The synthesis and relative acidity of substituted diphenylamines

Pigg, Brian

THE SYNTHESIS AND RELATIVE ACIDITY OF SUBSTITUTED DIPHENYLAMINES

by

BRIAN PIGG, B.Sc. (Hull)

A thesis submitted for the degree of Master of Science of The University of Durham

December 1970

ACKNOWLEDGEMENTS

I am indebted to the late Mr. N. Ferry for his helpful suggestions and encouragement throughout the course of the work.

I also wish to thank Dr. G. Kohnstam for acting as my University Supervisor and Mr. E. Lewis and the technical staff of the Chemistry Department for their help throughout.

MEMORANDUM

The work described in this thesis was carried out in the Chemistry Laboratories of The Sunderland Polytechnic.

This thesis has not been submitted for any other degree and is the original work of the author except where acknowledged by reference.

The objects of this study

(i) To synthesise various substituted diphenylamines and to report on the scope and limitations of the various methods of preparation.

It was hoped that the study would find a convenient method for the preparation of a wide range of substituted diphenylamines.

(ii) To determine the relative acidities of the diphenylamines and from the results obtain information about the transmission of electronic effects through molecules.

The study involved the attempt to develop an accurate method for the determination of the molar extinction coefficient for the diphenylamine anion, present in the equilibrium formed when 4-nitrodiphenylamine reacts with potassium isopropoxide in alcoholic solution, because of the wide disagreement among quoted values for this quantity in the chemical literature.

The reliable values for the molar extinction coefficients could then be used to determine accurate values for the relative acidities of the diphenylamines.

ABSTRACT

Synthetic Work

A study has been made of the scope and limitations of various methods of preparation of substituted diphenylamines. The study has led to extensions of the Chapman and Smiles rearrangements and a number of diphenylamines not previously prepared have been obtained.

Relative Acidities of Substituted Diphenylamines

The reaction between isopropoxides in alcoholic solution and substituted diphenylamines has been investigated spectrophotometrically. Variations in the apparent equilibrium constant may be explained by ion pair formation. A value of the ion pair dissociation constant has been determined which is of the expected order.

The suggestion of ion pair dissociation in dilute solution is further supported by the study of the reaction of lithium, sodium and potassium isopropoxides with nitrodiphenylamines.

A ρ value for proton removal for 4-nitrodiphenylamines has been found and an estimate of transmission of substituent effects through groups can be made.

CONTENTS

CHAPTER I

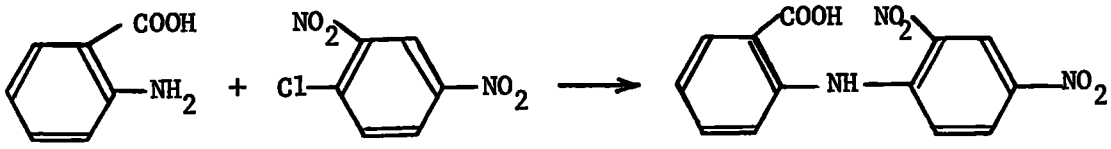
SYNTHETIC WORK

THE PREPARATION OF SUBSTITUTED DIPHENYLAMINES

There are three general methods for the preparation of diphenylamines (a) the Ullmann reaction (b) the Chapman reaction and (c) the Smiles rearrangement.

1.1 The Ullmann Reaction[1]

This is the commonest method of synthesis and involves the condensation of an aromatic amine with an alkyl halide.[2] The Ullmann diphenylamine synthesis was a development from a reaction carried out by Jourdan,[3] who condensed anthranilic acid with 2,4-dinitrochlorobenzene in boiling ethanolic ammonia.



Diphenylamine carboxylic acids have been reported to be readily decarboxylated by heating just above their melting points.[4]

Ullmann condensed orthochlorobenzoic acid with aniline in the presence of a trace of copper. Subsequently many substituted diphenylamines were synthesised, Ullmann and co-workers being responsible for a large amount of the work.

