*-Phenylthiomorpholine-1,1-dioxide (59e).

Dye	M.p./^{o}C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64;Y=$-CH_2SO_2CH_2-$)					
4'-OMe	227-9	59.15 59.3	5.5 5.3	12.2 12.45	9.3(S) 9.35
4'-H	—	Pure sample not isolated			
4'-Cl	238-40	54.95 55.25	4.6 4.45	12.0 11.75	10.15(Cl), 9.15(S) 10.45 9.25
4'-CF_3	220-23	53.25 53.25	4.2 4.2	11.0 11.15	14.9(F) , 8.35(S) 14.7 8.65
4'-CN	273-5	60.0 60.2	4.7 4.7	16.5 16.3	9.4(S) 9.05
4'-NO_2	279-81	53.35 53.7	4.45 4.65	15.55 15.3	8.9(S) 8.9
2'-CN,4'-NO_2	254-6	53.0 53.4	3.9 3.9	18.2 17.9	8.3(S) 8.05
(ii) Heterocyclic Dyes (65-66;Y=$-CH_2SO_2CH_2-$)					
65;6'-NO_2	276-7	48.9 48.7	3.6 3.75	16.8 16.95	15.35(S) 15.35
66;5'-NO_2	291-3	42.3 42.45	3.5 3.7	19.0 18.95	17.35(S) 17.55

Table 4.15. Melting Points and Elemental Analyses of Dyes Derived from N-Phenyl-N'-acetylpiperazine (59h).

Dye	M.p./°C	Elemental Analyses: Required/% Found/% C	H	N	Other
(i) Benzenoid Dyes (64;Y=-CH$_2$N(Ac)CH$_2$-)					
4'-OMe	213-4	67.45 67.1	6.5 6.65	16.55 16.8	
4'-H	209-10	70.15 70.45	6.5 6.45	18.2 18.25	
4'-Cl	226-7	63.05 63.0	5.55 5.65	16.35 16.3	10.35(Cl) 10.15
4'-CF$_3$	208-9	60.65 60.9	5.05 5.2	14.9 15.05	15.15(F) 15.3
4'-CN	207-9	68.45 68.8	5.7 5.6	21.0 21.2	
4'-NO$_2$	238-40	61.2 60.85	5.4 5.05	19.85 19.9	
2'-CN,4'-NO$_2$	179-80	60.3 60.5	4.75 4.85	22.2 21.95	
(ii) Heterocyclic Dyes (65-66; Y=-CH$_2$N(Ac)CH$_2$-)					
65;6'-NO$_2$	255-7	55.6 55.6	4.4 4.2	20.5 20.2	7.8(S) 8.1
66;5'-NO$_2$	224-5	50.0 50.1	4.45 4.4	23.35 23.7	8.9(S) 9.05

Table 4.16. Melting Points and Elemental Analyses of Dyes Derived from N-Phenyl-N'-ethylpiperazine (59f).

Dye	M.p./°C	Elemental Analyses: Required/% Found/% C	H	N	Other
(i) Benzenoid Dyes (64; Y=-CH$_2$N(Et)CH$_2$-)					
4'-OMe	—	Pure sample not isolated			
4'-H[a]	—	—	—	—	
4'-Cl[b]	186-8	—	—	—	—
4'-CF$_3$	202-5	63.0 63.05	5.8 5.8	15.45 15.35	15.75(F) 15.5
4'-CN	204-6	71.45 71.75	6.6 6.65	21.95 22.25	
4'-NO$_2$	178-80	63.7 63.8	6.2 6.1	20.65 21.0	
2'-CN,4'-NO$_2$	124-6	62.65 62.7	5.5 5.5	23.1 23.0	
(ii) Heterocyclic Dyes (65-66;Y=-CH$_2$N(Et)CH$_2$-)					
65;6'-NO$_2$	198-9	57.6 57.25	5.05 4.8	21.2 20.85	8.1(S) 8.45
66;5'-NO$_2$	171dec.	52.0 52.35	5.20 5.15	24.3 24.4	9.25(S) 9.1

[a] Mass spec. gives M^+, 294.1848; $C_{18}H_{22}N_4$ requires M, 294.1844

[b] Mass spec. gives M^+, 328.1451; $C_{18}H_{21}N_4Cl$ requires M, 328.1455

Table 4.17. Melting Points and Elemental Analyses of Dyes Derived from N-Phenyl-N'-methylpiperazine (59g).

Dye	M.p./°C	Elemental Analyses: Required/% Found/%			
		C	H	N	Other
(i) Benzenoid Dyes (64;Y=$-CH_2N(Me)CH_2-$)					
4'-OMe	—	Pure sample not isolated			
4'-H	—	Pure sample not isolated			
4'-Cl	207-9	64.85 65.2	6.05 6.0	17.8 17.45	11.3(Cl) 11.05
4'-CF_3	223-5	62.95 62.55	5.45 5.25	16.1 16.15	16.4(F) 16.6
4'-CN	235-7	70.8 70.55	6.25 6.1	22.95 22.95	
4'-NO_2	230-2	62.75 62.7	5.85 5.5	21.55 21.8	
2'-CN,4'-NO_2	172-4	61.7 61.65	5.15 5.0	24.0 24.05	
(ii) Heterocyclic Dye (65;Y=$-CH_2N(Me)CH_2-$)					
65;6'-NO_2[a]	211-3	—	—	—	

[a] Mass spec. gives M^+, 382.1224; $C_{18}H_{18}N_6O_2S$ requires M, 382.1212

4.6. Miscellaneous Preparations

(i) N-(4-Nitrophenyl)thiomorpholine (Scheme 4.11)

4-Nitrochlorobenzene (3.94 g, 0.025 mole) and thiomorpholine (6.45 g 0.062 mole) were heated under reflux in 1-butanol (20 cm ^{3}). After 12h the solvent was evaporated under reduced pressure and the residue was treated with dilute hydrochloric acid (5%, 200 cm^3). The resulting green precipitate was filtered off and the filtrate was extracted with dichloromethane until the yellow colour of the aqueous layer had disappeared. Evaporation of solvent from the dried ($MgSO_4$) organic layer gave a green oil which was combined with the filter cake and recrystallised from ethanol (using a little toluene to facilitate complete solution) to give N-(4-nitrophenyl)thiomorpholine as dark green leaflets (4.1 g, 73.1%) m.p. 140-42 °C (Found: C, 53.45; H, 5.2; N, 12.65; S, 14.2%. $C_{10}H_{12}N_2O_2S$ requires C, 53.55; H, 5.35; N, 12.5; S, 14.3%), δ ($CDCl_3$) 8.14(2H, d, J 9.0 Hz, H_a), 6.8 (2H, d, J 9.0 Hz, H_b), 3.75-4.0 (4H, m, H_c), 2.6-2.9 (4H, m, H_d).

(ii) N-(4-Cyanophenyl)thiomorpholine (Scheme 4.12)

4-Cyanofluorobenzene (5 g, 0.044 mole) and thiomorpholine (11.29 g, 0.11 mole) were heated under reflux in 1-butanol (20 cm^3). After 10 days, work up as in (i) gave a brown solid and a brown oil, which were combined and subjected to column chromatography (silica, toluene). Crystallisation of the main band from ethanol and then from toluene afforded white crystals of N-(4-cyanophenyl)thiomorpholine (6.0 g, 66.7%), m.p. 94-5 °C (Found:C, 64.45; H, 6.05; N, 14.05; S, 15.45%. $C_{11}H_{12}N_2S$ requires C, 64.7; H, 5.9; N, 13.7; S, 15.7%), ν_{CN} = 2210 cm^{-1}, δ($CDCl_3$) 7.50 (2H, d, J 9.0 Hz, H_a), 6.82 (2H, d, J 9.0 Hz, H_b), 3.65-3.9 (4H, m, H_c) 2.55-2.8 (4H, m, H_d).

(iii) N-(4-Bromophenyl)thiomorpholine (Scheme 4.13)

A stirred solution of N-phenylthiomorpholine (8 g, 0.045 mole) in acetic acid (25 cm^3) was treated dropwise over 20 min with a solution of bromine (2.3 cm^3, 0.045 mole) in acetic acid (15 cm^3) at room temperature. The resulting white suspension was stirred overnight and then poured into water (300 cm^3). Sodium metabisulphite solution was added to destroy any unreacted bromine. The basified suspension was extracted with dichloromethane (3 x 100 cm^3); drying ($MgSO_4$) and evaporation of solvent produced a crude solid which was crystallised from methanol to give off-white crystals of N-(4-bromophenyl)thiomorpholine (9.35 g, 80.5%), m.p. 96-7 °C (Found C, 46.75; H, 4.65; N, 5.55; S, 31.05; Br, 12.05%. $C_{10}H_{12}NSBr$ requires C, 46.5; H, 4.65; N, 5.45; S, 31.0; Br, 12.4%), δ ($CDCl_3$) 7.33 (2H, d, J 9.0 Hz, H_a), 6.74 (2H, d, J 9.0 Hz, H_b), 3.4-3.6 (4H, m, H_c), 2.6-2.8 (4H, m, H_d).

(iv) N-(4-Tolyl)thiomorpholine (Scheme 4.13)

A solution of N-(4-bromophenyl)thiomorpholine (8 g, 0.031 moles) in dry ether (25 cm^3) was added dropwise to a solution of butyl-lithium (33.5 cm^3 of a 15% w/w solution in hexane, 0.052 mole) in dry ether (20 cm^3) under a nitrogen atmosphere at room temperature. After stirring for 30 min to allow the aryl-lithium to form (confirmed by adding a few drops to a solution of Michler's ketone; addition of acetic acid then gives a violet colour), methyl iodide (1.93 cm^3, 0.031 moles) in dry ether (10 cm^3) was added dropwise. The mixture was stirred for 1h and then carefully poured into aqueous sodium hydroxide (10%, 300 cm^3). Evaporation of the dried ($MgSO_4$) ethereal extracts left a brown oil. Column chromatography (silica, toluene) gave a pale yellow oil (5.15 g, 86%), m.p. ∿ 20 °C which was shown to be N-(4-tolyl)thiomorpholine of reasonable purity by t.l.c. and ^{1}H-n.m.r., δ($CDCl_3$) 7.12 (2H, d, J 8.5 Hz, H_a), 6.83

(2H, d, J 8.5 Hz, H_b), 3.4-3.65 (4H, m, H_c), 2.65-2.85 (4H, m, H_d), 2.30 (3H, s, Me). However, to obtain a sample which remained solid at room temperature required an additional column chromatographic treatment [silica, light petroleum (b.p. 40-60 °C)] and several recrystallisations from ethanol and from light petroleum (b.p. 40-60 °C) to give a white crystalline powder, m.p. 30-31 °C (lit.,[176] 32.5-33 °C).

(v) 4,4'-Bisthiomorpholinobenzophenone (Scheme 4.14)

4,4'-Difluorobenzophenone (0.2 g, 0.02 mmole) and thiomorpholine (0.95 g, 9.2 mmole) were heated under reflux in dimethylsulfoxide (10 cm^3). After 90 min, the mixture was cooled and dichloromethane (50 cm^3) was added. After washing with water (3 x 100 cm^3) to remove unreacted thiomorpholine and dimethylsulfoxide, evaporation of solvent gave a dark brown oil. P.l.c. (silica, dichloromethane : toluene, 60 : 40) of the oil yielded two major products; a yellow fluorescent band of high R_f was identified as 4-fluoro-4'-thiomorpholinobenzophenone (41mg, 15%), m.p. 159 °C (Found: C, 67.65; H, 5.4; N, 5.1; S, 10.65; F, 7.05%. $C_{17}H_{16}NSOF$ requires C, 67.75; H, 5.3; N, 4.65; S, 10.65; F, 6.3%), δ ($CDCl_3$) 7.83 (2H, d, J 9.0 Hz, H_e), 7.77 (2H, d, J 9.0 Hz, H_a), 7.06 (2H, d, J 9.0 Hz, H_f), 6.85 (2H, d, J 9.0 Hz, H_b), 3.7-3.9 (4H, m, H_c), 2.6-2.8 (4H, m, H_d).

The yellow fluorescent band of lower R_f was subjected to a further p.l.c. treatment (silica, dichloromethane +0.5% AR acetone), to remove a slower moving blue fluorescent impurity, and was then crystallised from light petroleum (b.p. 100-120 °C), adding a little toluene to facilitate solution, to give 4,4'-bisthiomorpholinobenzophenone as a pale yellow powder (0.14 g, 40%), m.p. 147-9 °C (Found: C, 65.75; H, 6.4; N, 7.15; S, 16.45%. $C_{21}H_{24}N_2OS_2$ requires C, 65.63; H, 6.25; N, 7.29; S, 16.67%), δ ($CDCl_3$) 7.77 (4H, d, J 8.5 Hz, H_a), 6.87 (4H, d, J 8.5 Hz, H_b), 3.7-3.9 (8H, m, H_c), 2.65-2.85 (8H, m, H_d).

4.7. Preparation of the Dyes for Spectral Measurements

(i) Neutral Solution

A known weight of dye (5-10 mg) was dissolved in the appropriate solvent (ethanol or cyclohexane) in a volumetric flask (100,250 or 500 cm^3) and made up to the mark. A given amount of this stock solution was pipetted into a 25 cm^3 volumetric flask and diluted to the mark to give an absorbance value of 0.7-1.4. After leaving the solution in the dark overnight to ensure conversion of any cis-azo dye into the trans form, the absorption spectrum of the dye was measured.

(ii) Acid Solution

Ethanolic hydrogen chloride was prepared by passing dry hydrogen chloride gas (generated by the dropwise addition of concentrated hydrochloric acid to sulphuric acid) into ethanol for several hours. The resulting solution was standardised by titration against 0.1M aqueous sodium hydroxide using phenolphthalein as indicator (colourless to red at the end point). The amount of ethanolic hydrogen chloride required to give the desired number of equivalents was added to the appropriate volume of dye solution and made up to the mark in a 25 cm^3 volumetric flask. In the azobenzene series, an estimation of the amount of acid needed to fully protonate a dye was obtained by measuring the spectrum of the 4'-nitro derivative at several acidities. In cases where the concentration of the ethanolic hydrogen chloride was insufficient to produce full protonation, concentrated hydrochloric acid was used instead.

4.8. High Temperature Dyeings on Polyester

A 2% dyeing on polyester was carried out for each of the dyes as follows.[215]

A solution of the dye (20 mg, 2% on mass of fibre) in cellosolve (2-ethoxyethanol) was added with stirring to a solution of Dyapol T (0.1 g, 1g/l), the dispersing agent, in water (95 cm^3) to give a uniform dispersion of the dye in a dyebath of liquor ratio 100:1. A sample of polyester was immersed in the dyebath and the whole was heated to 120 °C (developing a pressure of 15 lb in^{-2}) over 30 min and maintained at this temperature for 90 min. The dyebath was cooled and the substrate was washed with cold water, then scoured at 90 °C for 15 min in a solution of Lissapol NC (1g/l) at a liquor ratio of 100:1. The cooled and rinsed polyester sample was dried at room temperature.

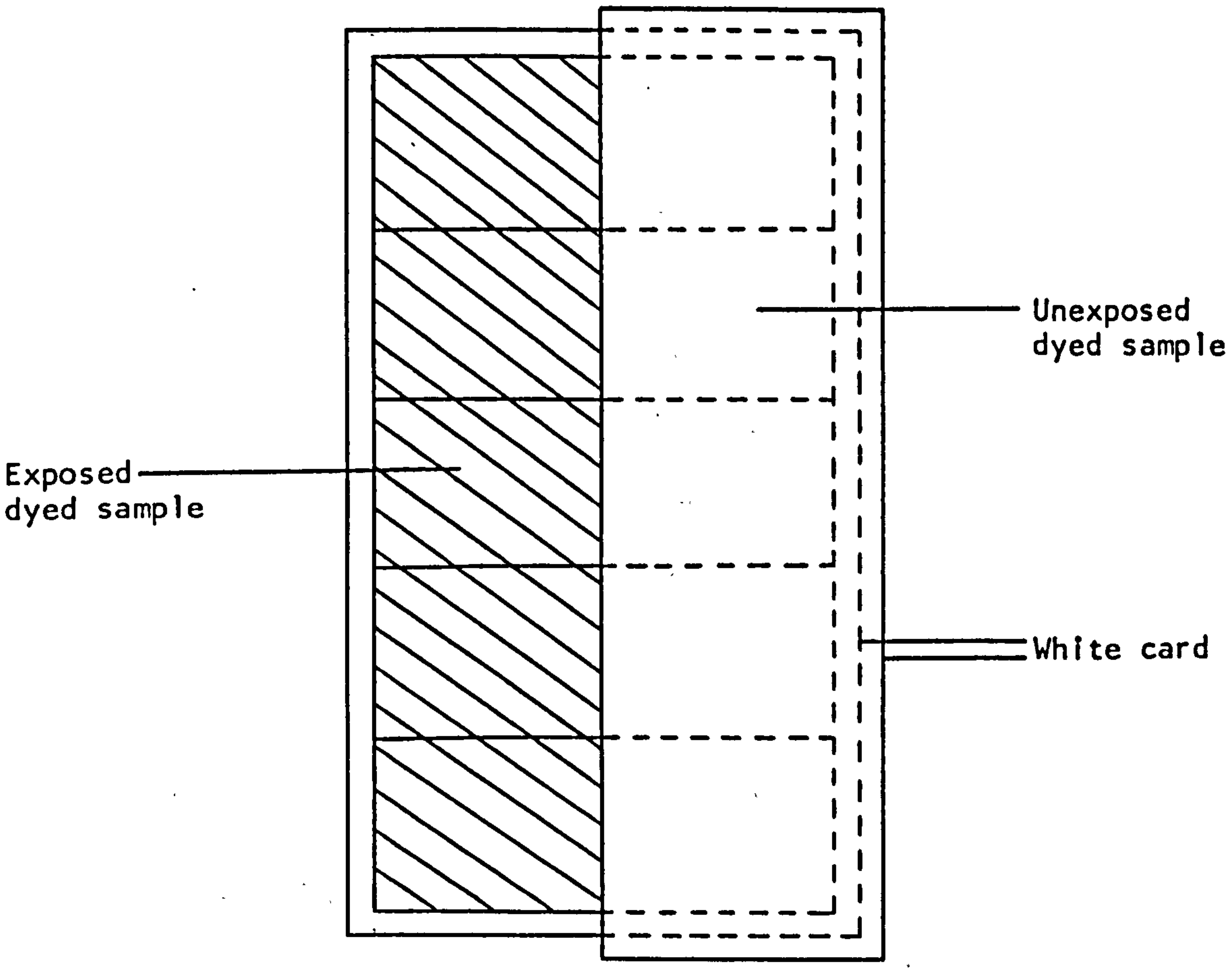
4.9 Fastness Tests[216]

(i) Fastness to Light: Xenon Lamp

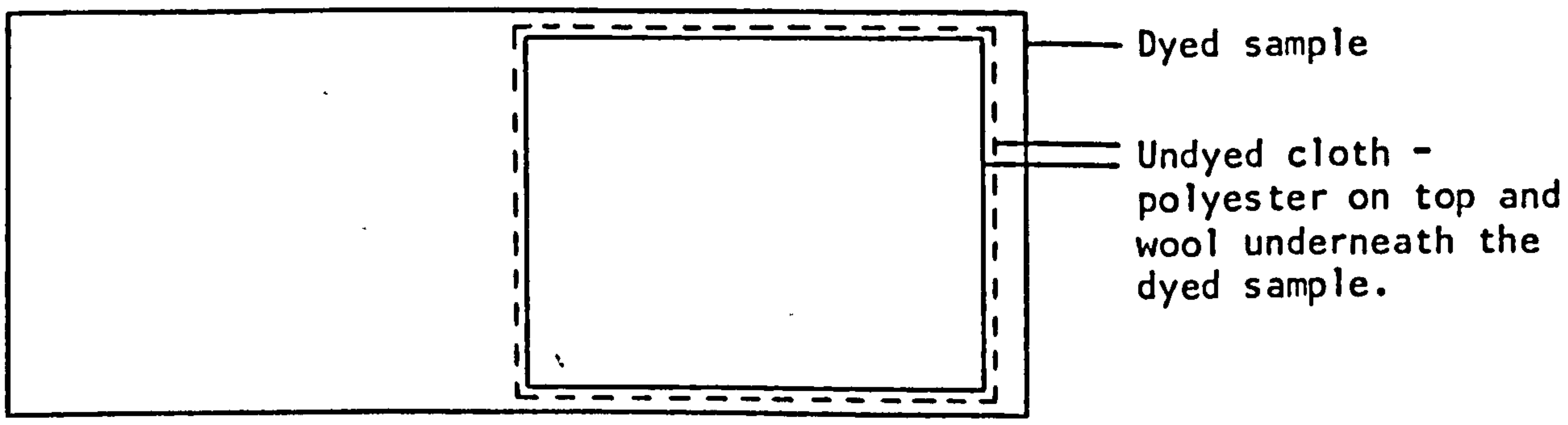
The samples to be examined were cut into pieces (2.5 cm x 1 cm) and mounted on strips of white card, with half the sample covered by a second strip of card [Fig. 4.2. (a)]. A set of blue standards was similarly mounted, and arranged together with the dyed samples around the xenon lamp . Exposure was continued until the light fastness of each sample had been assessed.[216]

(ii) Fastness to Washing

The ISO 3 method was used to evaluate wash-fastness ratings. The prepared dyed sample of polyester [Fig. 4.2 (b)] was placed in the container of a wash wheel together with a solution of soap flakes (5g/l) and anhydrous sodium carbonate (2g/l) at a liquor ratio of 50:1 for 30 min at 60 °C. The washed samples were rinsed in cold water and then dried at room temperature. The change in colour between the soaped sample and an unsoaped sample, and the staining of undyed cloths in the prepared sample, were assessed.[216]



(a)



(b)

Fig. 4.2. Preparation of samples for (a) light fastness and (b) wash fastness testing.

4.10 Measurement of pK_a Values[217]

For each dye, stock solutions containing a known mass concentration (*ca.* 2 mg dm^{-3}) in ethanol were prepared. A series of solutions in 50% ethanol by volume was produced in which the dye concentration was constant but the (known) concentration of sulphuric acid was changed to give a range which varied from that containing predominantly the non-protonated form to one involving mainly the protonated form of the dye. One strongly basic solution and a number of strongly acidic solutions were prepared for each dye. The solutions were thermostatted at 25 °C for at least thirty minutes before measuring their spectra in 4 cm silica cells contained in the thermostatted cell block of a Unicam SP 8-100 spectrophotometer.

For purposes of comparison, the pK_a value for 9-(4-cyanophenylazo)-julolidine was similarly obtained, although in this case the pH values of the dye solutions were measured since H_o values for the acidity range of protonation of the dye were not available. Standard buffer solutions[218] of 0.01 mol dm^{-3} lithium hydrogen oxinate/0.01 mol dm^{-3} oxalic acid in 50% ethanol and of 0.01 mol dm^{-3} lithium hydrogen succinate/0.01 mol dm^{-3} succinic acid in 50% ethanol were used to calibrate the pH meter (Philips PW9410 Digital).

The concentrated solutions of sulphuric acid were prepared and standardised by accurate dilution and titration with sodium hydroxide solution standardised with AR potassium hydrogen phthalate.

REFERENCES

1. R.D. Welham, J. Soc. Dyers and Colourists, 1963, 79, 98.
2. K. Venkataraman, 'The Chemistry of Synthetic Dyes,' Vol. I, Academic Press, London, 1952, p. 409.
3. F.M. Rowe, J. Soc. Dyers and Colourists, 1938, 54, 551.
4. E. Gurr, 'Synthetic Dyes in Biology, Medicine and Chemistry,' Academic Press, London, 1971, p.123.
5. W.H. Cliffe, J. Soc. Dyers and Colourists, 1959, 75, 278.
6. D.H. Wilcox Jr., Amer. Dyestuff Rep., 1958, 47, 539.
7. P.Griess, Ann., 1858, 106, 123.
8. P.Griess, Phil. Trans. Royal Soc. London, 1864, A154, 675, 683, 699, 706.
9. C.A.Martius, J.prakt. Chem., 1866, 98, 94.
10. Ref. 8, p.679.
11. F.M. Rowe, 'The Development of the Chemistry of the Commercial Synthetic Dyes (1856-1938),' Institute of Chemistry, 1938.
12. A.G. Green and K. H. Saunders, J. Soc. Dyers and Colourists, 1923, 39, 10; 1924, 40, 138.
13. E. Waters, J. Soc. Dyers and Colourists, 1950, 66, 609.
14. G. Hallas, J. Soc. Dyers and Colourists, 1979, 95, 285.
15. J. F. Dawson, Rev. Prog. Coloration, (a) 1972, 3, 18; (b) 1978, 9, 25.
16. C.Müller, Amer. Dyestuff Rep., 1970, 59, 37.
17. J.M. Straley, 'The Chemistry of Synthetic Dyes,' Vol. 3, Ed. K. Venkataraman, Academic Press, 1970, p. 385.
18. I.Bridgeman and A.T. Peters, J. Soc. Dyers and Colourists, 1970, 86, 519.
19. J.B. Dickey, E.B. Towne, M.S. Bloome, W.H. Moore, B.H. Smith Jr., and D.G. Hedberg, J. Soc. Dyers and Colourists, 1958, 74, 123.
20. M.F. Sartori, J. Soc. Dyers and Colourists, 1967, 83, 144.
21. J.B. Dickey, E.B. Towne, M.S. Bloome, W.H. Moore, H.M. Hill, H. Heynemann, D.G. Hedberg, D.C. Sievers and M.V. Otis, J. Org. Chem., 1959, 24, 187.
22. C.V. Stead, Rev. Prog. Coloration, 1970, 1, 27.
23. Eastman Kodak, USP,3,816,391, 1974.
24. J.M. Straley and D.G. Charmichael, Can. Text. J., 1959, 76, 49.
25. N.A. Evans and I.W. Stapleton, 'The Chemistry of Synthetic Dyes,' Vol. 8, Ed. K. Venkataraman, Academic Press, London, 1978, p.236.
26. S. Al-Kassim and A.T. Peters, J. Soc. Dyers and Colourists, 1973, 89, 359.
27. H. Aliwarga and G. Hallas, Dyes and Pigments, 1981, 2, 195.
28. K.L. Ng, M.Sc. Dissertation, University of Leeds, 1976, p.19.
29. J. Griffiths, Chem. Soc. Rev., 1970, 1, 481.
30. I. Bridgeman and A.T. Peters, Text.Res. J., 1974, 44, 645.
31. H.P. Mehta and A.T. Peters, Applied Spectrosc., 1974, 28, 241.
32. C.H. Giles, D.G. Duff and R.S. Sinclair, 'The Chemistry of Synthetic Dyes,' Vol. 8, Ed. K. Venkataraman, Academic Press, London, 1978, p. 319.
33. C.E. Vellins, ibid., p.191.
34. Ref. 15(b).
35. T. Reeves, Ph.D.Thesis, University of Leeds, 1979.
36. C. Graebe and C. Liebermann, Ber., 1868, 1, 106.
37. O.N. Witt, Ber., 1876, 9, 522.
38. J. Griffiths, 'Colour and Constitution of Organic Molecules,' Academic Press, London, 1976, p.82.
39. M. Schütze, Z. physik. Chem., 1892, 9, 109.
40. H.E. Armstrong, Proc. Chem. Soc., 1888, 4, 27.
41. J.T. Hewitt and H.T. Mitchell, J. Chem. Soc., 1907, 91, 1251.
42. P. Drude, Ann. Physik., 1904, 14, 677, 936.

43. G.N. Lewis and M. Calvin, Chem. Rev., 1939, 25, 273.
44. W. Dilthey and R. Wizinger, J. Prakt. Chem., 1928, 118, 321.
45. A. Hantzsch, Ber., 1906, 39, 1073.
46. A. von Baeyer, Ann., 1907, 354, 152.
47. E.R. Watson, Proc. Chem. Soc., 1913, 29, 348; J. Chem. Soc., 1914, 105, 759.
48. C.R. Bury, J. Amer.Chem. Soc., 1935, 57, 2115.
49. L. Pauling, Proc. Nat. Acad. Sci. USA, 1939, 25, 577.
49a. W. Heitler and F. London, Z. Phys., 1927, 44, 455.
50. M.J.S. Dewar, Chem. Soc. Special Publication, 1956, 4, 64.
51. N. Saadatjouyasr, Ph.D. Thesis, University of Leeds, 1980, p.101.
52. Ref. 38, p.76.
53. F.P. Chernyakovskii and A.V. Ryazanova, Uch. Zap. Yaraslov. Tekhnol. Inst., 1971, 26, 51; Chem. Abs., 1974, 80, 72059a.
54. Ref. 38, p.181.
55. L.M. Yagupol'skii and L.Z. Gandel'sman, J. Gen. Chem. USSR, 1965,35, 1259.
56. R.W. Castelino and G. Hallas, J.C.S. (B), 1971, 793.
57. G. Hallas, W.L. Ho and R. Todd, J. Soc. Dyers and Colourists, 1974, 90, 121.
58. G.B. Barlin and D.D. Perrin, Quart. Rev., 1966, 20, 75.
59. E. Sawicki, J.Org. Chem., 1957, 22, 915.
60. M. Martynoff, Compt. Rend., 1952, 235, 54.
61. W. Ross and G. Warwick, J. Chem. Soc., 1956, 1719.
62. R.J. Morris, F.R. Jensen and T.R. Lusebrink, J. Org. Chem., 1954, 19, 1306.
63. R. Wizinger, Chimia., 1965, 19, 339.
64. J. Griffiths and B. Roozpeikar, J. Chem. Soc. Perkin I, 1976, 42.
65a. Ref. 38, p.188.
65b. Ref. 38, p.104.
66. E. Hoyer, R. Schickfluss and W. Steckelberg, Angew. Chem., Int. Edn., 1973, 12, 926.
67. H.P. Mehta and A.T. Peters, Dyes and Pigments, 1981, 2, 259.
68. G. Hallas and K.L. Ng, J. Soc. Dyers and Colourists, 1977, 93, 284.
69. V.A. Ismailskii and A.V. Malygina, J. Gen. Chem. USSR, 1964, 34, 3602.
70. J. Griffiths and J. Thomasson, unpublished results.
71. D. Bontschev and E. Ratschin, Monatsh., 1970, 101, 1454.
72. J. B. Dickey, E.B. Towne, D.G. Hedberg, D.J. Wallace, M.A. Weaver and J.M. Straley, Amer. Dyestuff Rep., 1965, 54, 596.
73. P. Gregory and D. Thorp, J. Chem. Soc. Perkin I, 1979, 1990.
74. N. Ishikawa, M.J. Namkung and T.L. Fletcher, J.Org. Chem., 1965, 30, 3878.
75. K. Dimroth and H. Hafner, UV Atlas of Organic Compounds, Vol. 3, Butterworths, Verlag Chemie, 1967.
76. H.G. Wippel, Melliand Textilber., 1969, 50, 1090.
77. P.F. Polyevshchikov and V.A. Ismailskii, Uch. Zap. Kirov. Gos. Pedagog. Inst. No. 36, 1972, 118; Chem. Abs., 1973, 79, 93416j.
78. A.L. Kiprianov and I.M. Zhmurova, Zhur. Obsch. Khim., 1953, 23, 626; Chem. Abs., 1954, 48, 6981a.
79. Ref. 38, p. 186.
80. T.W. Campbell, D.A. Young and M.T. Rogers, J. Amer. Chem. Soc., 1951, 73, 5789.
81. G. Hallas, N. Saadatjouyasr, J.D. Hepworth, D.A. Ibbitson, A.M. Jones, T.P. Keane and A.R. Turton, J. Chem. Soc. Perkin II, 1981, 1292.
82. D.A. Ibbitson, P.C. James, and R.A. Knaust, J. Chem. Soc., 1961, 5163.

83. I. Ya Bershtein and O.F. Ginzburg, Russian Chem. Rev., 1972, 41, 97.
84. E. Sawicki, J. Org. Chem., 1957, 22, 365.
85. G. E. Lewis, Tetrahedron, 1960, 10, 129.
86. M. Liler, Adv. in Phys. Org. Chem., 1975, 11, 267.
87. S. Yeh and H.H. Jaffe, J. Amer. Chem. Soc., 1959, 81, 3283.
88. I. Ya Bershtein and O.F. Ginzburg, Doklady Akad. Nauk. SSSR, 1968, 180, 98.
89. S. Yamamoto, N. Nishimura and S. Hasegawa, Bull. Chem. Soc. Japan, 1973, 46, 194.
90. S. Yamamoto, ibid., 1973, 46, 3139.
91. S. Yamamoto, Y. Tenno and N. Nishimura, Aust. J. Chem., 1979, 32, 41.
92. E. Dubini—Paglia, B. Marcandalli, L. Pellicciari-Di Liddo, C. Leonardi and I.R. Bellobono, J. Chem. Soc. Perkin II, 1980, 937.
93. G. Hallas, Ph. D. Thesis, University of Hull, 1959.
94. J. Griffiths, J. Soc. Dyers and Colourists, 1972, 88, 106.
95. L.M. Yagupol'skii and L.Z. Gandel'sman, J. Gen. Chem. USSR, 1967, 37, 1992.
96. K.Y. Chu and J. Griffiths, Tetrahedron Letters, 1976, 405.
97. Ref. 38, p.104.
98. E. Sawicki, J. Org. Chem., 1957, 22, 1084.
99. F. Gerson and E. Heilbronner, Helv. Chim. Acta, 1962, 45, 42.
100. Y. Kuroda, H. Lee and A. Kuwae, J. Phys. Chem., 1980, 84, 3417.
101. E. Sawicki and F.E. Ray, J. Org. Chem., 1954, 19, 1686.
102. J.M. Carpentier and P. Dominique, J. Chem. Res., (S), 1981, 92, (M), 1981, 1001.
103. E. Sawicki, J.Org. Chem., 1957, 22, 621.
104. E. Sawicki, J. Org. Chem., 1956, 21, 605.
105. E. Sawicki and D. Gerber, J. Org. Chem., 1956, 21, 410.
106. A.T. Peters, Text. Res. J., 1974, 44, 719.
107. M.T. Rogers, T.W. Campbell and R.W. Maatman, J. Amer. Chem. Soc., 1951, 73, 5122.
108. H. Rau, Angew. Chem. Int. Edn., 1973, 12, 224.
109. M.J.S. Dewar, J. Amer. Chem. Soc., 1952, 74, 3341, 3345, 3350, 3353, 3357.
110. M.J.S. Dewar, J. Chem. Soc., 1950, 2329.
111. J. Griffiths, 'Developments in Polymer Photochemistry—1', Ed. N.S. Allen, Applied Science, London, 1980, p. 150.
112. H. Suzuki, 'Electronic Absorption Spectra and Geometry of Organic Molecules,' Academic Press, New York, 1967.
113. E.B. Knott, J. Chem. Soc., 1951, 1024.
114. L. Pentimalli, Tetrahedron, 1960, 9, 194.
115. Ref. 38, p.38.
116. Ref. 38, p.41.
117. J. Griffiths and J. Thomasson, unpublished results.
118. C.C. Barker and G. Hallas, J. Chem. Soc. (B), 1969, 1068.
119. P. Jones, Ph.D. Thesis, C.N.A.A., Preston Polytechnic, 1979.
120. G. Hallas, unpublished results.
121. T. Kameo, T. Hirashima and O. Manabe, Kogyo Kagaku Zasshi, 1971, 74, 1863.
122. C.P. Nash and G.E. Maciel, J. Phys. Chem., 1964, 68, 832.
123. A.T. Bottini and C.P. Nash, J. Amer. Chem. Soc., 1962, 84, 734.
124. W.D. Weringa and M.J. Janssen, Rec. Trav. Chim. des Pay-Bas, 1968, 87, 1372.
125. J.W. Eastes, M.H. Aldridge, R.R. Minesinger and M.J. Kamlet, J. Org. Chem., 1971, 36, 3847.
126. F. Effenberger, P. Fischer, W.W. Schoeller and W.D. Stohrer, Tetrahedron, 1978, 34, 2409.

127. M.J. Kamlet, R.R. Minesinger, E.G. Kayser, M.H. Aldridge and J.W. Eastes, J. Org. Chem., 1971, 36, 3852.
128. W.D. Gurowitz and M.A. Joseph, J. Org. Chem., 1967, 32, 3289.
129. G. Baddeley, J. Chadwick and H.T. Taylor, J. Chem. Soc., 1956, 451.
130. B.M. Wepster, 'Progress in Stereochemistry,' 1958, 2, 99, Ed. W. Klyne and P.B. de la Mare, Butterworth, London.
131. B. Fuchs, Topics in Stereochem., 1978, 10, 1.
132. W.J. Adams, H.J. Geise and L.S. Bartell, J. Amer. Chem. Soc., 1970, 92, 5013.
133. F.V. Brutcher Jr., T. Roberts, S.J. Barr and N. Pearson, J. Amer. Chem. Soc., 1959, 81, 4915.
134. B.C. Gilbert, R.O.C. Norman and M. Trenwith, J. Chem. Soc. Perkin II, 1974, 1033.
135. H.B. Klevens and J.R. Platt, J. Amer. Chem. Soc., 1949, 71, 1714.
136. E.A. Braude and F. Sondheimer, J. Chem. Soc., 1955, 3754.
137. M.J. Kamlet, H.G. Adolph and J.C. Hoffsommer, J. Amer. Chem. Soc., 1964, 86, 4018.
138. J. Griffiths, B. Roozpeikar and J. Thomasson, J. Chem. Res., (S), 1981, 302,(M), 1981, 3722.
139. M.J.S. Dewar,'Steric Effects in Conjugated Systems,' Ed. G.W. Gray, Butterworths, London, 1958, p.46.
140. G. Hallas and N. Saadatjouyasr,J. Soc. Dyers and Colourists, 1981, 97, 281.
141. H.C. Brown, J.H. Brewster and H. Schechter, J. Amer. Chem. Soc., 1954, 76, 467.
142. Ref. 28, p.15.
143. G. Cilento, E.C. Miller and J.A. Miller, J. Amer. Chem. Soc., 1956, 78,1718.
144. S.V. Sunthankar and V. Thanumoorthy, Textile Res. J., 1969, 39, 606.
145. Idem., Indian J. Chem., 1970, 8, 598.
146. I.H. Leaver in 'Photochemistry of Dyed and Pigmented Polymers,' Ed. N.S. Allen and J.F. McKellar, Applied Science, London, 1980, p. 161.
147. Ref. 111, p.145.
148. J. Griffiths and S. Murray, unpublished results.
149. T.K. Wu and B.P. Dailey, J. Chem. Phys., 1964, 41, 2796.
150. W.G. Hehre, R.W. Taft and R.D. Topsom, Prog. Phys. Org. Chem., 1976, 12, 169.
151. J. Niwa, Bull. Chem. Soc. Japan, 1975, 48, 1637.
152a. L.M. Jackson and S. Sternhell, 'Applications of Nuclear Magnetic Resonance Spectroscopy in Organic Chemistry,' 2nd edn., Pergamon, 1969, p. 307.
152b. Idem., ibid., p. 209.
152c. Idem., ibid., p. 199, 200.
152d. Idem.,ibid., p. 164.
153. P.W. Hickmott and O. Meth-Cohn, in 'An Introduction to Spectroscopic Methods for the Identification of Organic Compounds,' Vol. 1, Ed. F. Scheinmann, Pergamon, 1970, p.69.
154. G. Hallas, J. Chem. Soc., 1971, 2847.
155. D. Simov, V. Koleva, A. Penchev and B. Gulubov, God. Sofii. Univ., Khim. Fak., 1980, 71, 81; Chem. Abs., 1981, 95, 5940c.
156. W.L. Ho, M. Sc. Dissertation, University of Leeds, 1973, p.47.
157. J.S. Martin and B.P. Dailey, J. Chem. Phys., 1963, 39, 1722.
158. J.D. Hepworth, unpublished results.
159. A. Foris, in 'The Analytical Chemistry of Synthetic Dyes,' Ed. K. Venkataraman, Wiley-Interscience, London, 1977, p.233.

160. Yu.K. Yur'ev and G.A. Minkina, J. Gen. Chem. USSR, 1937, 7, 2945; Chem. Abs., 1938, 32, 5399(2).
161. Yu.K. Yur'ev and I.K. Korobitsyna, Vestnik Moskov. Univ., 8, No.5, Ser. Fitz. - Mat. i Estestven. Nauk. No. 3, 73, 1953; Chem. Abs., 1955, 49, 6225c.
162. Yu.K. Yur'ev and I.K. Korobitsyna, R.D. Ben-Yakir,L.A. Savina and P.A. Akishin, Vestnik Moskov. Univ.,6, No. 2, Ser. Fiz. - Mat. i Estestven. Nauk.No. 1, 37, 1951; Chem. Abs., 1953, 47, 124f.
163. F.K. Signaigo and H. Adkins, J. Amer. Chem. Soc., 1936, 58, 709.
164. K.C. Scheiber and V.P. Fernandez, J. Org. Chem., 1961, 26, 1744.
165. D.D. Reynolds and W.O. Kenyon, J. Amer. Chem. Soc., 1950, 72, 1597.
166. R. Huisgen and J. Sauer, Chem. Ber.,1958, 91, 1453.
167. A.N. Bourns, H.W. Embleton and M.K. Hansuld, Org. Synth., 1954, 34, 79; idem, Can. J. Chem., 1952, 30, 1.
168. Fr. patent, 880,986, Feb. 8, 1943.
169. G.Baddeley, J. Chadwick and H.T. Taylor, J. Chem. Soc.,1956, 448.
170. H. Bock and K.L. Kompa, Chem. Ber., 1966, 99, 1347.
171. G. Wittig and W. Merkle, Ber., 1943, 76B, 109.
172. G. Ehrhart, Ber., 1963, 96, 2042.
173. C.H. Horning and F.W. Bergstrom, J. Amer. Chem. Soc., 1945, 67, 2110.
174. P. Caubere and N. Derozier, Bull. Soc. Chim. Fr., 1969, 5, 1737.
175. B.P. 133,108, June 26, 1918.
176. Yu.K. Yur'ev and S.V. Dyatlovitskaya, Zhur. Obshchei. Khim., 1957, 27, 3148; Chem. Abs., 1958, 52, 9077a.
177. M. Nakajima, J. Pharm. Soc. Japan, 1946, 66, 15; Chem. Abs., 1951, 45, 6575d.
178. O.B. Helfrich and E.E. Reid, J. Amer. Chem. Soc., 1920, 42,1208.
179. A.H. Ford-Moore, J. Chem. Soc., 1949, 2433.
180. P. Malatesta and B.D 'Atri, Ricerca sci., 1952, 22, 1589; Chem. Abs., 1953, 47, 10478b.
181. V.Prelog and V. Stepan, Coll. Czech. Chem. Comm., 1935, 7, 93; Chem. Abs., 1935, 29, 4013(3).
182. D. Kohlbach,Arhiv Hem. Farm., 1937, 11, 99; Chem. Abs., 1939, 33, 2897(4).
183. W.T. Forsee Jr. and C.B. Pollard, J. Amer. Chem. Soc., 1935, 57, 1788.
184. J.M. Khanna, V.M. Dixit and N. Anand, Synthesis, 1975, 9, 607.
185. V. Prelog and G.J. Driza, Coll. Czech. Chem. Comm., 1933, 5, 497; Chem. Abs., 1934, 28, 1348.
186. G.N. Ford and F.F. Nord, J. Org. Chem., 1955, 20, 1353.
187. C.D.Hurd and K.L. Kreuz, J. Amer. Chem. Soc., 1952, 74, 2965.
188. H.E. Fierz-David and L.Blangley, 'Fundamental Processes of Dye Chemistry,' 5th Edn., Interscience, 1949.
189. J.M. Tedder, in 'The Chemistry of Synthetic Dyes,' Ed. K. Venkataraman, Academic Press, London, 1970, p.233.
190. E.D. Hughes, C.K. Ingold and J.H. Ridd, J. Chem. Soc., 1958, 58, 65, 70, 77, 82, 86.
191. J.H. Ridd, J. Soc. Dyers and Colourists, 1965, 81, 355.
192. Ref. 28, p.52.
193. M. Ellwood and J. Griffiths, J. Chem. Soc. Chem. Comm., 1980, 81.
194. Idem., unpublished results.
195. G.S. Egerton and A.G. Morgan, J. Soc. Dyers and Colourists, 1970, 86, 242.
196. A. Thiel, Fortschr. Chem. Physik u. Physik Chem., 1924, 18, 38.