To improve the yield and perform more difficult condensation variations in the catalyst, acid-binding agent and the use of solvents were tried.

The original catalyst "Nature Kupfer C" has been replaced by spongy precipitated copper. For more reactive substances only a trace of copper is required for most condensations (approximately 1% of copper based on the aromatic halide). The presence of too much catalyst leads to tar formation.

The original acid-binding agent, ammonia, was replaced by potassium carbonate.[5] Sodium acetate has been used for reactions in which hydrolysis must be avoided.[6] Calcium carbonate is often used in the preparation of diphenylamine sulphonic acids.[7]

Although no solvents, apart from the reactants, were initially employed, it has been found advantageous to use various solvents. High boiling alcohols, which are readily removed by steam distillation after the reaction, are used with success. Volatile alcohols have been frequently used and often give a much cleaner product than in the absence of solvent. Nitrobenzene is used for more difficult condensations at high temperatures. A recent review of the Ullmann diphenyl synthesis[8] suggests the use of many solvents and it is probable that some of these may be used for the diphenylamine synthesis. The reaction time can be decreased by the use of moderate amounts of amides, such as dimethylformamide, hexamethylphosphoramide and N methylpyrrolidone.

Improvements in yields have been obtained by variation of the reactants. Goldberg used acetyl derivatives of the amines.[9] This method enables aromatic amines to react with bromobenzene or its homologues. The amine is acetylated and reacted with the halogen compound in nitrobenzene solution in the presence of anhydrous potassium carbonate as an acid-binding agent and cuprous iodide as a catalyst.

According to a patent specification submitted by United States Rubber Company on June 29th 1960, the disadvantage of the Goldberg synthesis is that the yields are very small (ca. 1% of theory). The yield of p-nitro diphenylamine is increased some seventy fold by continuously removing the water formed by neutralisation of the liberated hydrogen chloride by the carbonate acid-acceptor.

Closely related to the preparation of diphenylamines via the diphenylamine-2-carboxylic acids is the method via the diphenylamine-2-sulphonic acids. The sulphonic acids, in many cases, can be readily desulphonated to the corresponding diphenylamine by heating for two hours at 100° with 70% v/v sulphuric acid or by refluxing with constant boiling hydrochloric acid. The solvent used in this method is usually water, chalk is often used as the acid-binding agent and no catalyst is required.

1.2 Preparation of 2-, 3- and 4-nitrodiphenylamines by the Ullmann reaction

1.2.1 Preparation of 4-nitrodiphenylamines

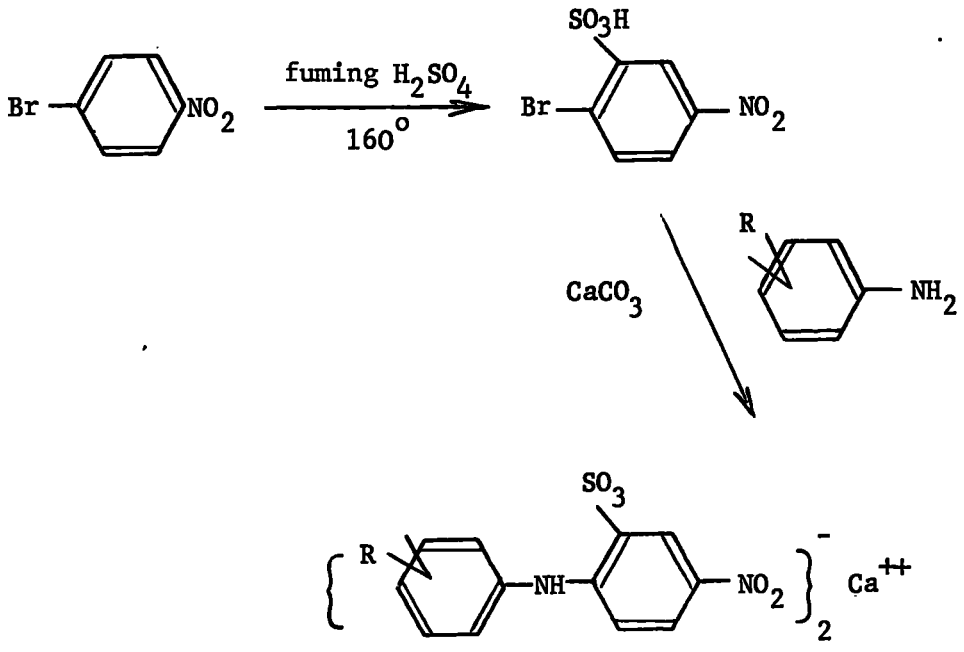
The preparation of 4-nitrodiphenylamines by the Ullmann reaction using 4-bromo-nitrobenzene is not a convenient process (see Chapter VIII, p.146 for details of preparation of 4-nitrodiphenylamine). The time of heating is long and varies from 10 hours to 24 hours. The product is often very impure, separating as a tar which is decolourised by charcoal. The yield is small and in an attempted preparation 2'-chloro-4-nitrodiphenylamine no product was obtained.

1.2.2 Preparation of 2-nitrodiphenylamine

For the preparation of the 2-nitrodiphenylamines using the Ullmann reaction, the variation of McCombie, Scarborough and Waters was used[10] (see Chapter VIII p.146 for details of preparation of 2-nitro-4'-methyldiphenylamine). This method involves the prolonged heating of 2-bromonitrobenzene with the appropriate amine in alcoholic solution in a sealed tube. Dark coloured residues were obtained, requiring extensive purification and in some cases pure products were difficult to obtain. It is not a suitable method for the preparation of a wide range of nitrodiphenylamines in a pure condition.

1.2.3 Modifications to Ullmann Reaction

(i) Activation of the bromine atom in 4-bromonitrobenzene by sulphonation enabled the reaction to be performed under mild conditions using water or glycerol as solvent and calcium carbonate as acid-binding agent (see Chapter VIII p.147 for details of preparation of 2'-methyl-4-nitrodiphenylamine).



The sulphonic acids were readily obtained in a pure condition and some were readily desulphonated by heating with 50% w/w sulphuric acid or constant boiling hydrochloric acid. The diphenylamines were obtained in a pure condition and in good yield (60-70%).

The following 4-nitrodiphenylamines were prepared by this method:

Substituent	Colour	Recryst. Solvent	M.p.
2'CH_3	Orange plates	ligroin-benzene	115°
3'CH_3	Orange plates	ligroin-benzene	131°
4'CH_3	Yellow needles	ethanol	138°
2'CH_3O	Yellow needles	ligroin-benzene	111°
4'CH_3O	Red leaflets	xylene	151°

The following compounds however resisted desulphonation: 3'-methoxy, 2'-chloro, 3'-chloro and 4'-chloro-4-nitro-diphenylamine-2-sulphonic acids.

Sulphonation of 2-chloronitrobenzene formed 2-nitrochlorobenzene-4-sulphonic acid which could be used in a similar manner to prepare certain 2-nitrodiphenylamines. The following 2-nitrodiphenylamines were prepared by this method:

Substituent	Colour	Recryst. Solvent	M.p.
3'CH_3	Orange needles	ethanol	92°
4'CH_3	Orange needles	"	68°
2'CH_3O	Red needles	"	83°
4'CH_3O	Orange prisms	"	91°
4'Cl	Orange prisms	"	146°

3'-methoxy-2-nitrodiphenylamine could not be prepared by this method since the corresponding sulphonic acid resisted desulphonation.