197. L.A. Flexser, L.P. Hammett and A. Dingwall, J. Amer. Chem. Soc., 1935, 57, 2103.
198. M.T. Rogers, T.W. Campbell and R.W. Maatman, J. Amer. Chem. Soc., 1951, 73, 5122.
199. R.L. Reeves, J. Amer. Chem. Soc., 1966, 88, 2240.
200. M. Safta and B. Ostrogovich, Rev. Roum. Chim., 1974, 19, 1621.
201. Yu. L. Haldna, Reaktsionnaya. Sposobnost. Organicheskikh Soedinenii, 1964, 1, 110.
202. A.R. Katritzky, A.J. Waring and K. Yates, Tetrahedron, 1953, 19, 4651.
203. W.N. White, T. Vogelmann, M. Morse and H.S. White, J. Org. Chem., 1977, 42, 162.
204. P. Vetesnik, K. Rotschein, J. Socha and M. Vecera, Coll. Czech. Chem. Comm., 1969, 34, 1087, and 1970, 35, 3128.
205. M.A. Paul and A.F. Long, Chem. Rev., 1957, 57, 1.
206. P. Tickle, A.G. Briggs and J.M. Wilson, J. Chem. Soc.(B), 1970, 65.
207. A.I. Gel'bshtein, G.C. Scheglova and M.I. Temkin, Doklady Akad.Nauk. SSSR, 1956, 107, 108.
208. Idem., Zhur. neorg. Khim., 1956, 1, 282.
209. D.R. Waring, private communication.
210. J. v. Braun, Ber., 1922, 55, 3556.
211. J. v. Braun, Ber., 1904, 37, 3212.
212. V.V. Korshak and Yu.A. Strepikheev, J. Gen. Chem. USSR., 1944, 14, 312; Chem. Abs., 1945, 39, 3790(2).
213. U.S. patent, 3,585,182, June 15th,1971.
214. Yorkshire Chemicals, private communication.
215. C.H. Giles, 'A Laboratory Course in Dyeing,' 3rd Edn., Soc. Dyers and Colourists, 1974.
216. 'Standard Methods for the Determination of the Colour Fastness of Textiles and Leather,' Soc. Dyers and Colourists, 4th Edn., 1978.
217. D. Mason, private communication.
218. D.D. Perrin and B. Dempsey, 'Buffers for pH and Metal Ion Control,' Chapman and Hall, London,1974, p.89.
219. Ref. 38, p.18 and subsequent bibliography.
220. E. Hückel, Z. Phys., 1931, 70, 204.
221. Idem., ibid., 1931, 72, 310.
222. Idem., ibid., 1932, 76, 628.
223. Idem., ibid.,1933, 83, 632.
224. G.W. Wheland and D.E. Mann, J. Chem. Phys.,1949, 17, 264.
225. R. Pariser and R.G. Parr, J. Chem. Phys., 1953, 21, 466, 767.
226. J.A. Pople, Trans. Faraday Soc., 1953, 49, 1375.
227. K. Nishimoto and N. Mataga, Z. Phys. Chem., 1957, 12, 335.
228. R.S. Mulliken, J. Chem. Phys., 1939, 7, 14, 20, 121.
229. J. Griffiths, Rev. Prog. Coloration, 1981, 11, 37.
230. J. Griffiths, Dyes and Pigments,in press.
231. J. Thomasson, Ph.D.thesis, University of Leeds, 1981, p.205.
232. Y. Kogo and H. Kikuchi, Nippon Kagaku Kaishi, 1979, 11, 1524; Chem. Abs., 1980, 92, 128204m.
233. J. Griffiths, B. Roozpeikar and J. Thomasson, J. Chem. Res.,(S), 1981, 302, (M), 1981, 3722.
234. J. Griffiths and K.Pender, Dyes and Pigments, 1981, 2, 49.
235. Y. Kogo, H. Kikuchi, M. Matsuoka and T. Kitao, J. Soc. Dyers and Colourists, 1980, 96, 475, 526.
236. K. Y. Chu and J. Griffiths, J. Chem. Res., (S), 1978, 180, (M), 1978, 2319.
237. Idem., J. Chem. Soc. Perkin I, 1979, 696.
238. G. Green-Buckley and J. Griffiths, J. Chem. Soc. Perkin I, 1979, 702.

239. Ref. 38.
240. J. Fabian and H. Hartmann, 'Light Absorption of Organic Colorants,' Springer-Verlag, Berlin, 1980.
241. K.A. Woode, J.C.J. Bart and M. Calcaterra, Dyes and Pigments, 1981, 2, 271.
242. H. Frühbeis, Melliand Textilber., 1973, 955.
243. I. Fischer-Hjalmars and S. Meza, Acta Chem. Scand., 1972, 26, 2991.
244. Ref. 231, p.210.
245. Ref. 38, p.182.
246. R.N. Beale and E.M.F. Roe, J. Amer. Chem. Soc., 1952, 74, 2302.

5. APPENDIX I

5. Appendix I. Quantitative Applications of Molecular Orbital Theory to the Spectral Properties of Dyes.[219]

5.1. General Considerations

The absorption of ultraviolet and visible light leads to a disturbance of the electronic distribution in a molecule, resulting in the formation of an electronically excited state. Quantum theory states that a molecule can exist only in a limited number of discrete energy states, E_n, as described by the wave functions Ψ_n in the equation

$$\underline{H}\Psi_n = E_n\Psi_n \qquad (5.1)$$

where $\underline{H}$ is the Hamiltonian operator. In physical terms, $\Psi_n^2 d\tau$ represents a probability function for the state in a small volume element $d\tau$, so that integrated over all space the product will be equal to unity, as shown by the normalising equation:

$$\int_{-\infty}^{+\infty} \Psi_n^2 \, d\tau = 1 \qquad (5.2)$$

Values of Ψ_n(often called eigenfunctions) which satisfy the equation can be regarded as the various possible electronic states of the molecule, each having an energy value E_n (often called eigenvalues). The lowest energy eigenfunction is the ground state of the molecule; the energy of the radiation absorbed is then given by

$$E_{\text{excited state}} - E_{\text{ground state}} = h\nu \qquad (5.3)$$

where h is Planck's constant and ν is the frequency.

If the eigenvalues of a molecule were known precisely, all possible electronic transitions could be assigned energy values. Unfortunately, the exact solution of eqn. (5.1) is not possible for complex molecules using present mathematical techniques, and approximations have therefore to be made. Empirical parameters are often utilised to overcome theoretical difficulties and absorb these approximations.

A particularly valuable approximation assumes that the complete electronic wave function for the ground state of a molecule can be factorised out into a series of simpler wave functions, ψ, each of which describes the behaviour of one electron only; these one-electron wave functions are the familiar molecular orbitals. The electronic structure of a molecule can then be built up by feeding electrons in pairs into the various orbitals, in order of increasing energy, and the longest-wavelength absorption band can be attributed to the promotion of an electron from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO).

The one-electron wave function approach is implicit in the Hückel molecular orbital (HMO) method and the superior Pariser-Parr-Pople (PPP) method, both of which are outlined briefly below.

5.2 The Hückel Molecular Orbital (HMO) Method.[220-223]

This approach invokes the σ-π separation principle in which it is assumed that the σ and π electrons can be treated independently (in fact, the σ electrons are effectively ignored). One-electron wave functions and related energies are obtained by using the linear combination of atomic orbitals (LCAO) procedure. Hence, for a system of n overlapping p orbitals the molecular orbital wave function (ψ) is expressed as a linear sum of the component atomic orbital wave functions (ϕ):

$$\psi = c_1\phi_1 + c_2\phi_2 + \ldots\ldots\ldots c_n\phi_n \qquad (5.4)$$

The mixing coefficients (or eigenvectors), c_n, can have any value between ± 1 and denote the relative contributions of each atomic orbital to ψ; adjacent coefficients of like algebraic sign correspond to in-phase overlap, whilst those of opposite sign correspond to out-of-phase overlap.

The energy (or eigenvalue), E, of the molecular orbital is defined by

$$H\psi = E\psi \qquad (5.5)$$

This equation refers to the energy and wave function of a molecular orbital, rather than to those of a molecular state as in eqn.(5.1). Mathematical manipulation gives an expression for the energy of the molecular orbital, in terms of ϕ, c and the operator H. Utilisation of the variation principle gives n secular equations, containing integrals of the form

$$\int \phi_n H \phi_n d\tau = H_{nn} \qquad (5.6a)$$

$$\int \phi_m H \phi_n d\tau = H_{mn} \qquad (5.6b)$$

$$\int \phi^2{}_n d\tau = S_{nn} \qquad (5.6c)$$

$$\int \phi_m \phi_n d\tau = S_{mn} \qquad (5.6d)$$

The normalisation requirement of atomic orbital wave functions causes all S_{nn} integrals to be equated to unity. The S_{mn} integrals, or overlap integrals, are a measure of the degree of overlap of the two orbitals m and n. These values are taken as zero, in the zero differential overlap (ZDO) approximation, despite the fact that formation of a molecular orbital requires spatial overlap of atomic orbitals. This assumption greatly simplifies the calculations without greatly affecting their outcome.

Each H_{nn} integral (5.6a) represents the energy of an electron whilst it occupies the atomic orbital ϕ_n. This energy is called the Coulomb integral, α_n, and in HMO theory it is assumed that all H_{nn} integrals for carbon atoms have the same numerical value, α. The H_{mn} integral can be regarded as the energy of an electron whilst it occupies the region of overlap of orbital ϕ_m with ϕ_n, and is termed the resonance integral. In the HMO method, resonance integrals relating to non-adjacent atoms are given a value of zero (owing to the negligible degree of overlap), and those between adjacent pairs of carbon atoms are assumed to have the same value, β.

The secular equations can now be greatly simplified and written in the form of a determinant (having extracted the coefficients c_n) for a molecule containing n conjugated p orbitals:

$$\begin{vmatrix} \alpha_1-E & \beta_{12} & \beta_{13} \cdots\cdots & \beta_{1n} \\ \beta_{21} & \alpha_2-E & \beta_{23} \cdots\cdots & \beta_{2n} \\ \beta_{31} & \beta_{32} & \alpha_3-E \cdots\cdots & \beta_{3n} \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \cdot & \cdot & \cdot & \cdot \\ \beta_{n1} & \beta_{n2} & \beta_{n3} \cdots\cdots & \alpha_n-E \end{vmatrix} = 0 \qquad (5.7)$$

The aforementioned approximations concerning α_n and β_{mn} enable a solution to the determinant to be obtained; in general, for a system of n overlapping p orbitals (giving a determinant of order n), n molecular orbital eigenvalues are obtained, expressed in terms of α and β, which are treated as empirical parameters. Application of the ZDO approximation to the normalisation requirement of a molecular orbital gives eqn (5.8) which, in addition to the secular equations, enables the mixing coefficients c_n to be calculated for each orbital. Each c_n^2 term can be identified

$$c_1^2 + c_2^2 + c_3^2 \ldots\ldots\ldots + c_n^2 = 1 \qquad (5.8)$$

with the fraction of an electron in an orbital associated with atomic centre n, i.e., the fractional electron density on atom n. In a typical molecule, there will be several π-orbitals and many will contain two electrons, such that the net electron density Q_n on atom n is given by:

$$Q_n = \sum_r c_{r,n}^2 . N_r \qquad (5.9)$$

where N_r is the number of electrons (1 or 2) in each orbital r.

Considering the region of overlap between two adjacent atoms, m and n, the quantity $c_m.c_n$ can be associated with the probability of finding an electron in the region of overlap, or in other words the degree of bonding. Hence the term $c_m.c_n$ is referred to as the partial bond order for the bond between atoms m and n due to one electron in one molecular orbital. Total bond order, $P_{m,n}$, is given by the sum of the partial bond orders due to all the various π-electrons in the molecular orbitals r:

$$P_{m,n} = \sum_r c_{r,m} . c_{r,n} . N_r \qquad (5.10)$$

and lies between zero (pure single bond) and unity (pure double bond). Thus, electron densities and bond orders in both ground and excited states can be obtained by means of eqns. (5.9) and (5.10), using the appropriate orbital occupancies.

In its original form, as outlined above, the HMO procedure specifically refers to hydrocarbons. The presence of heteroatoms makes the inherent approximations concerning α and β less valid. Although modifications to account for heteroatoms (e.g., the ω-technique[224]) have been developed, the fact that the HMO approximation neglects electronic interactions makes it rather unreliable for the prediction of transition energies, except in certain favourable cases.

5.3. The Pariser-Parr-Pople (PPP) Self Consistent Field (SCF) Molecular Orbital (MO) Method.[225,226]

This method retains the σ-π separation principle of the HMO method but specifically includes interelectronic effects in the calculations. The LCAO approach is again used to give a general determinant similar to eqn.(5.7), the fundamental difference being in the α_n and β_{mn} electron energy terms. In the HMO method, repulsion energies due to the presence of other π-electrons are not included in the α and β values. The PPP method, however, does include the effects of electron interaction. Thus, the magnitude of these terms depends on the electron occupancy of the π-orbitals. In the PPP procedure, each α_n and β_{mn} term in the determinant is given a specific numerical value; solution of the determinant again gives the molecular orbital eigenvalues for the system. The LCAO coefficients are found in the same way as in the HMO method, leading to electron densities and bond orders for the molecule.

The main problem in the PPP method lies in the assignment of appropriate values to each α_n and β_{mn}, ensuring that electronic interactions are well accounted for. These values may be expressed as follows:

$$\alpha_n = \alpha_n^{core} + (RE)_n \qquad (5.11)$$

$$\beta_{mn} = \beta_{mn}^{core} + (RE)_{mn} \qquad (5.12)$$

The one-centre core term, α_n^{core}, is the attraction energy experienced by an electron on an atom n, due to the positively charged nuclear framework, assuming that all the other π-electrons have been removed, and is given approximately by minus the valence state ionisation potential (VSIP) of the atom on which the electron is residing, added to the sum of each of the attractive energies, $-\gamma_{mn}$, between the electron on atom n and a remote positive centre m, where γ_{mn} is the repulsion energy that would result if the positive charge in the system were replaced by an electron. These γ_{mn} terms can be calculated from experimental data (see eqn. 5.15), and are dependent on the geometry of the molecule.

The β_{mn}^{core} values can be regarded as the energy of an electron residing between atoms m and n, experiencing the total attractive force of the positively charged nuclear framework. They are usually determined empirically for specific bonds and can be related to bond lengths. The β_{mn}^{core} term for non-adjacent atoms is taken as zero, as in the HMO method. PPP calculations appear to be less sensitive to the choice of β_{mn}^{core} values than to other parameters.

The one-centre repulsion term $(RE)_n$ arises from the interaction of the electron localised on atom n with all the other π-electrons, and is given by the expression

$$(RE)_n = \frac{1}{2}Q_n \cdot \gamma_{nn} + \sum_{m \neq n} Q_m \cdot \gamma_{mn} \qquad (5.13)$$

where Q_n and Q_m are the π-electron densities on atoms n and m, respectively, as evaluated from eqn.(5.9), and γ_{nn} is the repulsion energy between two p electrons on the same atom n, and is obtained from

$$\gamma_{nn} = VSIP_n - A_n \qquad (5.14)$$

where A_n is the experimentally determined electron affinity of atom n. The two-centre electron repulsion integrals γ_{mn} are found from some average of the one-centre terms for atoms m and n. The empirical relationship of Nishimoto and Mataga[227] (eqn.5.15), where d_{mn} is the distance through space between atoms m and n, gives good results in many cases. Thus, a geometry dependence is again introduced into the calculations.

$$\gamma_{mn} = \frac{14.39(\gamma_{mm} + \gamma_{nn})}{[(\gamma_{mm} + \gamma_{nn})d_{mn} + 28.78]} \qquad (5.15)$$

The two-centre repulsion energy term $(RE)_{mn}$ is given by

$$(RE)_{mn} = -\frac{1}{2} P_{mn}.\gamma_{mn} \qquad (5.16)$$

where P_{mn} is the π-bond order between atoms m and n.

Thus,it is seen that eigenvalues for the system can be obtained if the following parameters are known:

(a) interatomic distances and bond angles,

(b) VSIP and A values for all atoms,

(c) all β_{mn}^{core} values,

(d) π-electron densities and π-bond orders.

Unfortunately, the electron densities and bond orders can only be determined after the LCAO coefficients for all the occupied orbitals are known, i.e.,after the eigenvalues have been calculated. This problem is negotiated by carrying out a preliminary Hückel calculation, without specifying exact α and β values, to give a rough set of eigenvectors. The resultant calculated bond orders and electron densities are then used to set up the PPP secular determinant, solution of which affords an improved set of coefficients. This process is then repeated until successive cycles give the desired degree of consistency. This iterative approach introduces a degree of self consistency into the PPP method.

In addition to calculating eigenvalues for the system (of both singlet and triplet states), from which λ_{max} values are derived, together with the LCAO coefficients c_n, from which π-electron densities and π-bond orders are obtained, output from the PPP computation also includes dipole moment magnitudes and directions in the ground and excited states, the transition moment vector, and oscillator strengths, f, [228] as defined by the expression

$$f = 4.703 \times 10^{29}.\nu_m.\underline{M}^2 \qquad (5.17)$$

where ν_m is the mean absorption frequency of the band (in cm^{-1}) and $\underline{M}$ is the transition dipole moment. Oscillator strength is related to the area under an absorption band covering frequencies ν_1 to ν_2:

$$f = 4.32 \times 10^{-9} \int_{\nu_1}^{\nu_2} \varepsilon \, d\nu \sim 4.32 \times 10^{-9}.\varepsilon_{max}.\Delta\nu_{\frac{1}{2}} \qquad (5.18)$$

The approximation, where $\Delta\nu_{\frac{1}{2}}$ is the width of the band (in cm^{-1}) at $\varepsilon = \varepsilon_{max}/2$, holds for reasonably symmetrical curves. Thus, oscillator strengths are directly proportional to molar extinction coefficients provided that half-band widths are constant for the dyes studied. Values of f range from zero for a very weak band to unity for a very intense band. Computed values are often greater than unity, presumably because the calculated transition dipole moment is too large. Thus, although absolute values are inaccurate, relative values within a series are of predictive value.

The vast majority of stable organic molecules have an orbital arrangement consisting of sets of paired electrons of opposite spin, i.e., possess singlet ground states. If, after promotion to a higher orbital, an electron retains its spin, the resultant excited state is also a singlet state, whereas if the electron reverses its spin a triplet excited state is obtained. Quantum mechanical restrictions render ground (singlet) state to excited triplet state transitions highly forbidden, leading to exceedingly weak absorption bands.Corresponding singlet to singlet transitions, on the other hand, are allowed and therefore intense and are normally responsible for the visible absorption bands of molecules. Thus, calculated λ_{max} values are for this latter transition, although it should be noted that the PPP method is able to distinguish between singlet and triplet states (by its consideration of electronic repulsion effects), making it possible to calculate energy values for both states.

5.3.1. Configuration Interaction (CI).

The results of a PPP calculation strictly refer to the ground state molecule, since the electron repulsion energies are based on the ground state orbital occupancy. Promotion of an electron to an unoccupied orbital results in a new occupany, and it is not valid to assign to the electron an eigenvalue that is based on a ground state calculation. Thus, a PPP calculation has to be refined in order to calculate electronic transition energies in a reliable manner.

It is common practice to designate electronic states of a molecule by orbital occupancy descriptions. These representations are better described as electronic configurations, and are often a poor representation of a true molecular state since they are a theoretical concept, based on the assumption that a many-electron state wave function can be factorised out into a product of one-electron molecular orbital functions. Better approximations to the true state wave functions, Ψ^{state}, can be obtained by a linear combination of the various configuration wave functions, Ψ,in a manner similar to the LCAO treatment of molecular orbital wave functions (eqn. 5.19).

$$\Psi^{\text{state}} \sim \Psi^{\text{improved}} = c_1\Psi_1 + c_2\Psi_2 + \dots\dots c_n\Psi_n \qquad (5.19)$$

Solution of the resulting new determinant gives a series of improved state energies (and hence better transition energies) and the mixing coefficients, or configuration vectors, c_n, some of which will be finite (in which case the relevant configurations will interact) and some zero (no configuration interaction). This treatment leads to the concept that an absorption process can be represented either by one electronic configuration (i.e., by the transition of an electron from one orbital to another, as was entirely the case before CI), or by a transition to which more than one electronic configuration contributes. The latter type often occurs strongly if the initial PPP calculation predicts degenerate configurations and involves the degenerate configurations only. For instance, the transitions of buta-1,3-diene were initially predicted at 213, 162 (two bands) and 123 nm. After CI, the revised values were 214, 175, 150 and 122 nm. Some transitions, however, may involve several electronic configurations. Thus, CI is essential in many cases to remove the artifical degeneracy of certain excited configurations, and hence to predict the correct number of absorption bands, and also to increase the accuracy of the calculated data. Configuration vectors are calculated in the computation, and these vectors give an indication of how best the electronic transition can be represented.

5.4. Practical Applications of the PPP Method.[229,230]

The PPP-SCF-MO method has been used in the study of the colour and constitution of a wide range of dyes, including aminoazo compounds[229-233] di- and tri-arylmethanes,[234] anthraquinones,[235], naphthoquinones[236,237] and heterocyclic analogues of the anthraquinones.[238] Calculations of a more specific nature in other dye classes have also been carried out.[239,240]

In the present work, a standard PPP-MO procedure was employed, within the fixed β approximation. Two-centre electron repulsion integrals were determined by the previously described Nishimoto-Mataga relationship (eqn. 5.15), and electronic excitation energies were refined by a limited CI treatment involving the nine singly excited singlet configurations obtained by promoting an electron from the three highest occupied orbitals to the three lowest unoccupied orbitals. It was found that the limited CI treatment generally produced a bathochromic shift of the longest wavelength absorption band of 0-5%, although in some heterocyclic dyes shifts of up to 10% were calculated. Extension of CI had little additional effect, as other workers have also found.[231]

The calculated configuration vectors indicate that in most cases the contribution of the HOMO ⟶ LUMO electronic transition to the visible absorption band is about 95% (although for the 4'-nitrophenyl and 6'-nitrobenzthiazolyl dyes the amount drops to 80-85%), i.e., a description of the first excited states of these types of molecules in terms of orbital occupancies is quite reasonable.

Calculations have been restricted in the main to the pyrrolidinoazo dye series, since (by analogy with recent work on aminoazo dyes[241]) these dyes can reasonably be assumed to have planar structures, and will therefore show any trends more clearly than if steric factors had also to be considered. Parameters used in the calculations are shown in Table 5.1, with calculated visible absorption data being given in Table 5.2. It should be noted that, since the experimental λ_{max} values of corresponding pyrrolidinoazo and <u>NN</u>-diethylaminoazo dyes are essentially the same, the parameters for the terminal nitrogen atom will also be the same, hence the PPP method is insensitive to any differences in experimental

Table 5.1. PPP-MO Parameters used for the Calculation of Electronic Absorption Spectral Data for Derivatives of 4-Aminoazobenzene.[229,230,242,243]

Bond Type X-Y		Atom Y	$VSIP_Y$[a] (eV)	A_Y[b] (eV)	β_{XY}[c] (eV)	Z_Y[d]	r_{XY}[e] (Å)
C$\overset{\cdots}{-}$C aromatic		C	11.16	0.03	-2.39	1	1.40
C-$\ddot{N}Me_2$[f]		N	18.0	8.0	-2.75	2	1.40
C-$\ddot{N}$ (pyrrolidino)[g]		N	17.5	7.5	-2.75	2	1.40
C-$\ddot{O}$Me (and $\ddot{O}$Et)		O	32.9	11.43	-2.60	2	1.36
Cl-C[h]		C	12.0	0.61	-	1	-
C-$\ddot{Cl}$[i]		Cl	23.3	12.5	-1.36	2	1.34
C-C	acetyl	C	11.16	0.03	-2.30	1	1.45
C=O		O	15.0	0.71	-2.46	1	1.22
C-C	cyano	C	11.19	0.1	-2.30	1	1.40
C≡N		N	14.18	3.5	-2.67	1	1.15
C-N	nitro	N	24.8	12.53	-2.00	2	1.49
N-O		O	21.0	2.5	-2.80	1	1.21
C-N	azo	N	14.7	2.3	-2.48	1	1.40
N=N		N	14.7	2.3	-2.90	1	1.23
C-S[f,j]	heterocyclic	S	20.0	10.0	-1.00	2	1.71
C-N[f,k]		N	12.0	0.5	-2.40	1	1.38
C=N[f]		N	12.0	0.5	-2.00	1	1.33
R-$\overset{+}{N}$		$\overset{+}{N}$	21.0	9.26	-2.40	2	1.35

[a] Valence state ionisation potential of atom Y

[b] Electron affinity of atom Y

[c] Resonance integral for bond X-Y

[d] Core charge of atom Y

[e] Bond length

[f] Parameters reoptimised (c.f. refs. 229,230,242,243).

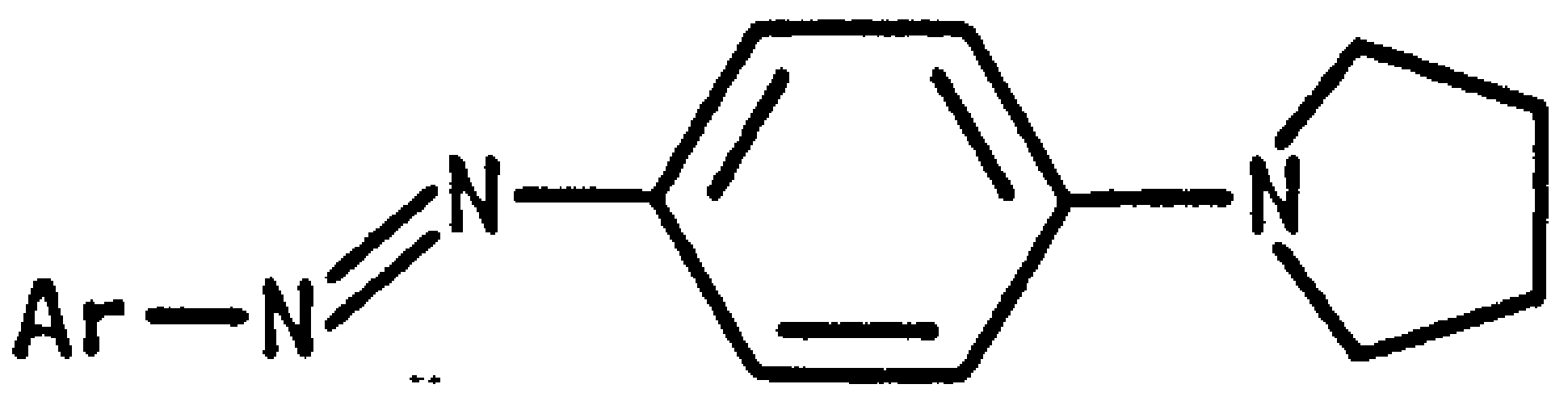
[g] Identical to reoptimised C-$\ddot{N}Et_2$ parameters

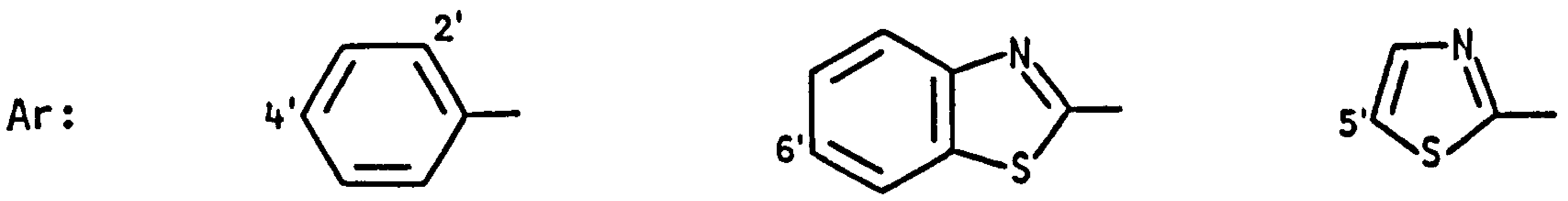
[h] Parameters of carbon atom modified to account for -I effect of Cl

[i] Cl considered to be part of π-electron system, with its own parameters

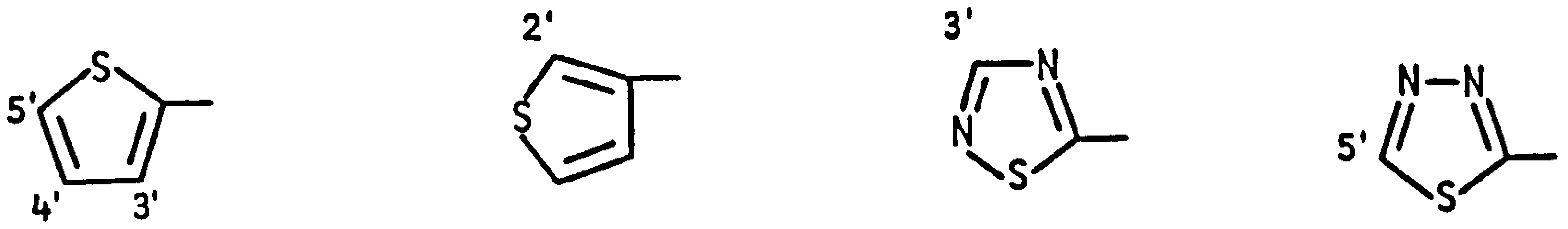
[j] N-S given same parameters

[k] N-N given same parameters

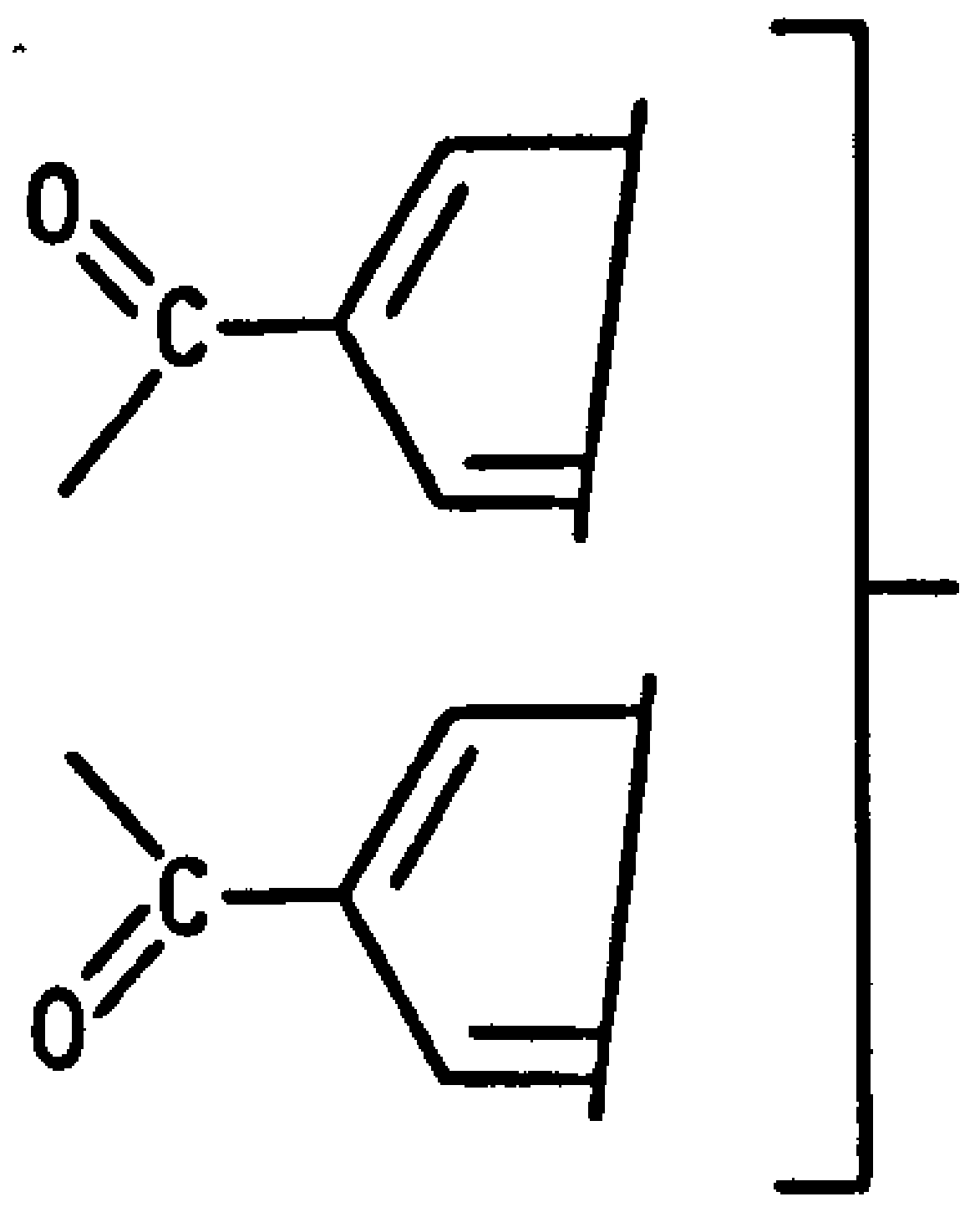




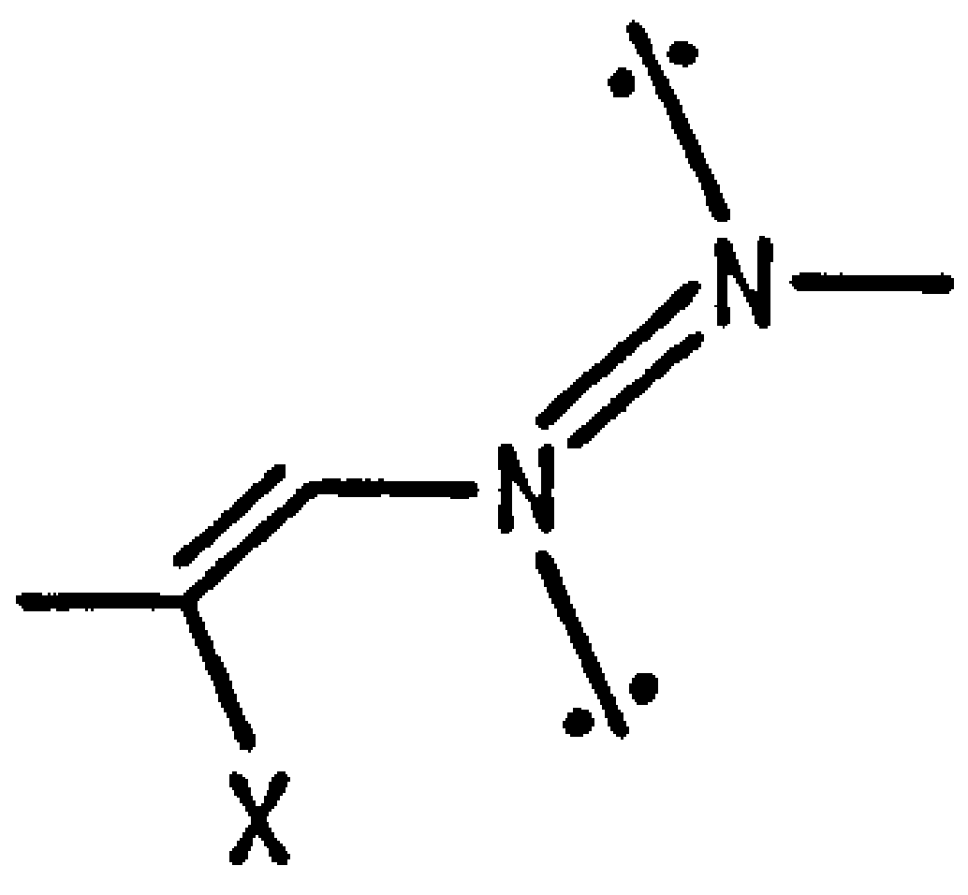
(I) (II) (III)



(IV) (V) (VI) (VII)



Data given are for the average of the two structures.



Conformation of <u>ortho</u>-substituted dyes used in the calculations.

Scheme 5.1. Model systems (with stereochemistry as shown) used in PPP-MO calculations.

Table 5.2. Comparison of Experimental and Calculated Electronic Absorption Spectral Data for Dyes Derived from N-Phenylpyrrolidine (I-VII).

Dye	λ_{max}/nm (calc.)	f[a] (calc.)	λ_{max}/nm[b] (exp.)	$10^{-4}\varepsilon$ (exp.)
I;4'-OMe	412	1.51	407	2.98[b]
I;4'-H	411	1.45	407	2.86[b]
I;4'-Cl	413(411)[d]	1.45(1.47)[d]	416	3.08[b]
I;4'-Ac	431	1.63	434	3.25[b]
I;2'-CN	442.5	1.30	438	3.08[b]
I;4'-CN	439.5	1.66	438	3.52[b]
I;4'-NO_2	464(452.5)[e]	1.48	459	3.43[b]
I;2'-CN,4'-NO_2	482.5(473)[e]	1.44	503	4.44[b]
II;6'-OEt	475.5	1.79	478	5.51[c]
II;6'-H	475	1.73	471	5.48[c]
II;6'-NO_2	509.5	1.85	505	6.48[c]
III;5'-H	466	1.52	452	3.93[c]
III;5'-NO_2	533	1.75	529	5.17[c]
IV;3',5'-$(CN)_2$-4'-Me	524[f]	1.61[f]	538	5.79[c]
IV;3'-NO_2,5'-Ac	547.5	1.29	547	4.28[c]
IV;3',5'-NO_2	556	1.47	589	5.94[c]
IV;3'-Ac	464	1.32	-	-
IV;5'-Ac	481	1.77	-	-
V;2'-Ac	448.5	1.31	440	2.73[c]
V;2'-CO_2Me	439	1.29	430	2.83[c]
V;3'-Ph	466	1.58	472	4.86[c]
VI;3'-SMe	471[g]	1.53[g]	474	4.60[c]
VII;5'-SEt	476[g]	1.57[g]	467	5.24[c]

---

[a] Oscillator strength

[b] Solvent cyclohexane

[c] Solvent ethanol

[d] Consideration of -I effect of Cl atom gives λ_{max} value outside brackets. Incorporation of Cl atom into the π-electron system gives λ_{max} value inside brackets

[e] Value outside brackets is for β_{N-O} (nitro)=-2.8; value inside brackets is for β_{N-O}(nitro) = -3.05

[f] 4'-Me group not included in calculations

[g] Calculated value is for methoxy analogue

data caused by the different terminal alkyl groups, such as dipole moment values and electron density distributions (as indicated by n.m.r.).

Standard bond lengths and angles were used in the computations wherever possible, and literature β values were utilised unless otherwise stated. The most critical parameters of a PPP calculation are the valence state ionisation potential (VSIP) and the one-centre electron repulsion integral (γ_{nn}) for each atom. If the PPP method is of genuine wide applicability it should not be necessary to change any of these parameters from those derived for similar atoms in other systems. Thus, the VSIP and γ_{nn} values were those used elsewhere wherever possible. However, in order to optimise the agreement between experimental and calculated results over the range of azo dyes studied, certain parameters were reassessed by trial and error calculations. Thus, the resonance integral (β) for the N-O bonds of the nitro group was changed from -3.05 eV to -2.8 eV. This modification provided a bathochromic shift of the calculated λ_{max} values of 5-15 nm (see, for example, I; 4'-NO_2, Table 5.3). The VSIP and A values for the π-excessive sulphur atom of the heterocyclic ring systems were modified slightly, from 22.2 eV and 9.16 eV, to 20.0 eV and 10.0 eV, respectively, in order to give the best fit for all the heterocyclic systems. The most important change occurs in the parameters for the π-equivalent C=N bond(s) of the heterocyclic rings. The β value for the C=N bond is moved from -2.6 eV to -2.0 eV, producing a significant bathochromic shift in the first absorption band, whilst the VSIP and A values are reduced from 16.0 and 2.5, to 12.0 and 0.5, respectively, thereby separating the originally similar λ_{max} values of the parent thiazole and benzthiazole azo dyes, and of the 6'-nitrobenzthiazole derivative (Table 5.3). Hence, the new parameters enable the absorption bands to be reasonably well predicted, free from other visible bands and of high oscillator strength. The applicability

Table 5.3. The Effect of Parameter Modification on the Calculated Absorption Spectral Data of Some Pyrrolidinoazo Dyes.

DYE	ORIGINAL PARAMETERS λ_{max}/nm(f)	MODIFIED PARAMETERS λ_{max}/nm(f)	EXPERIMENTAL λ_{max}/nm $(10^{-4}\varepsilon)^{f}$
I;4'-NO_2	452.5(1.52)^{a}	464(1.48)^{b}	459(3.43)
II;6'-H	451(1.69)^{c}	442.5(1.67)^{d}	
		483.5(1.73)^{e}	
		475(1.73)^{d,e}	471(5.48)
II;6'-NO_2	456(1.81)^{a,c}	471.5(1.75)^{b,d}	
	[460(1.83) ^{b,c}]	490.5(1.92)^{b,e}	
		509.5(1.85)^{b,d,e}	505(6.48)
(III);5'-H	453(1.46)^{c}	438.5(1.51)^{d}	
		480.5(1.52)^{e}	
		466(1.52)^{d,e}	452(3.93)
(III);5'-NO_2	478.5(1.71)^{a,c}	533(1.75)^{b,d,e}	529(5.17)
(VI),3'-Ph	432.5(1.38)^{c}	466(1.58)^{d,e}	472(4.86)

[a] β_{N-O} (nitro) = -3.05

[b] β_{N-O} (nitro) = -2.8

[c] Heterocyclic aza: $VSIP_N$, = 16.0, A_N = 2.5, $\beta_{C=N}$ = -2.6, β_{C-N} = -2.4

[d] As [c], except $VSIP_N$ = 12.0, A_N = 0.5

[e] As [c], except $\beta_{C=N}$=-2.0

[f] Solvent cyclohexane

of these new values to other systems is uncertain; it may be that they are useful only in azo dye systems. Nevertheless, the modifications are justified by the considerable improvements found in λ_{max} values, relative to the original parameters (see Table 5.3). It is probable that the appropriate parameters can be still further optimised so as to remove any discrepancies in the calculated trends.