(ii) Dipolar aprotic solvents have been observed to increase the rate of a number of reactions.[8] Dimethylsulphoxide was unsuccessful. Considerable decomposition occurred and dark coloured products were formed. N-methyl-pyrrolidone, however shows promise as a solvent. The time of heating is reduced, the yields are larger and the product purer.

The 3'-methoxy, 3'-methyl and 4'-methyl substituted derivatives of 4-nitrodiphenylamine were prepared by this method (see Chapter VIII, p.147 for details of preparation of 3'-methoxy-4-nitro-diphenylamine).

1.2.4 Preparation of 3-nitrodiphenylamines

Only the 4'CH_3 and 4'CH_3O-3-nitrodiphenylamines have been prepared with small yields.

3-nitrodiphenylamine

The Goldberg modification of the Ullman reaction gave only a 10% yield, so a method of Albert and Gledhill was adopted.[11] (See Chapter VIII, p.148 for details).

3-nitro-4'-methyldiphenylamine

The method of Albert and Gledhill was adopted. Charring occurred when the intermediate, 4'-methyl-5-nitrodiphenylamine-2-carboxylic

acid, was heated to just above its melting point. The final diphenylamine was obtained in only 10% yield, and quite a large quantity of unchanged acid was recovered after 30 minutes heating at 240°. No reference to 3-nitro-4'-methyldiphenylamine could be found in the literature, m.p. 240°C. (Found: C,67·81; H,5·26; $C_{13}H_{12}N_2O_2$ requires C,68·4; H,5·26).

3-nitro-4'methoxydiphenylamine

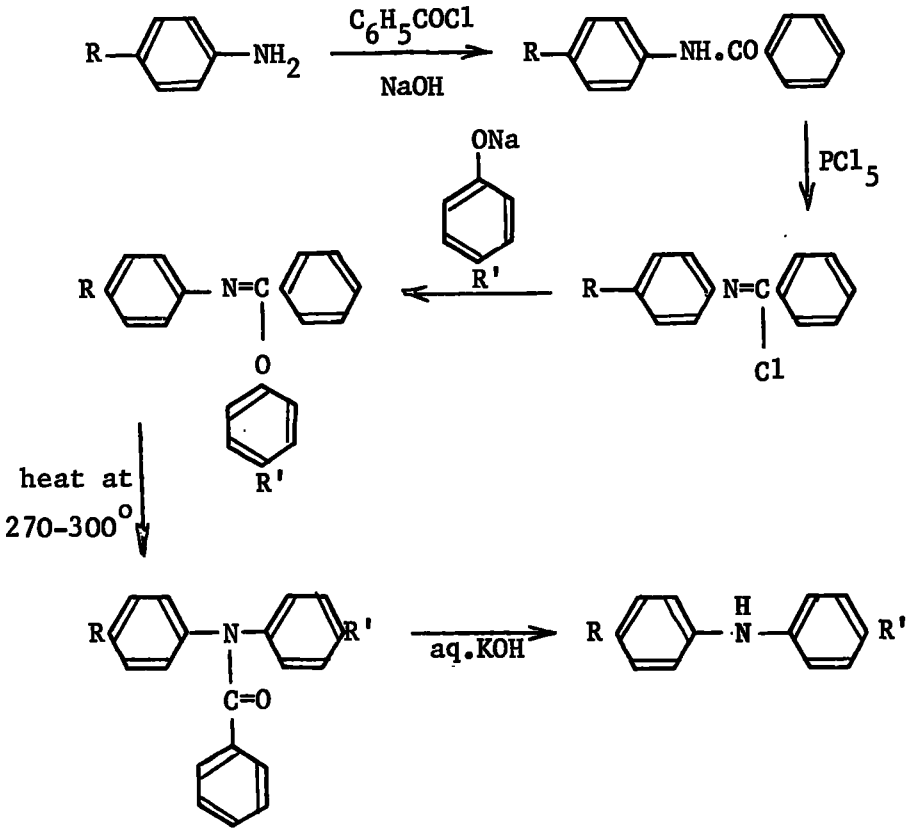
This compound was prepared in small yields by the Ullmann reaction.