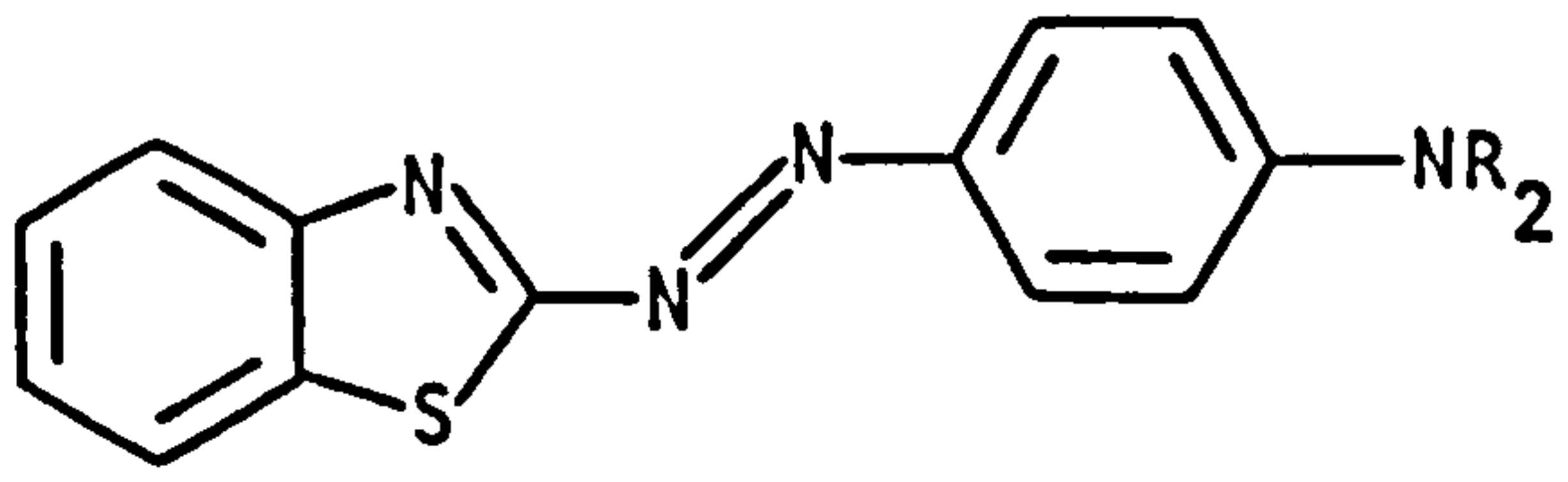
Study of Table 5.2 reveals that in most cases the calculated λ_{max} value of each dye in the pyrrolidinoazo series is predicted to within 5-10 nm. Obvious exceptions are (I; 2'-CN, 4'-NO_2) and (IV;3'5'-$(NO_2)_2$) which are, respectively, about 20 nm and 30 nm too hypsochromic. These discrepancies may arise from the parameters of the nitro group (common to both dyes) or the complications arising from a substituent in an <u>ortho</u> position.

The experimentally observed small effect of a 4'-donor substituent in 4-aminoazobenzene derivatives is predicted (dyes I; 4'-OMe and 4'-H, Table 5.2), as are the relative bathochromicities of the 4'-acceptor dyes. In the case of dye (I; 4'-Cl), λ_{max} values can be obtained by considering only the inductive effect of the Cl atom, simulated by a modification of the parameters of the carbon atom to which it is attached, or by incorporating a lone pair of electrons on the Cl atom into the π-electron system of the molecule. Both methods give similar results; in this case, the former approach is slightly better. The isomeric cyano dyes (I; 2'-CN and 4'-CN) are predicted to have similar λ_{max} values, a prediction observed experimentally.

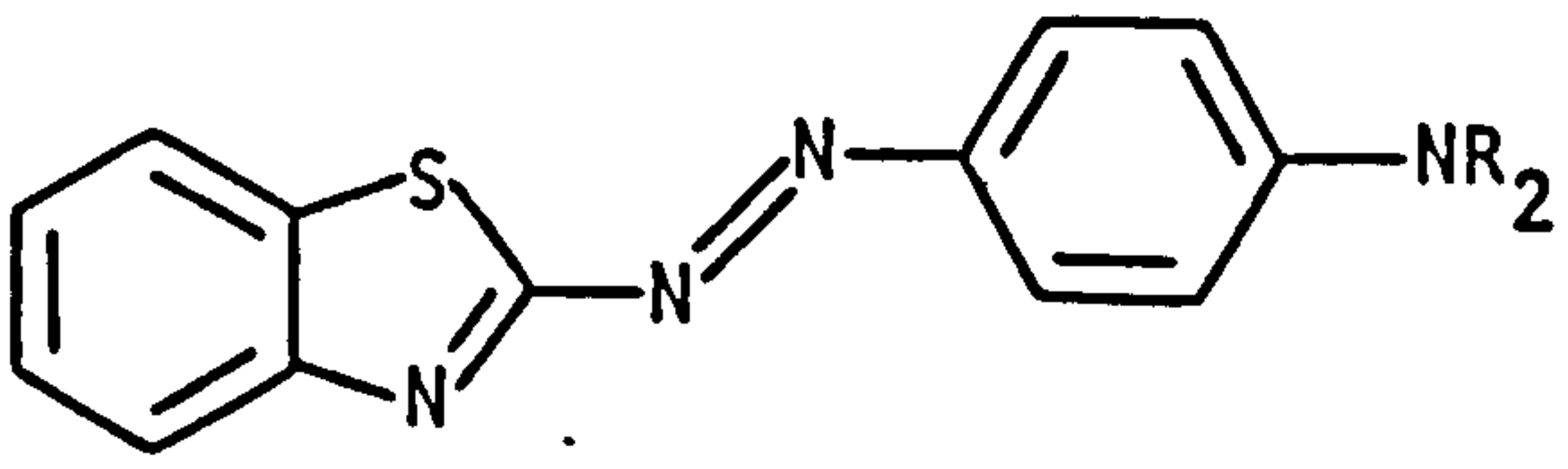
Oscillator strength, f, can be directly related to molar extinction coefficients (eqn. 5.18) if half-band widths (in cm^{-1}) are constant for the dyes studied. As this is not always the case, predicted f values give only a rough guide to the expected intensity of a dye. Oscillator strengths obtained from eqn. 5.18 for dyes (I) range from about 0.6 to 0.7, whereas calculated values are near 1.5. The reason for this overestimation of oscillator strength is uncertain. In almost every case, all other calculated absorption bands (in the u.v. region of the spectrum) have predicted oscillator strengths below 0.5, as is expected from experimental data.

In the benzthiazolylazo series, the experimentally observed small effect on λ_{max} of a 6'-donor substituent (65;6'-OEt, Table 2.5, 2.6 and 2.7) is again predicted. The calculated relative positions of the parent thiazolyl- and benzthiazolylazo compounds, and their nitro derivatives, agree with experimental data, reflecting the easier polarisability of the thiazolyl- types.

It is noteworthy that conformational changes such as that between (124) and (125) cause a change in λ_{max} of 1-2 nm. Similar small changes are observed in calculated oscillator strengths, electron densities and dipole moments.



(124)



(125)

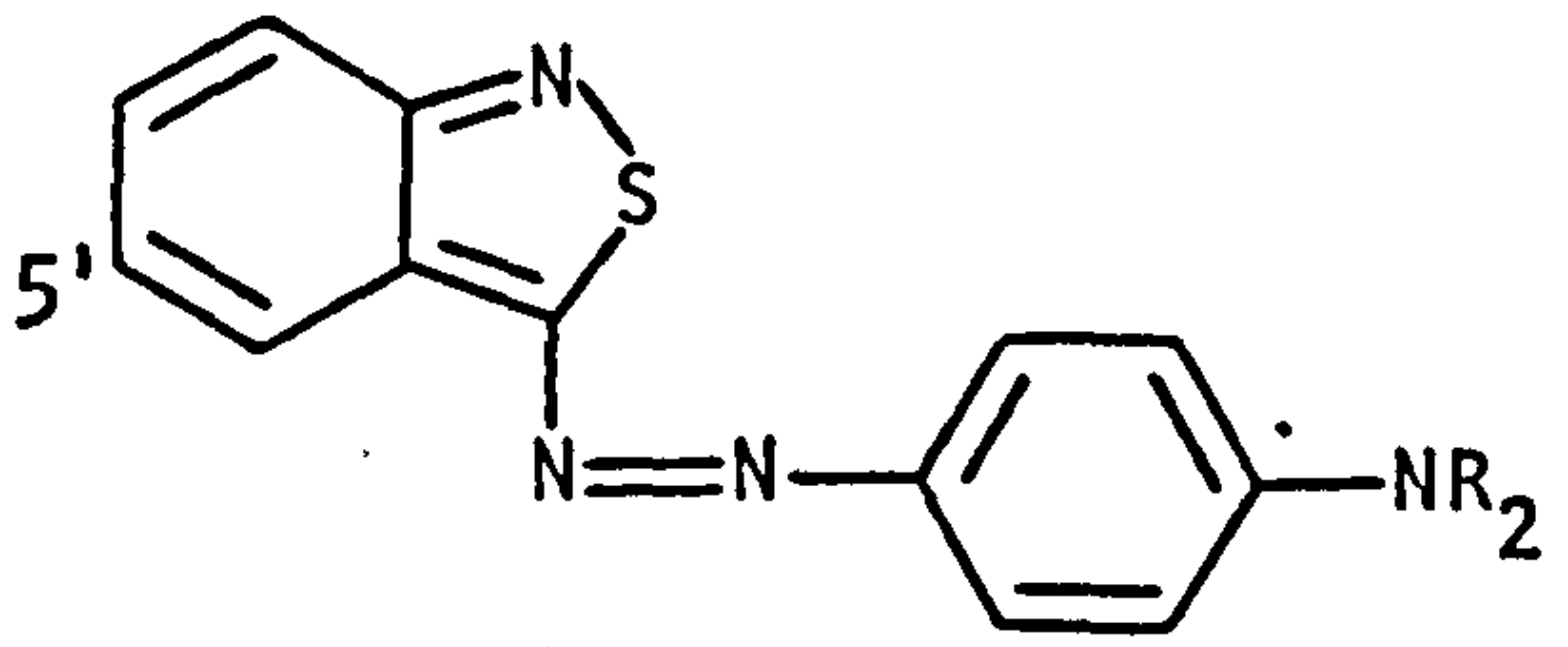
Text cut off in original

The relative bathochromic effects of the acetyl and methoxycarbonyl groups in the thienyl dyes (V; 2'-COMe and 2'-CO_2Me, respectively) are well reproduced in the calculated values. Calculations also indicate that dyes of the thienyl-2-azo class should absorb at longer wavelengths than the -3-azo analogues; experimental data from related systems support this view (see Section 2.3.1). The similarity between λ_{max} values of the parent benzthiazole (II;6'-H) and the 1,2,4- and 1,3,4,-thiadiazoles (VI and VII, respectively) is reproduced, but unfortunately the 1,3,4-thiadiazoles are erroneously predicted to absorb at longer wavelengths than their 1,2,4-isomers.

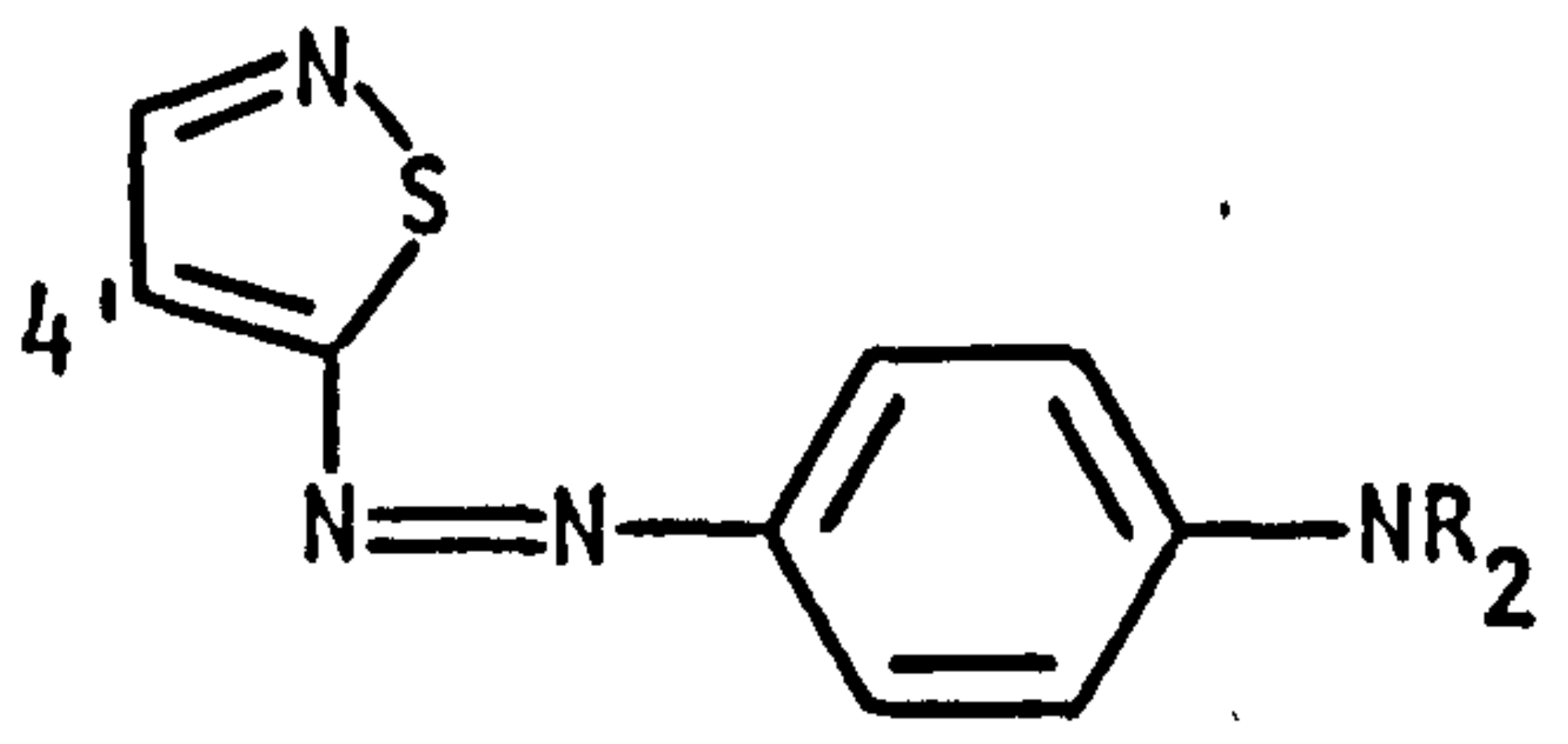
Calculated oscillator strengths of the heterocyclic types (II-VII) are again overestimated, values obtained from eqn. 5.18 being in the region of 0.8-0.9. Relative values are somewhat variable, although the high intensities produced by the benzthiazolyl system are predicted qualitatively.

As a further test of the applicability of the modified parameters, calculations were carried out on the benzisothiazole (VIII) and isothiazole (IX) dyes, and also on dye (X) in which the terminal amino group is attached to a heterocyclic ring rather than a phenyl ring. The predictions reproduce the exceptionally bathochromic properties of these dyes, in particular that the 5'-nitrobenzisothiazole residue imparts larger wavelength shifts than any of the other systems studied, and that the parent benzisothiazole dye (VIII;5'-H) is nearly as bathochromic as the 4'-nitroisothiazole dye (IX;4'-NO_2). Dye (X) is also correctly predicted to absorb at significantly longer wavelengths than its phenyl parent, which absorbs at 478 nm in ethanol and 444 nm in cyclohexane $[\lambda_{max}(\text{calc})=452 \text{ nm}]$.

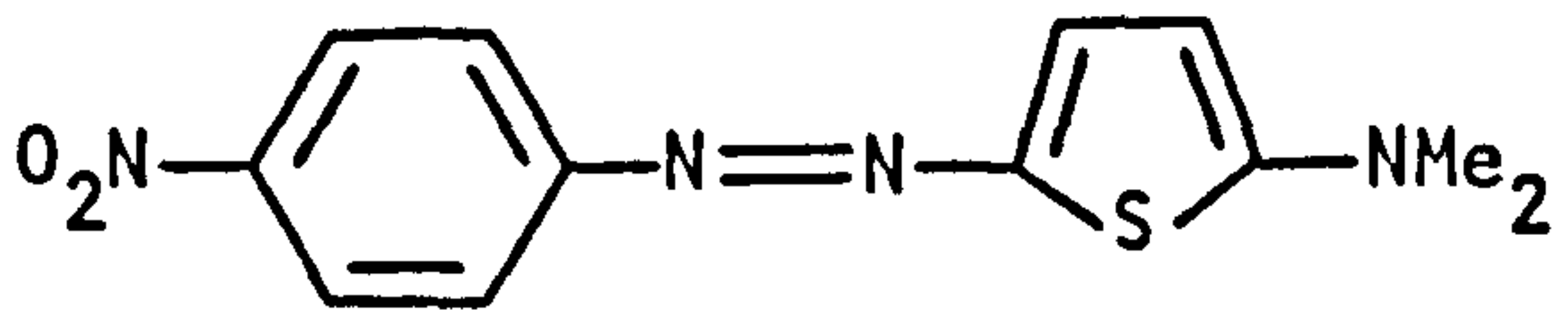
Table 5.4. Comparison of Experimental and Calculated Electronic Absorption Spectral Data for Some Azo Dyes (VIII)-(X).



(VIII)



(IX)



(X)

Dye	λ_{max}(calc) /nm	f(calc)	λ_{max}(exp.)^{a} /nm	$10^{-4}\varepsilon$(exp.)
VIII,R=Me;5'-H	521.5	1.71	548^{b}	-
VIII,R=Me;5'-NO_2	599	1.15	598^{b}	-
VIII,R=Et;5'-H	530	1.75	-	-
VIII,R=Et;5'-NO_2	611	1.18	-	-
IX,R=Me;4'-H	445	1.44	482.5^{c}	-
IX,R=Me;4'-NO_2	536	0.91	558^{c}	-
IX,R=Et;4'-H	453.5	1.48	-	-
IX,R=Et;4'-NO_2	547.5	0.94	-	-
X	495	1.63	554^{d}	5.00^{d}

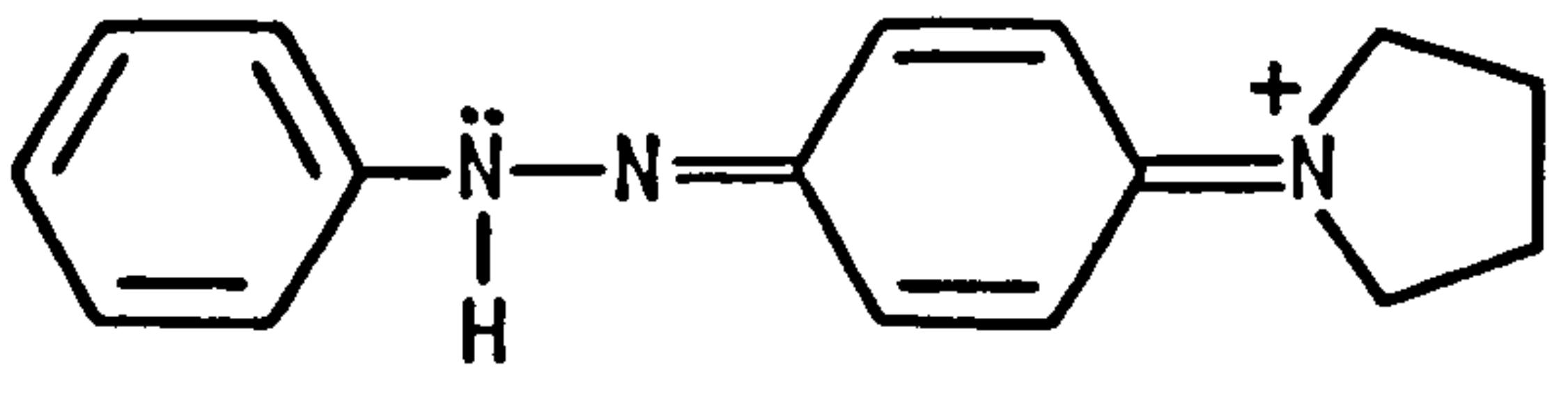
[a] Solvent ethanol?