CHAPTER II

CHAPMAN REACTION

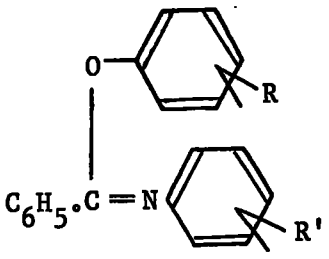
2.1 The Chapman reaction has been reviewed recently.[12]

Chapman[13] discovered a suitable method of preparing imidates consisting of the addition of an ethereal solution of an iminochloride to a solution of a sodium phenate in absolute alcohol. Following a report by Munm, Hesse and Volquartz,[14] Chapman found that benzoyldiphenylamine was formed in theoretical yield by heating N-phenylbenziminophenyl ether at 270-300° for two hours.



The rearrangement is facilitated by electron withdrawing groups in the migrating nucleus and electron donating groups in the stationary one. Chapman found that compounds with ortho-substituents in the migrating nucleus rearranged at a faster rate than the corresponding p-substituted compounds.[15]

He found that in the case of the imidate:



where R is o-NO_2 and R' is H, 2-Br or 4-CH_3, conversion to the desired benzoyldiarylamines occurred by heating for 1 hour at less than 200°. Under similar conditions, when R is p-NO_2 and R' is H, the imidate decomposed to form tarry materials.[1] Wheatley[16] however succeeded in preparing 4-nitrodiphenylamine by the Chapman rearrangement.

The Chapman reaction presents a suitable method of preparing various substituted diphenylamines. However although this method results in a clean reaction and gives good yields it has the disadvantage of involving the preparation of a separate imidoyl-chloride for each diphenylamine.

2.2 Preparation of 4-nitrodiphenylamines

Contrary to the findings of Chapman,[15] who reported tar formation at 150°, the imidate of 4-nitrodiphenylamine was rearranged by heating at 160° for 30 mins. (See Chapter VIII, p.148 for details of preparation of 4-nitrodiphenylamine). Tar formation was not observed even at 220°.

The reaction does not appear to be general for the preparation of 4-nitrodiphenylamines. From the appropriate imidates of 2', 3' and 4'-methyl and 2', 3' and 4'Cl compounds only that of the 3'-chloro was rearranged successfully and the diphenylamine obtained (see Chapter VIII, p.149 for details of preparation of 3'-chloro-4-nitrodiphenylamine).

Substituent	Colour	Recryst. solvent	M.p.
H	Yellow needles	ethanol	114°
3'Cl	Yellow needles	ethanol	143°

2.3 Preparation of 2-nitrodiphenylamines

The Chapman reaction was fairly successful for preparing 2-nitrodiphenylamines. In spite of the reaction being a many stage process the final yield is about 10% based on the amine. The Chapman reaction was used successfully for the preparation of the following substituted 2-nitrodiphenylamines.

Substituents	Colour	Recryst. Solvent	M.p.
2'CH_3	Red needles	ethanol	76°
3'CH_3	Orange needles	"	96°
2'Cl	Orange needles	"	152°
3'Cl	Orange needles	"	91°
3'Br	Orange prisms	"	127°

Chapman[11] showed that ortho-substituents in the migrating nucleus of the imidates rearranged at a faster rate than the corresponding para-substituents. This was supported by the work of Wiseberg and Rowland.[17]

Although the Chapman rearrangement gave reasonable yields of 2-nitrodiphenylamines and was a clean reaction, the method was not as convenient as the Smiles rearrangement.