[b] Ref.76

c 3'-Methyl derivative, ref. 76

[d] Ref. 14

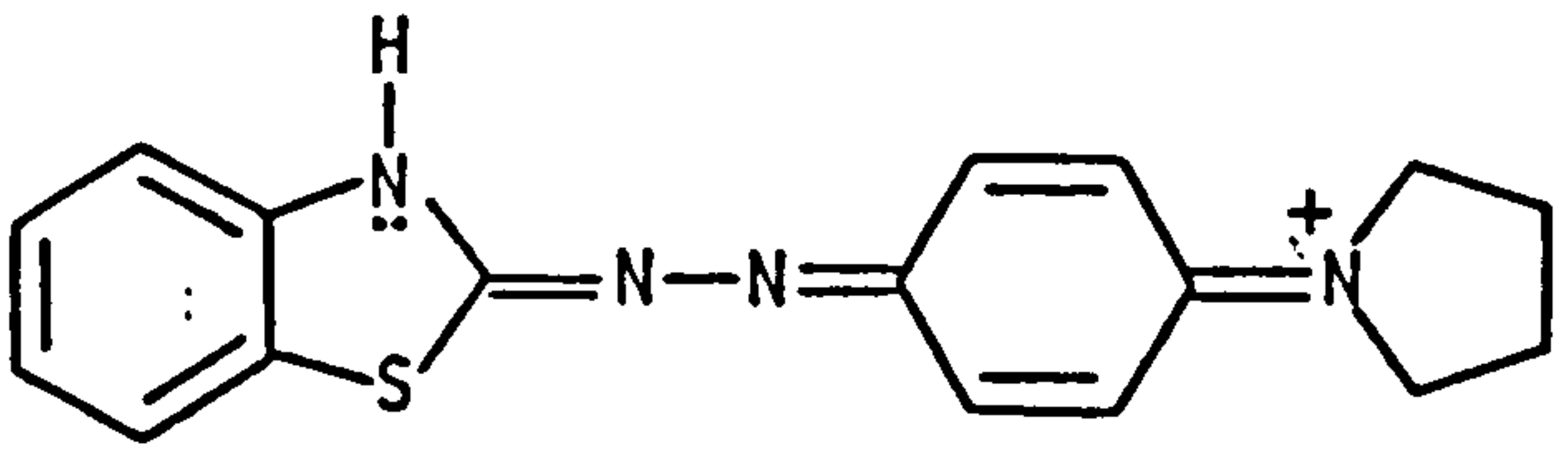
The protonated phenylazo dyes generally absorb at longer wavelengths than their neutral precursors. PPP calculations (Table 5.5) are in line with this fact [e.g.,4-pyrrolidinoazobenzene, observed wavelength shift (in ethanol) on protonation = 106 nm, calculated shift = 67 nm], although trends within the pyrrolidinoazo series are poorly predicted. Due to the low solubility of these cationic molecules in non-polar solvents, spectral measurements are usually obtained in ethanol, introducing a measure of uncertainty into such comparisons. However, the relatively small wavelength shifts caused by 4'-acceptor groups is reproduced, and the 4'-methoxy dye is correctly predicted to be the most bathochromic member of the series. The additional bathochromic effect of protonation at the ring nitrogen in thiazolyl and benzthiazolyl dye systems is also predicted, for instance dyes (126) to (128), as are the increased intensities of the protonated dyes (assuming protonation occurs at the β-azo - or heterocyclic ring - nitrogen atom rather than the terminal nitrogen atom) compared with the neutral precursors (Table 5.5).



(126)

λ_{max}(calc.) = 478 nm

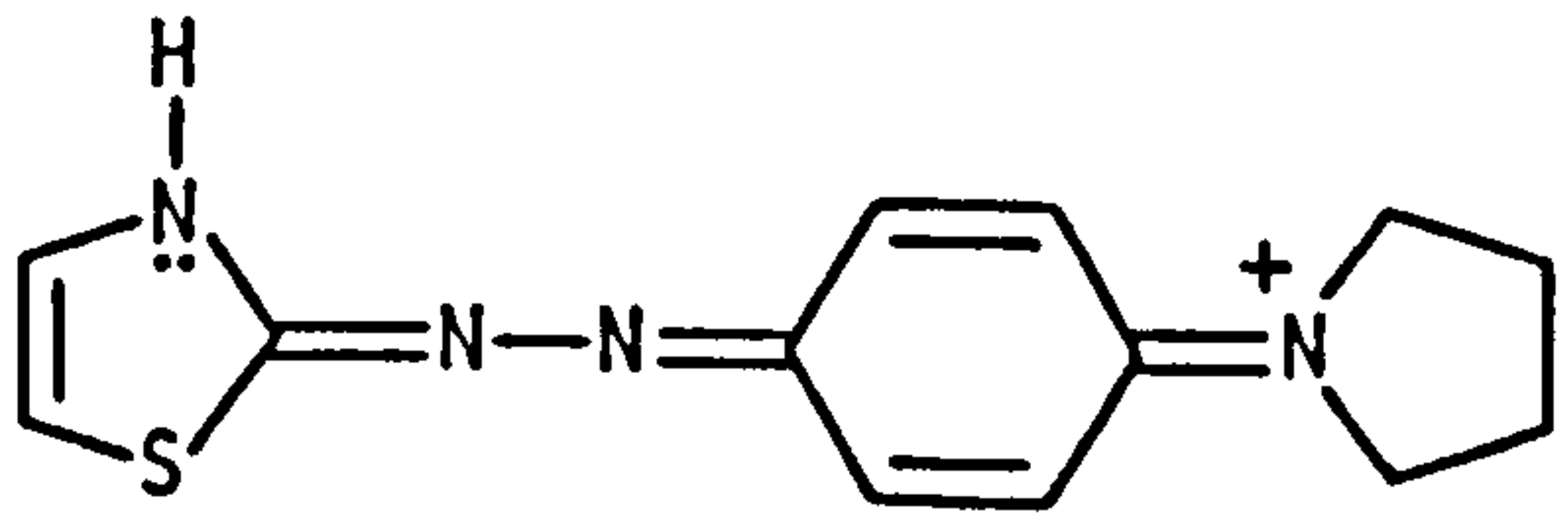
λ_{max}(exp.) = 517 nm



(127)

λ_{max}(calc.) = 535 nm

λ_{max}(exp.) = 600 nm



(128)

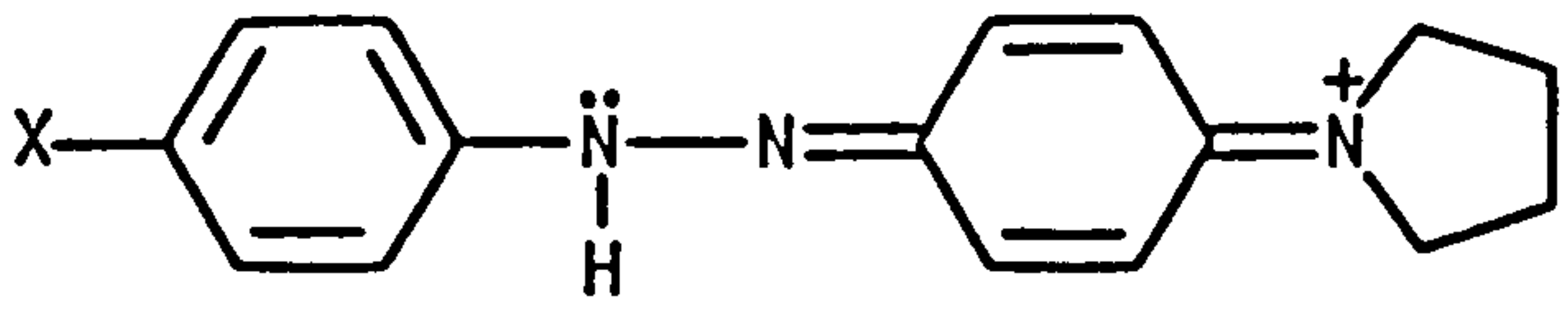
λ_{max}(calc.) = 542 nm

λ_{max}(exp.) = 589 nm

It is probable that the VSIP and A values for the β-azo nitrogen atom (the site of protonation) were developed on the assumption that the protonated dyes would show positive solvatochromism in a manner similar to that of the neutral dyes. However, recent work[244] has suggested that the opposite is true, i.e. these systems will shift to longer wavelengths in non-polar solvents. If this is indeed the case, then a re-evaluation of the β-azo nitrogen parameters is required.

Electron densities of the ground and excited states of some azo dyes (as calculated by the PPP method) are shown in Figs. 5.1—5.7

Table 5.5. Comparison of Experimental and Calculated Electronic Absorption Spectral Data for Some Protonated Dyes Derived from 4-Aminoazobenzene.

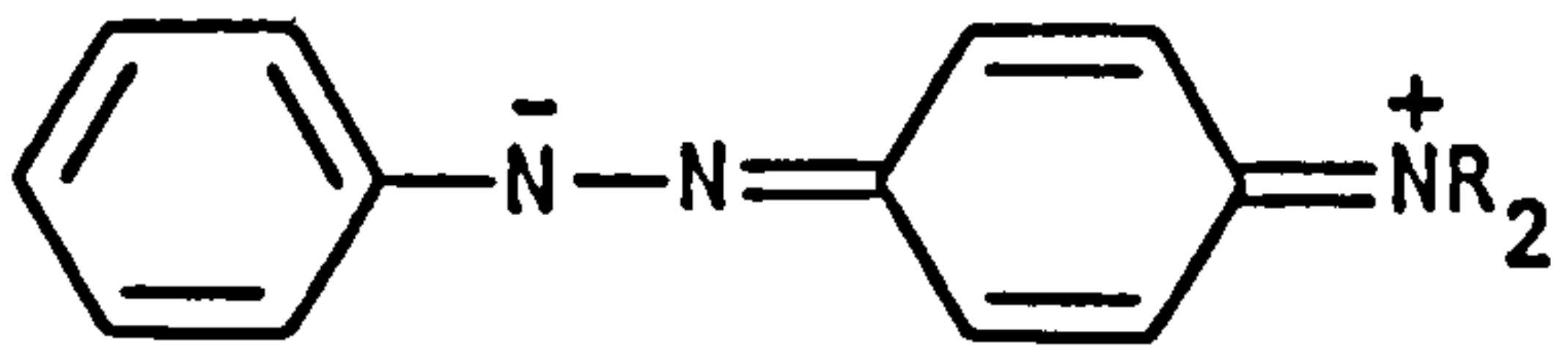


X	λ_{max}(calc) /nm	f(calc)	λ_{max}(exp) /nm	$10^{-4}\varepsilon$
4'-OMe	502	2.02	559	5.90
4'-H	478	2.01	519	5.77
4'-Cl	479[a](498)[b]	2.02[a](2.01)[b]	524	5.88
4'-Ac	490	2.20	520	6.34
4'-CN	488	2.26	512	6.19
4'-NO_2	483	2.18	512	6.82

[a] Cl not part of π-electron system

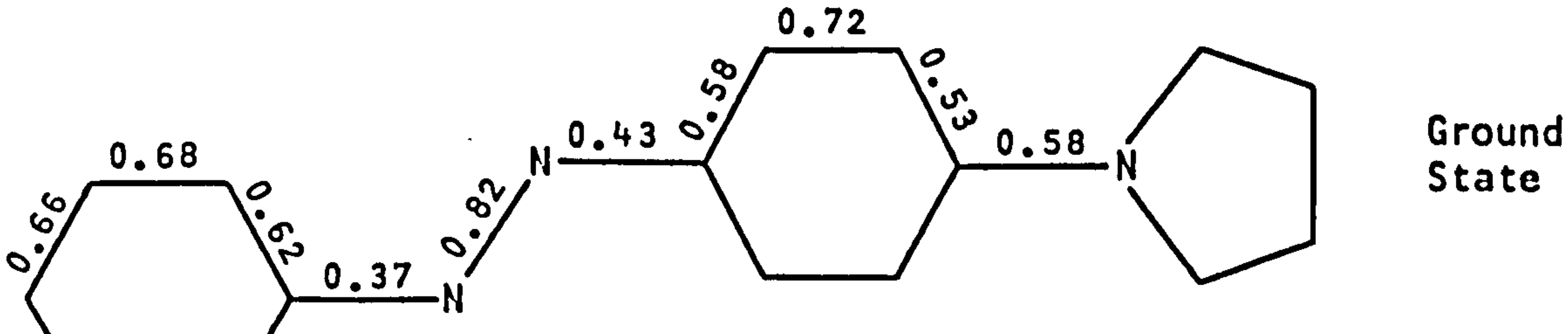
[b] Cl part of π-electron system

(conformations as shown). With reference to the parent dye, 4'-pyrrolidinoazobenzene (Fig. 5.1), the ground state of the molecule shows a considerable loss of electron density at the terminal nitrogen atom, the main electron rich centres being the <u>ortho</u> and <u>para</u> carbon atoms of the donor ring together with the β-azo nitrogen atom (as predicted by ground state resonance theory) and also, but to a lesser extent, the α-azo nitrogen atom. Excitation is seen to result in even more conjugation by the terminal nitrogen lone pair and also in reductions in electron density at the <u>ortho</u> and <u>para</u> positions, whilst a build up of electron density occurs at the azo link, in particular at the α-nitrogen atom, as has previously been stated.[245] Gains in electron density (of variable amounts) are seen at all the carbon atoms of the acceptor ring. These trends are clearly incompatible with resonance ideas, which suggest a build up of electron density at the β-azo nitrogen atom due to the contribution of structures such as (129) to the excited state, but, on the other hand, they are closely related to the results of similar calculations on 4-aminostilbene,[246] where electron density build up at the α-carbon atom is observed on excitation.

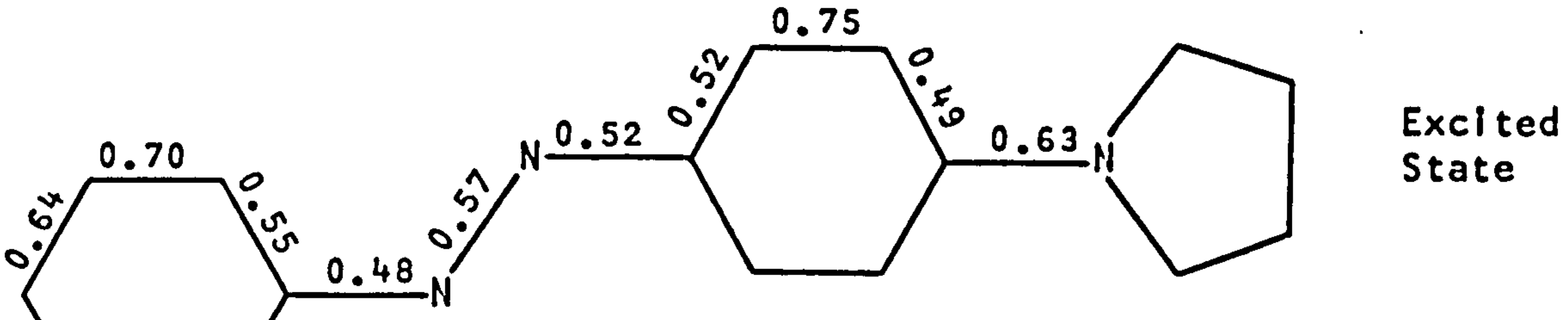


(129)

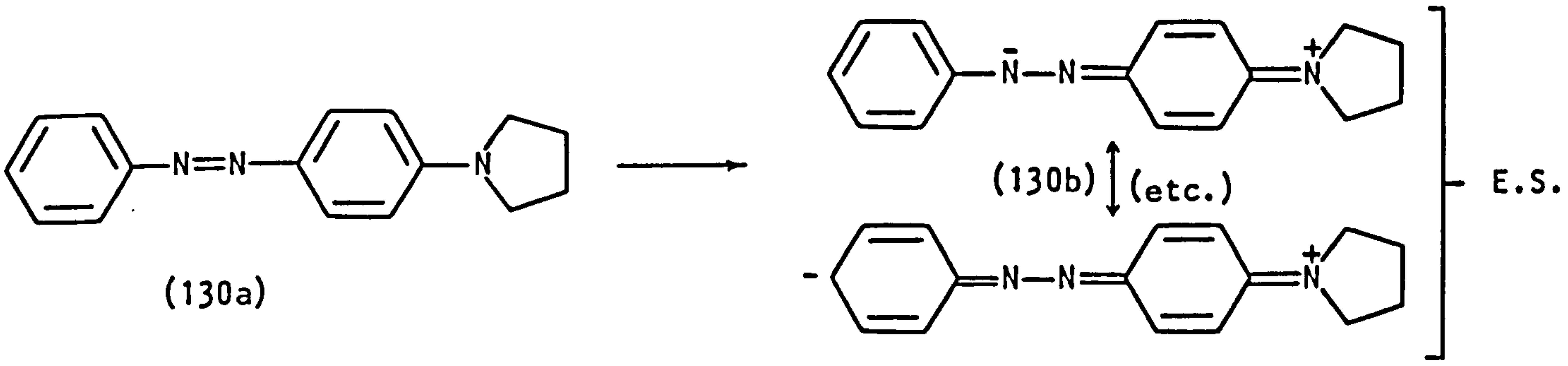
Bond order calculations for 4-pyrrolidinoazobenzene (130) do, on the other hand, suggest a movement towards a more quinonoid structure (130b) in the excited state, as witnessed by the increased bond order at the C_{ar}-N, C_2—C_3, both C_{ar}-N(azo), and $C_{2'}$-$C_{3'}$ bonds, and decreases in bond order at the other bonds, especially at the azo link.



(130a)



(130b)



Introduction of a methoxy group at the 4'-position (Fig. 5.2) causes a slight reduction in the conjugation of the terminal nitrogen lone pair, but the trends are similar to those of the parent dye. It is noticeable that the oxygen lone pair plays a negligible part in the excitation process, which may help to explain why the methoxy group has little effect on the λ_{max} value. Replacement of methoxy by an electron withdrawing group causes a reduction in the build up of electron density at the β-azo nitrogen, leading eventually to an overall loss on excitation, as shown for the 4'-nitro derivative (Fig. 5.3). The terminal nitrogen lone pair shows increased conjugation in both ground and excited states, whilst the nitro group shows a major build-up of electron density at all

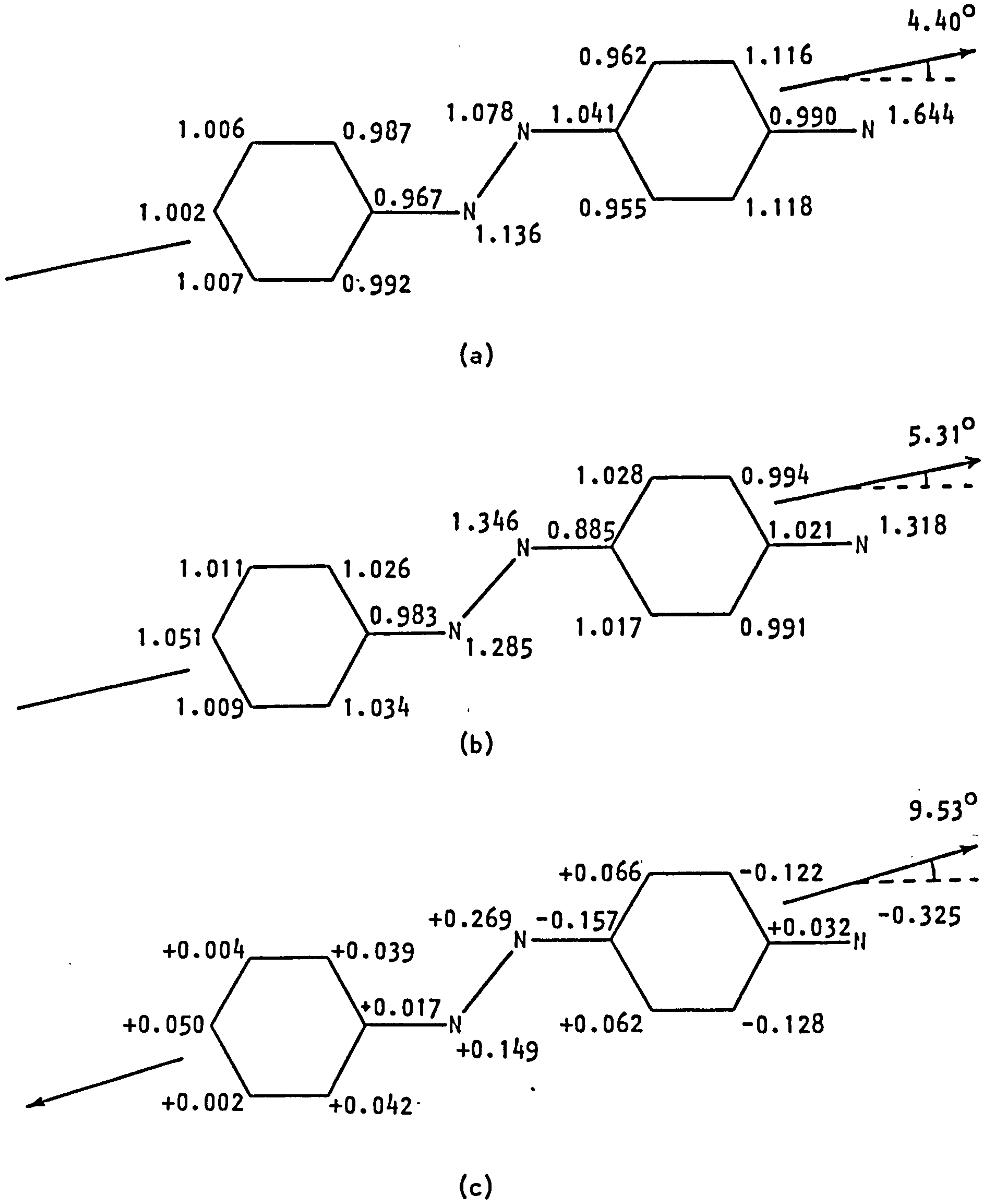
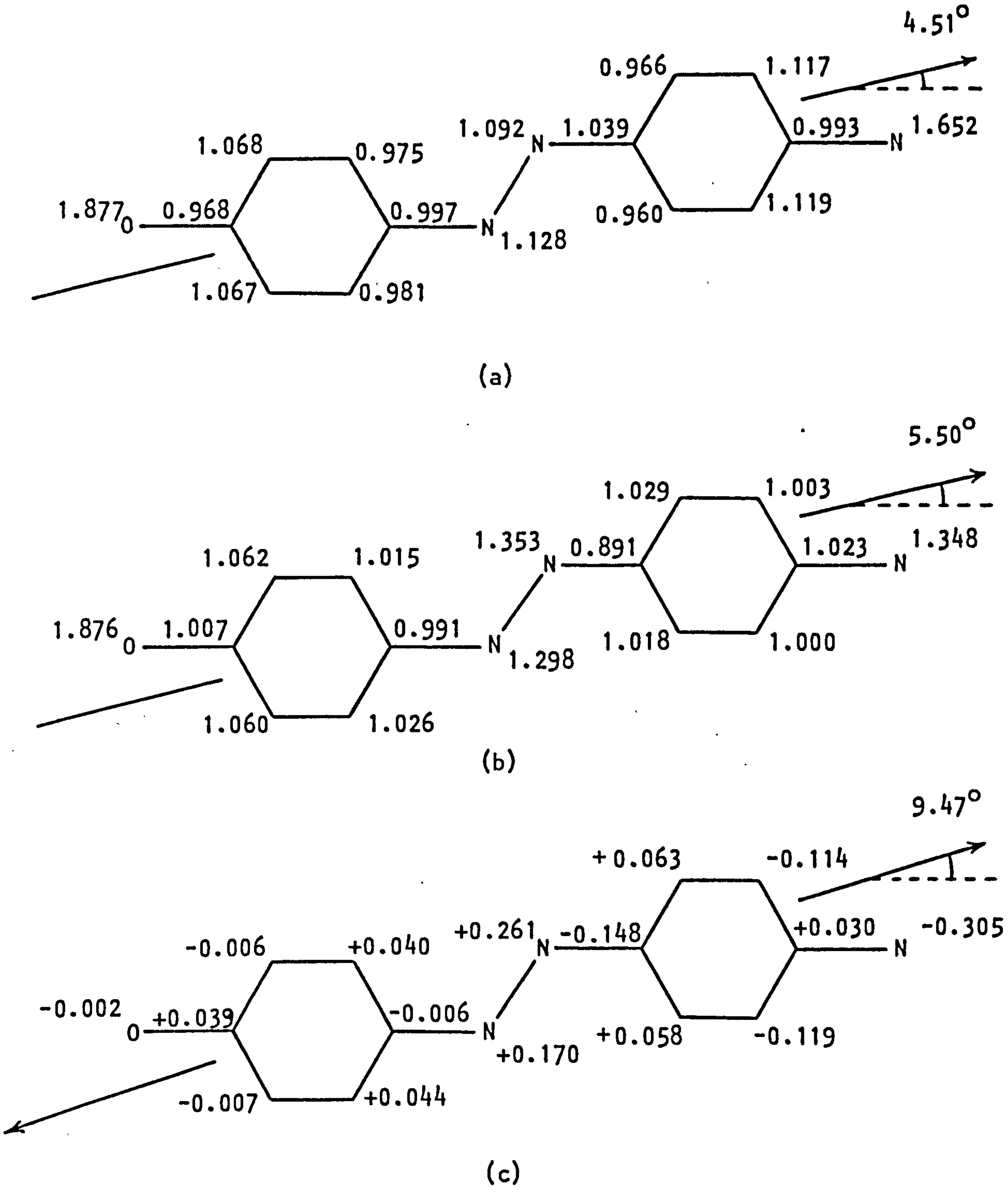


Fig. 5.1. The HOMO ⟶ LUMO electronic transition for 4-pyrrolidinoazobenzene:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.



(a)

(b)

(c)

Fig. 5.2. The HOMO→LUMO electronic transition for 4'-methoxy-4-pyrrolidinoazobenzene:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

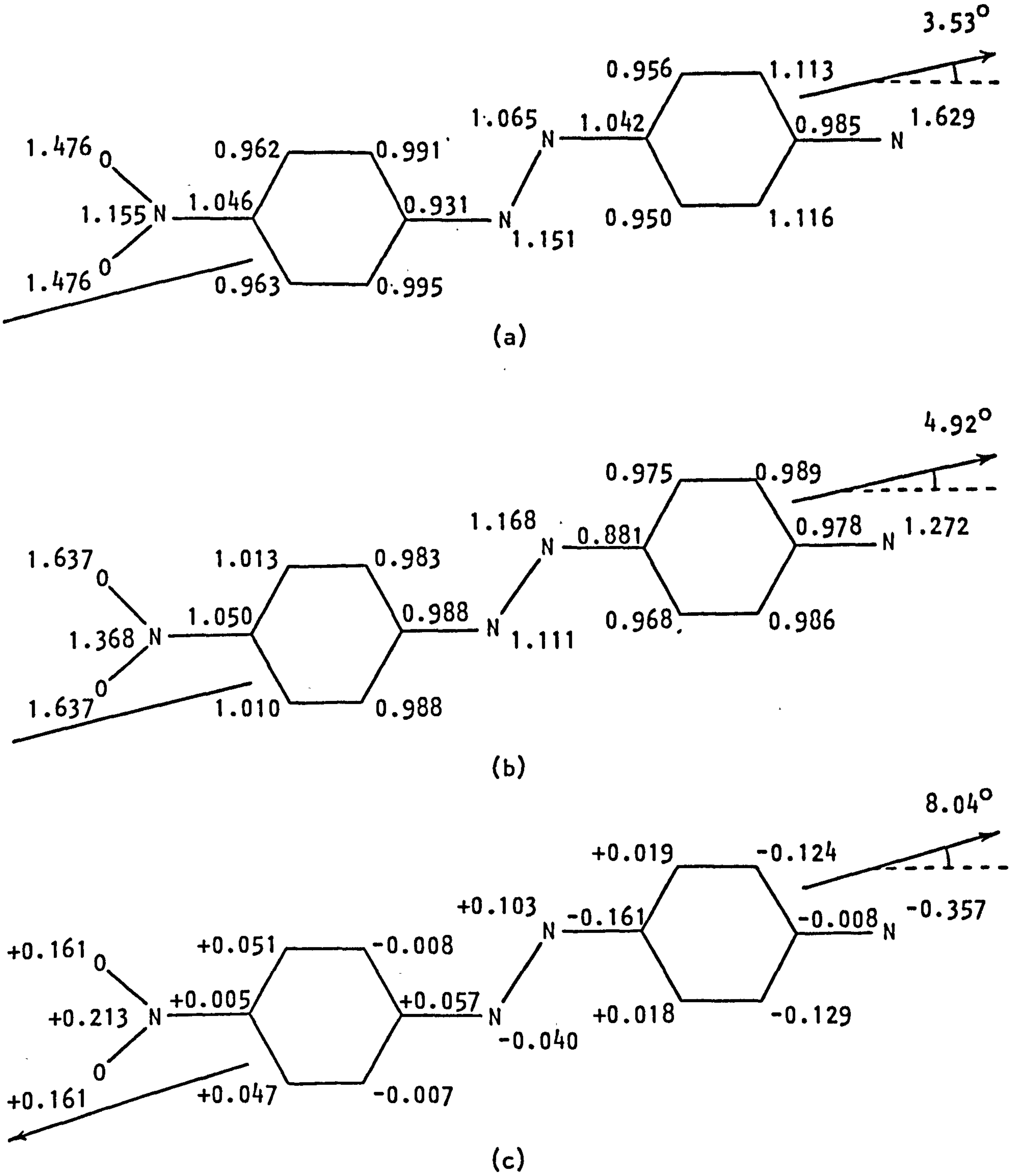


Fig. 5.3. The HOMO→LUMO electronic transition for 4'-nitro-4-pyrrolidinoazobenzene:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

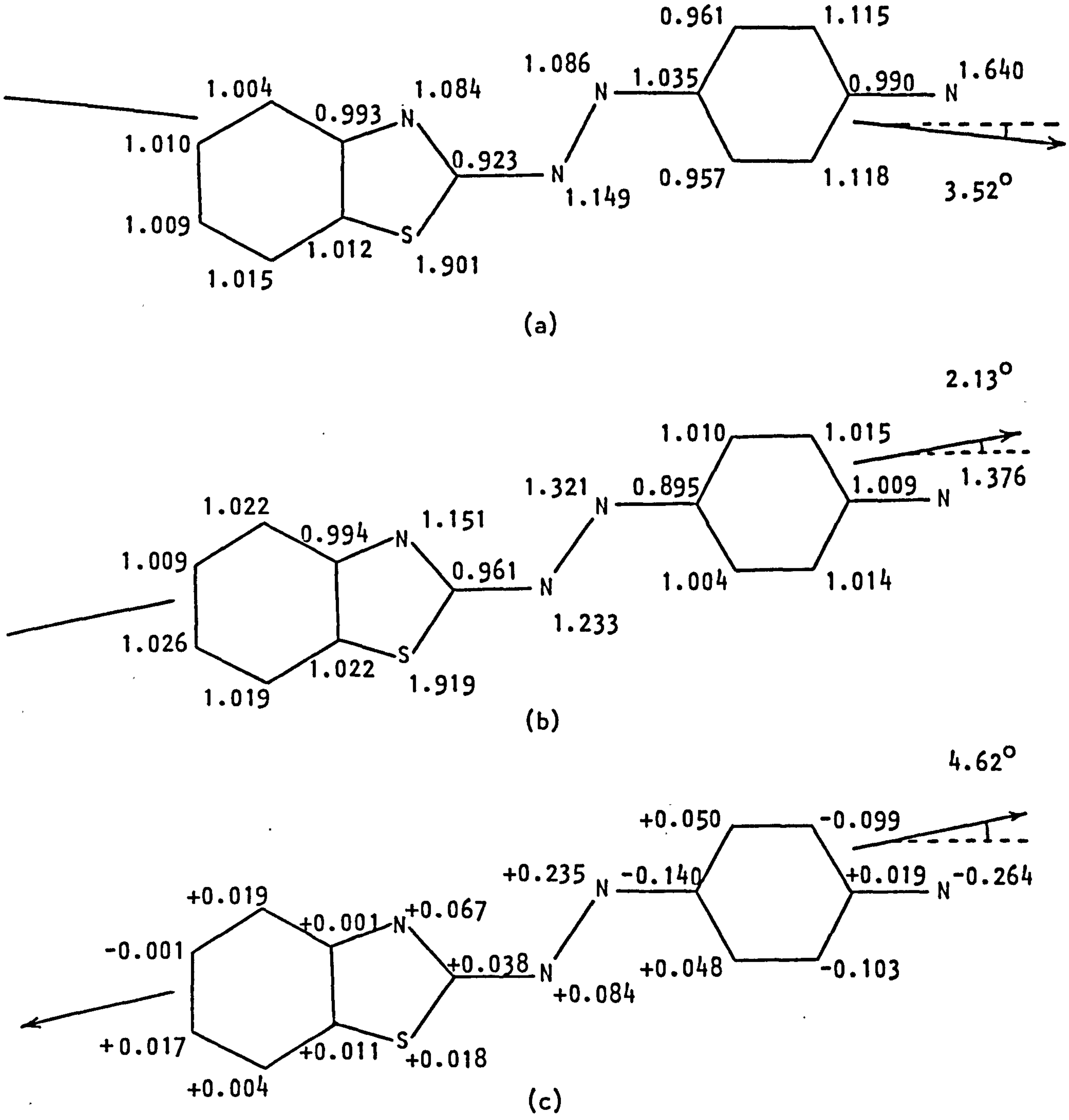


Fig. 5.4. The HOMO→LUMO electronic transition for N-[4-(benzthiazol-2'-ylazo)phenyl]pyrrolidine:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

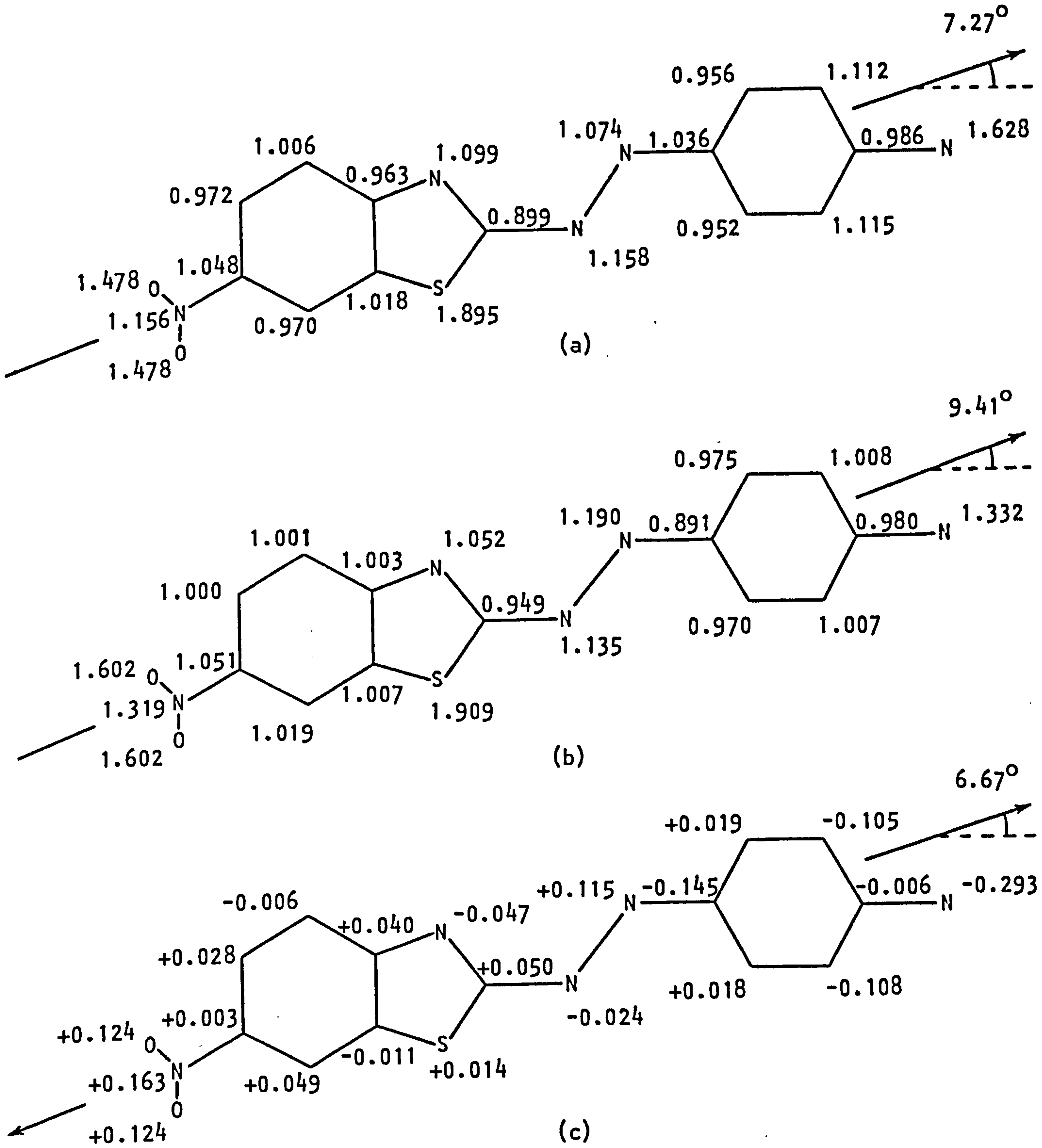


Fig. 5.5. The HOMO ⟶ LUMO electronic transition for N-[4-(6'-nitrobenzthiazolyl-2'-azo)phenyl] pyrrolidine:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

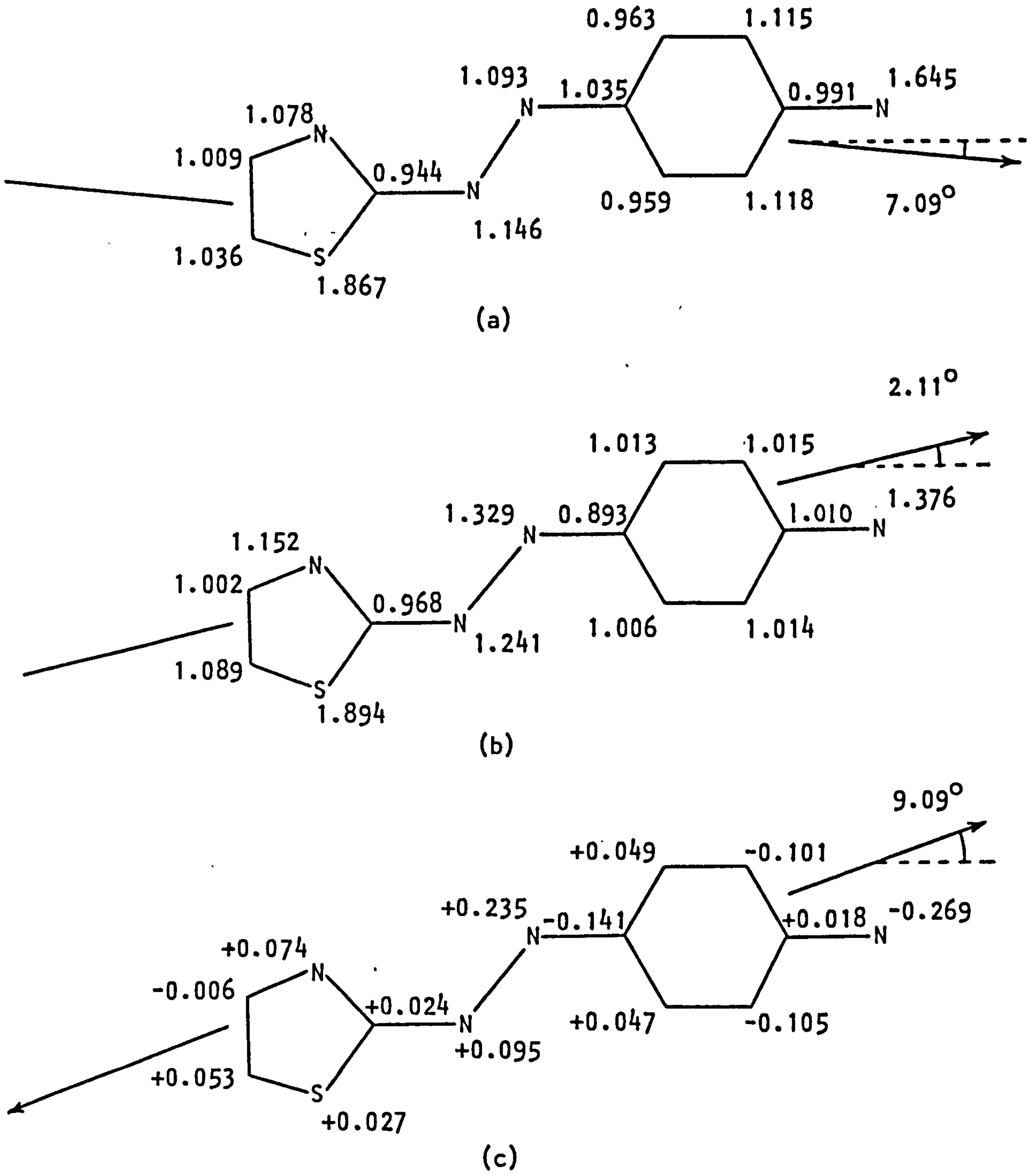


Fig. 5.6. The HOMO ⟶ LUMO electronic transition for N-[4-(thiazol-2'-ylazo)phenyl] pyrrolidine:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

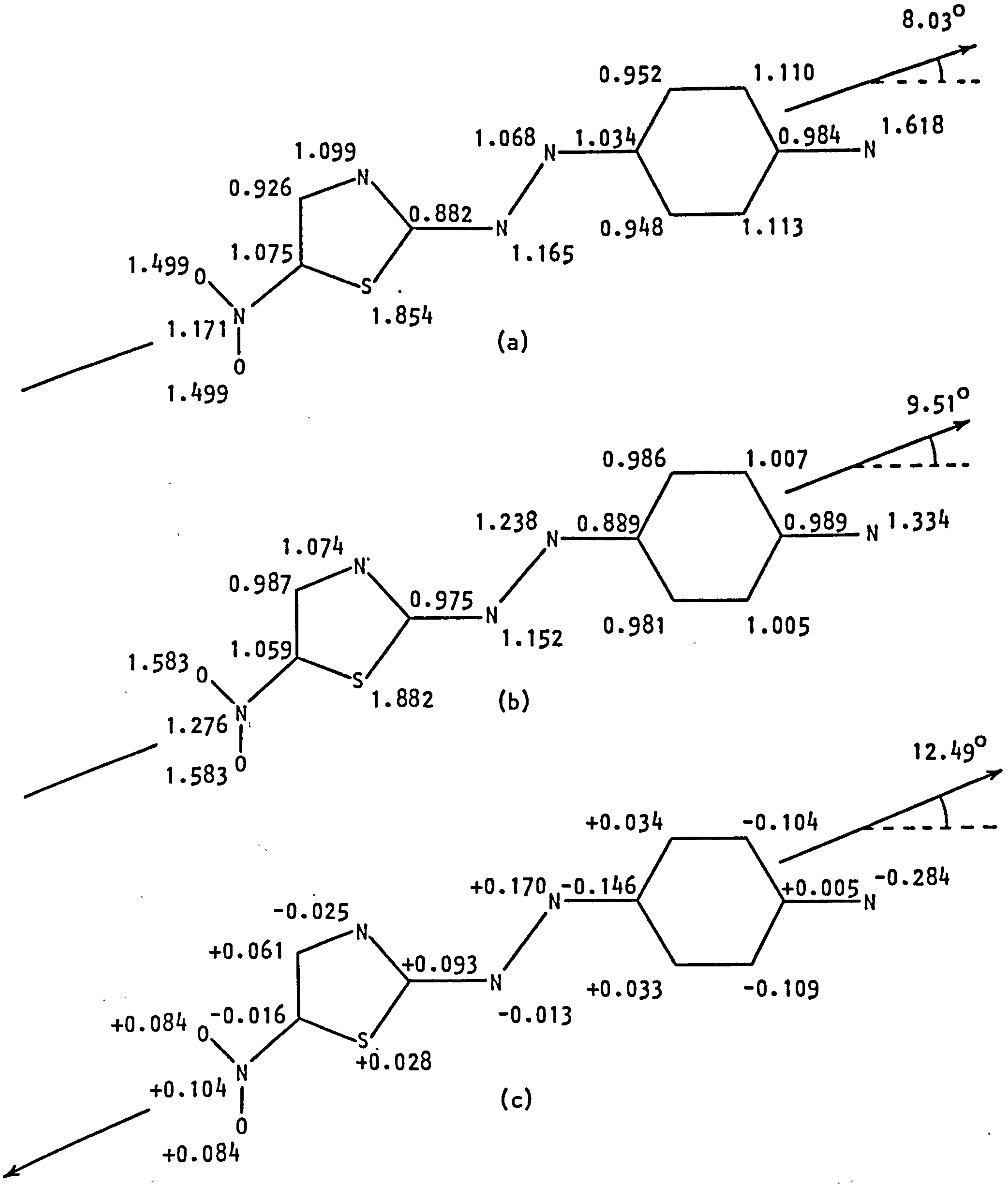


Fig. 5.7. The HOMO ⟶ LUMO electronic transition for N-[4-(5'-nitrothiazol-2'-ylazo)phenyl]pyrrolidine:

(a) Ground state π-electron densities and dipole moment angle,

(b) Excited state π-electron densities and dipole moment angle,

(c) Changes in π-electron densities and transition moment angle.

three atoms in the excited state.

In each of the above dyes, the ground state electron density at the terminal nitrogen atom is greater than at the β-azo nitrogen atom. The fact that protonation occurs to a large extent in many azo dyes at the latter site suggests that other factors are important, such as the ease of attack by the proton, and resonance stabilisation of the resulting cation.

The parent dyes and nitro derivatives of the benzthiazolyl and thiazolyl dyes show similar trends to their phenyl counter-parts. The change of electron density at the terminal nitrogen atom in the 5'-nitrothiazolyl dye (Fig. 5.7) is rather less than with the other nitro derivatives. Presumably this situation arises because the ground state of this molecule is already very polar. The sulphur atom of the heterocyclic rings of these systems appears to play only a small part in the redistribution of electronic charge accompanying excitation, suggesting that this atom is not important in terms of the bathochromicity of these dyes. The ring nitrogen atom behaves rather like the β-azo nitrogen atom, its net profit or loss depending on the type of substituent at the 5'-position.

Calculated dipole moment values tend to exceed those obtained from experimental observations (Table 5.6). This finding may arise from the fact that the contribution of the σ electron core to the overall dipole moment of the molecule is not considered. As stated earlier, the PPP method cannot distinguish between the pyrrolidino- and NN-diethylamino-groups, so that calculated dipole moments are identical for both types. However, it is noticeable that the excited state moment is higher than the ground state moment for each dye, suggesting an excited state more polar than the ground state, and this is reflected in the positive solvato-

Table 5.6. Calculated π-Contribution to the Dipole Moments of Some Pyrrolidinoazo[a] Dyes (I-III).[b]

DYE	CALC. μ/D GROUND STATE	CALC. μ/D EXCITED STATE	EXP. μ/D GROUND STATE P[c]	EXP. μ/D GROUND STATE D[d]
I;4'-OMe	4.06	17.49	-	-
I;4'-H	6.50	21.53	3.76	3.40
I;4'-Cl	7.12(5.87)[e]	22.51(20.57)[e]	5.13	5.01
I;4'-Ac	8.45	26.77	-	-
I;4'-CN	10.60	31.01	-	8.17
I;4'-NO_2	12.22	46.19	-	8.43
II;6'-H	7.16	20.32	-	-
II;6'-NO_2	13.00	45.18	-	-
III;5'-H	6.31	19.37	-	-
III;5'-NO_2	13.79	35.26	-	-

[a] Calculated values apply equally to the analogous NN-diethylaminoazo dyes

[b] Conformations as shown in Scheme 5.1

[c] Pyrrolidinoazo dyes (ref. 89)

[d] NN-Diethylaminoazo analogues (ref.81)

[e] Value outside brackets refers to consideration of -I effect of Cl atom only; value inside brackets considers the Cl atom as part of the π-electron system

chromism of these dyes. Predicted ground state moments increase as the strength of the electron acceptor residue of the dye increases, as would be expected due to the increased conjugation of the nitrogen lone pair.

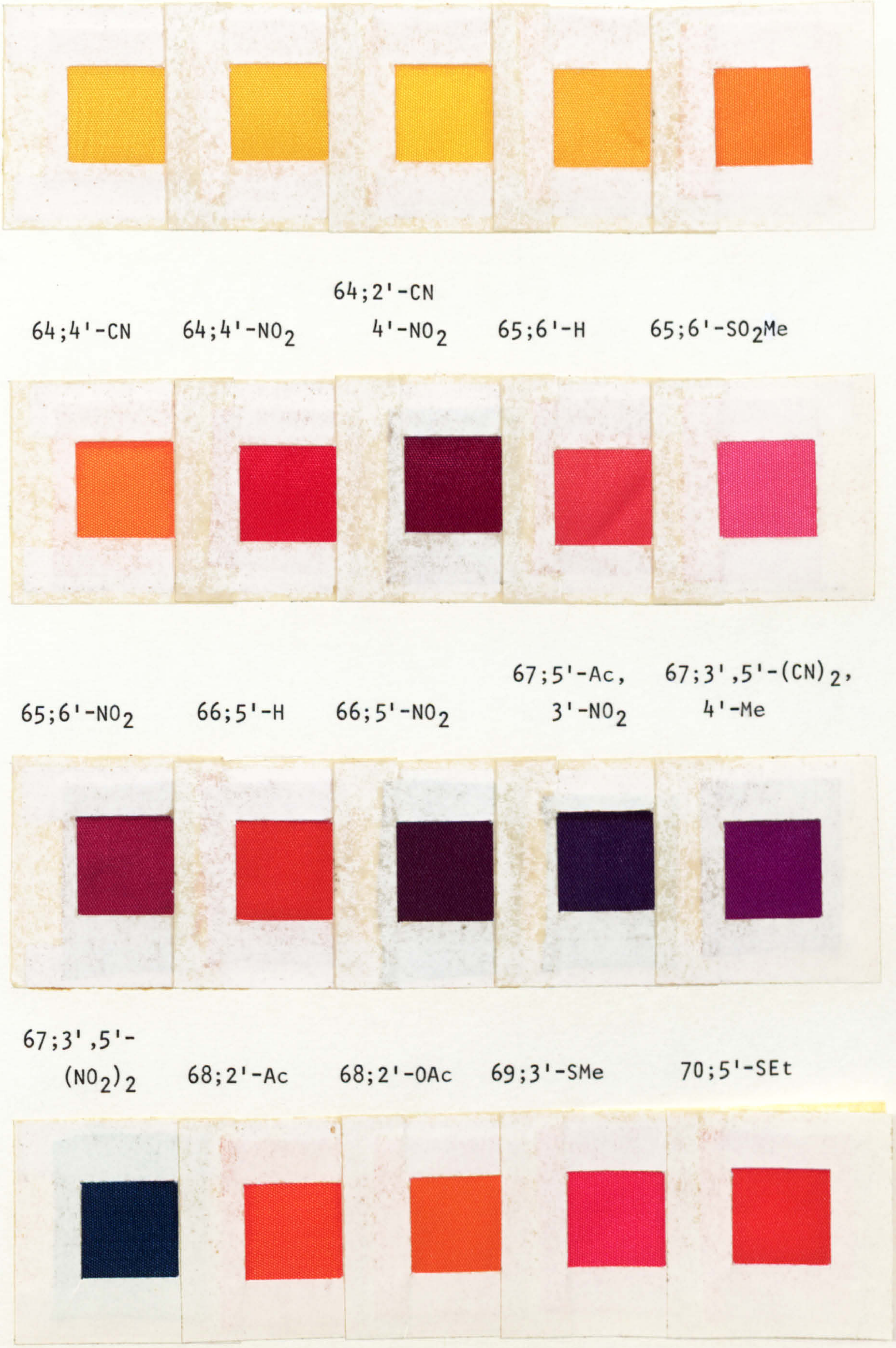
Experimental dipole moment studies on the pyrrolidinoazo dyes are being undertaken at the present time. These results will shed more light on the relationship between calculated and experimental values.

The transition moment vector ($\underline{M}$) of a dye molecule (arising from the temporary increase in asymmetry of the electron density distribution which occurs during the transition of a molecule from one state to another) has assumed a technical significance in recent years in connection with coloured liquid crystal display systems, which depend on the polarisation of dye absorption bands, i.e., on the criterion that for light absorption to occur the electric vector of the incident light must oscillate in the same direction as the transition moment. In such display systems, the dye is dissolved in a liquid crystal host (the components of which are usually long and highly polar molecules) and must align itself as closely as possible with the liquid crystal so that as the molecules of the latter are switched from one orientation to another, by application of an electric field, the orientation of the dye molecules will follow suit. Thus, the dye molecule should ideally be a long planar molecule, such as an azo dye, with its ground state dipole moment vector (μ) along the long axis. These two factors can be assumed to dictate the orientation axis of the dye molecule with respect to the host. The PPP model suggests that azo dyes fit the latter requirements [see Figs. 5.1 (a)-5.7(a)], and computed μ values may be of considerable use in comparing the alignment properties of related dyes; alignment will be reinforced as μ for the dye increases.

In the absence of an electric field the cell will appear coloured, but when a voltage is applied the dye molecule aligns with its orientation axis parallel to the direction of the light wave, i.e., perpendicular to the electric vector of the wave. For light absorption not to occur in this orientation, M must also lie along the orientation axis of the molecule or, to a first approximation in azo dyes, parallel to μ. PPP calculations (Figs. 5.1-5.7) predict similar directions for M and μ, suggesting that azo dyes may be useful in liquid crystal systems, and recent studies [35] have confirmed the promise of this class of chromogens. Although other factors, such as photochemical stability, are important in determining the suitability of dyes for use in liquid crystal devices, the PPP method may prove to be a valuable tool in their initial evaluation.[230]

6. APPENDIX II

Plate 6.1. High Temperature Dyeings on Polyester of Some Dyes Derived from N-Phenylpyrrolidine (64-70; Y = $-CH_2CH_2-$).



64;4'-OMe 64;4'-H 64;4'-Cl 64;4'-CF_3 64;4'-Ac

64;4'-CN 64;4'-NO_2 64;2'-CN, 4'-NO_2 65;6'-H 65;6'-SO_2Me

65;6'-NO_2 66;5'-H 66;5'-NO_2 67;5'-Ac, 3'-NO_2 67;3',5'-$(CN)_2$, 4'-Me

67;3',5'-$(NO_2)_2$ 68;2'-Ac 68;2'-OAc 69;3'-SMe 70;5'-SEt

Plate 6.2. High Temperature Dyeings on Polyester of Some Dyes Derived from (a) *N*-Phenylpiperidine (64-67;Y = $-CH_2CH_2CH_2-$) and (b) *N*-Phenylmorpholine (64-67;Y = $-CH_2OCH_2-$).

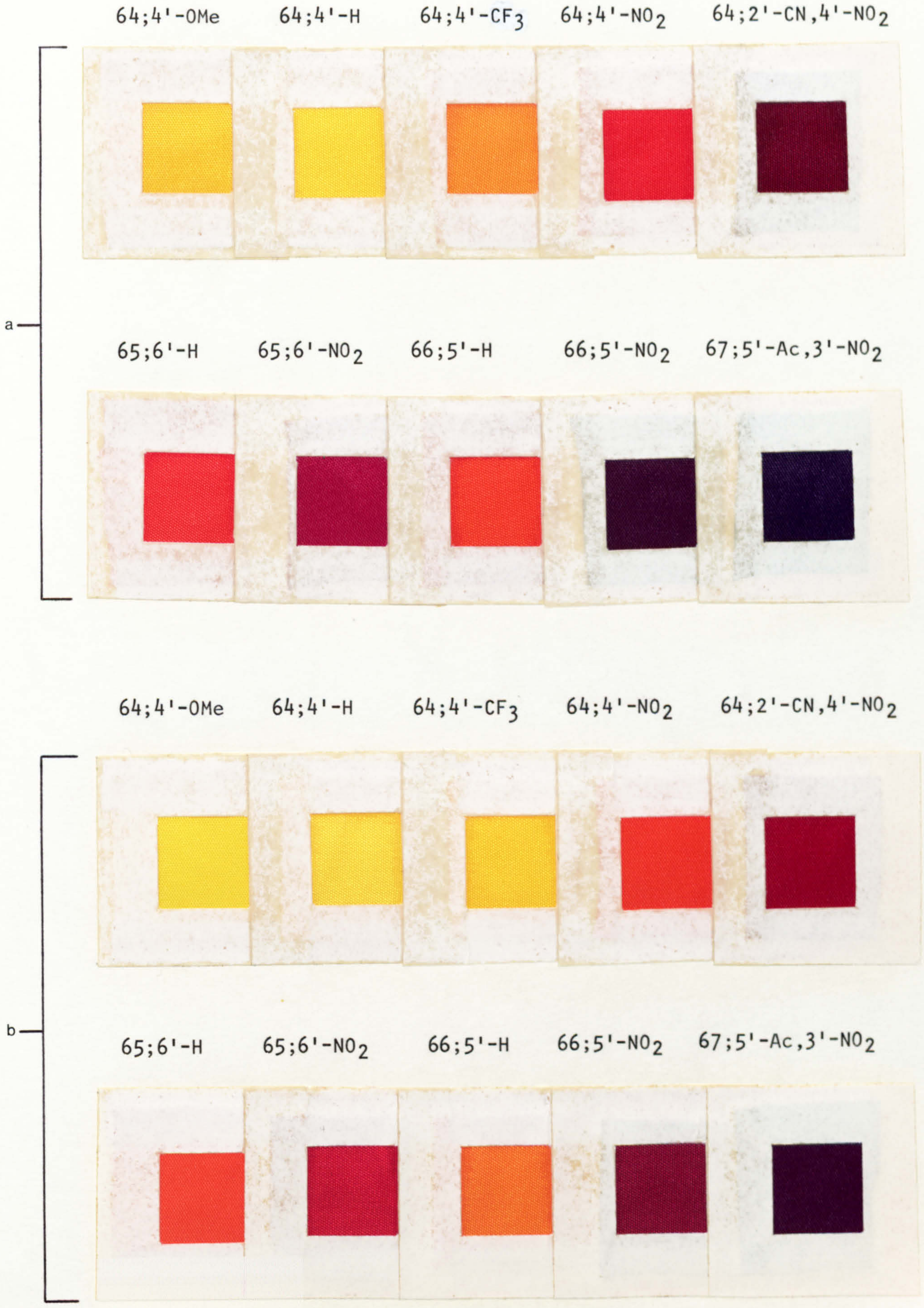
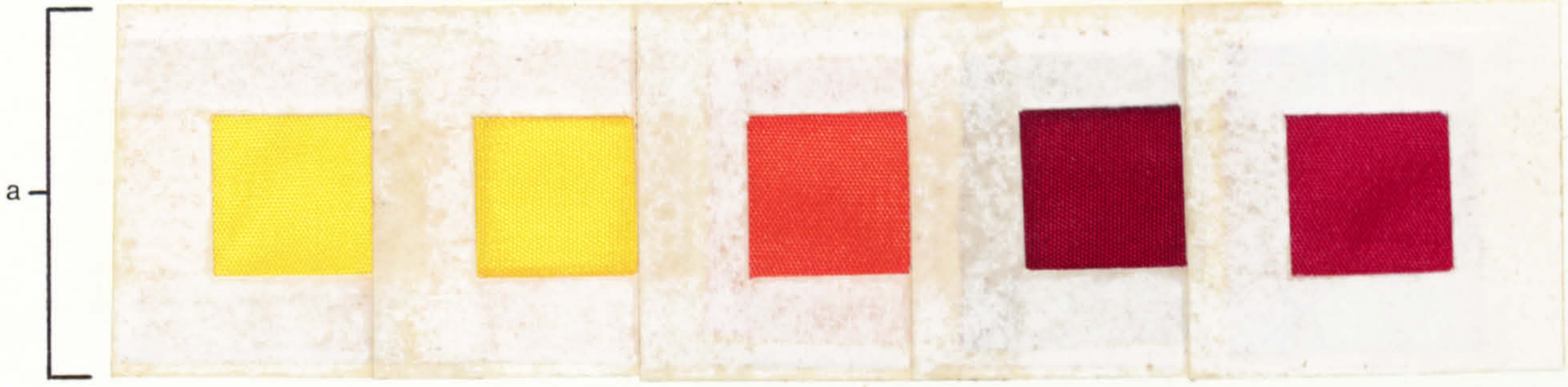


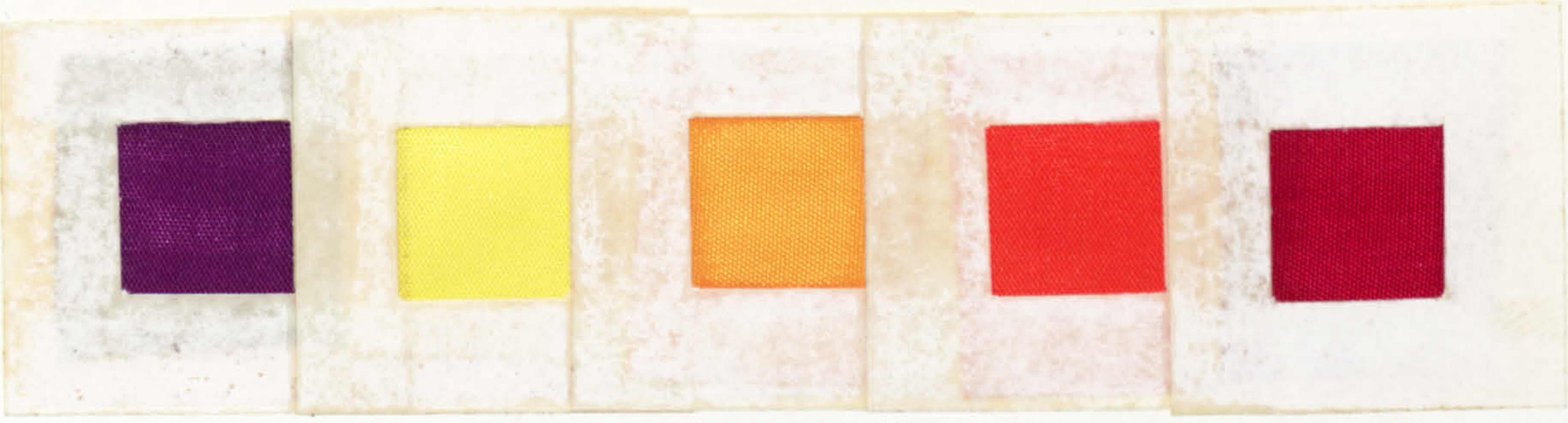
Plate 6.3. High Temperature Dyeings on Polyester of Some Dyes Derived from (a) N-Phenylthiomorpholine (64-66;Y = $-CH_2SCH_2-$), (b) N-Phenylthiomorpholine-1,1-dioxide (64;Y = $-CH_2SO_2CH_2-$), (c) N'-Ethyl-N-phenylpiperazine (64;Y = $-CH_2N(Et)CH_2-$), (d) N'-Acetyl-N-phenylpiperazine (64-65;Y = $-CH_2N(Ac)CH_2-$) and (e) NN-Diethylaniline (30).

64;4'-OMe 64;4'-H 64;4'-NO$_2$ 64;2'-CN, 4'-NO$_2$ 65;6'-NO$_2$

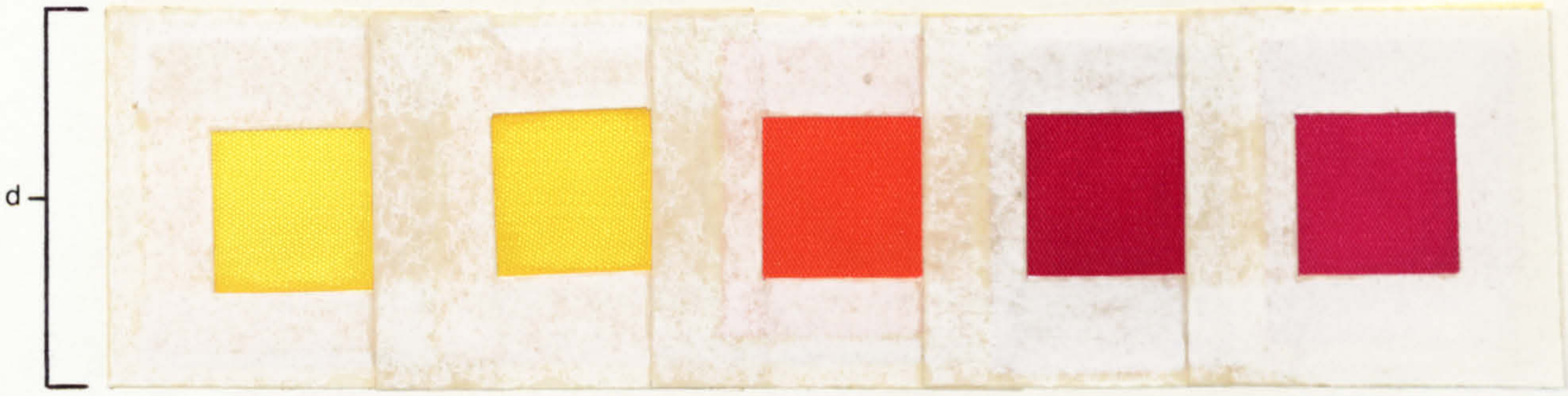


a b c

66;5'-NO$_2$ 64;4'-OMe 64;4'-NO$_2$ 64;4'-NO$_2$ 64;2'-CN,4'-NO$_2$



64;4'-OMe 64;4'-H 64;4'-NO$_2$ 64;2'-CN, 4'-NO$_2$ 65;6'-NO$_2$



30;4'-OMe 30;4'-H 30;4'-NO$_2$