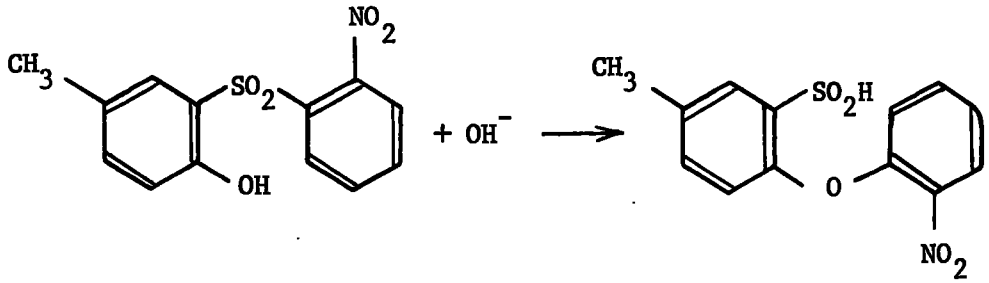
CHAPTER III

3.1 The Smiles Rearrangement

A group of intramolecular nucleophilic aromatic substitution reactions investigated by Smiles[19] may be represented by the general expression:

A variety of such arrangements have been observed in which -ZH may be -OH, -SH, -NHR, -CONHR, $-SO_2NHR$, or $-SO_2H$, while X may be O, S, SO or SO_2; although not all combinations of -ZH and X are allowed.[20] The reaction is usually conducted in basic media and it is generally agreed that the mechanism involves ionisation of -ZH to $-Z^-$ followed by nucleophilic attack of $-Z^-$ on C_1 (ring B) displacing $-X^-$.[21]

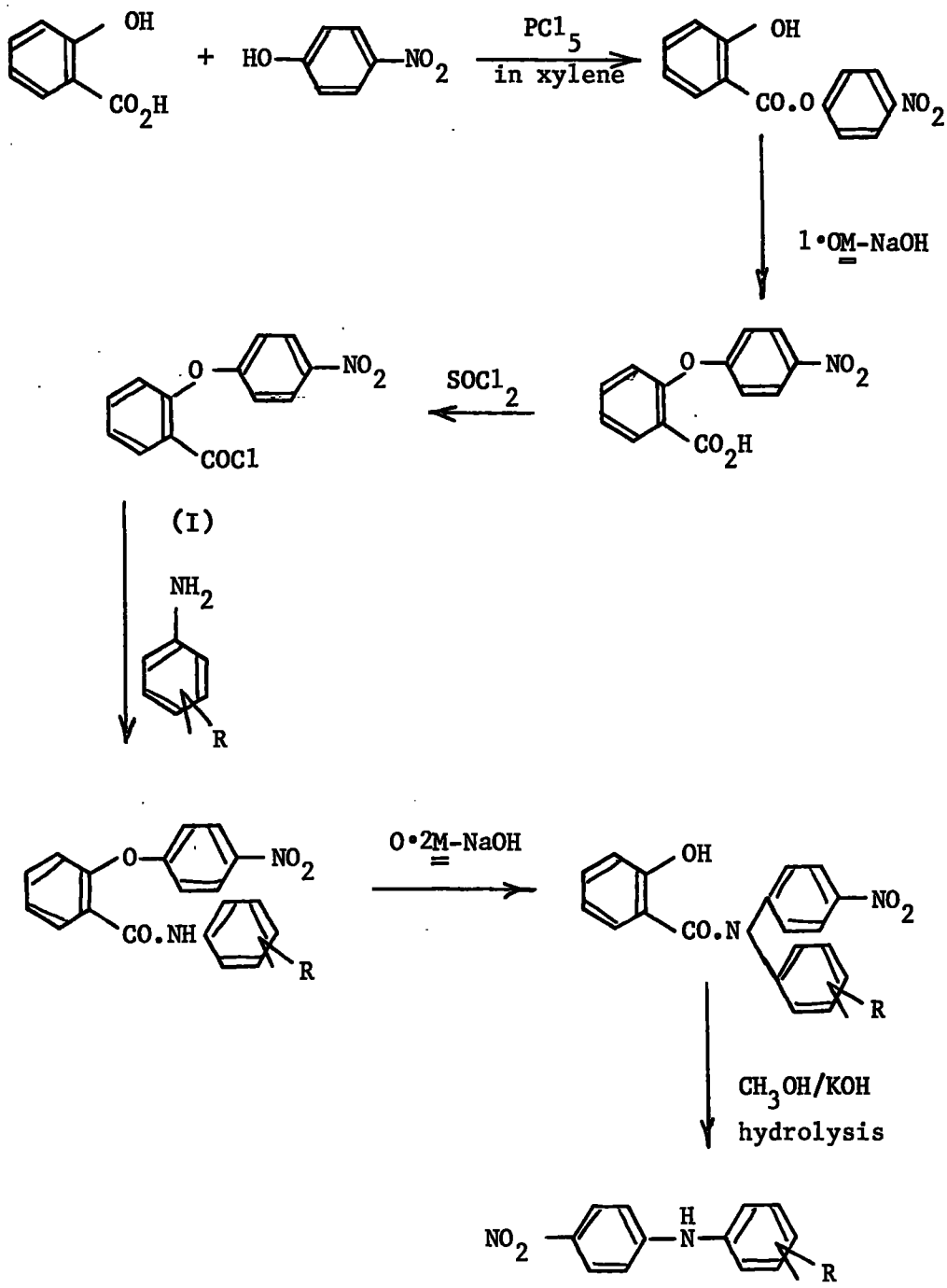
A typical example of this transformation is:



McClement and Smiles[22] and more recently, Bunnett[23] have studied the effects that substituents exert on the rate of rearrangement of a series of sulphones. The use of the rearrangement as a method for the preparation of substituted diphenylamines has largely been neglected.

3.2 Preparation of 4-nitrodiphenylamines

The following method was found to be the most convenient for the preparation of 4-nitrodiphenylamines.



The acid chloride (I) may be prepared in bulk and the remaining stages are rapid, and give good yields.

A literature search failed to reveal an application of the Smiles rearrangement to prepare substituted diphenylamines.[1,13]

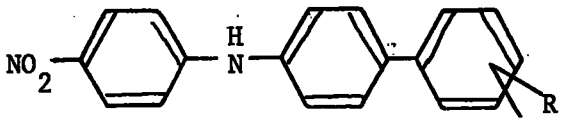
The following 4-nitrodiphenylamines have been prepared by the Smiles rearrangement (see Chapter VIII, p.149 for preparation of 4-nitrodiphenylamines).

Substituent	Colour	Recryst. solvent	M.pt.
H	Yellow needles	Ethanol	114°
3'-CH_3O	Yellow needles	"	112°
4'-CH_3O	Orange needles	"	150°
3'-CH_3	Orange needles	"	131°
4'-CH_3	Orange needles	"	138°
3'-F	Yellow plates	"	127°
4'-Cl	Yellow plates	"	146°
3'-NO_2	Orange plates	"	220°
2'-Cl	Yellow needles	"	104°

Difficulty was met when attempting to prepare a pure sample of 4-nitro-4'-formyldiphenylamine by the Smiles rearrangement (see Chapter VIII, p.151 for details). Attempts to purify the 4-nitro-4'-formyldiphenylamine by recrystallisation, regeneration from the

oxime and by thin layer chromatography failed.

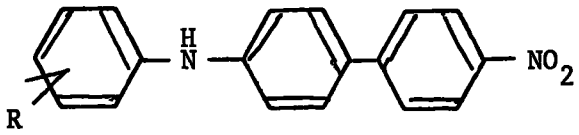
Diphenylamines of the types:



(where R = 4' NO_2 and H)

I

and

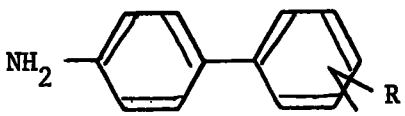


(where R = H)

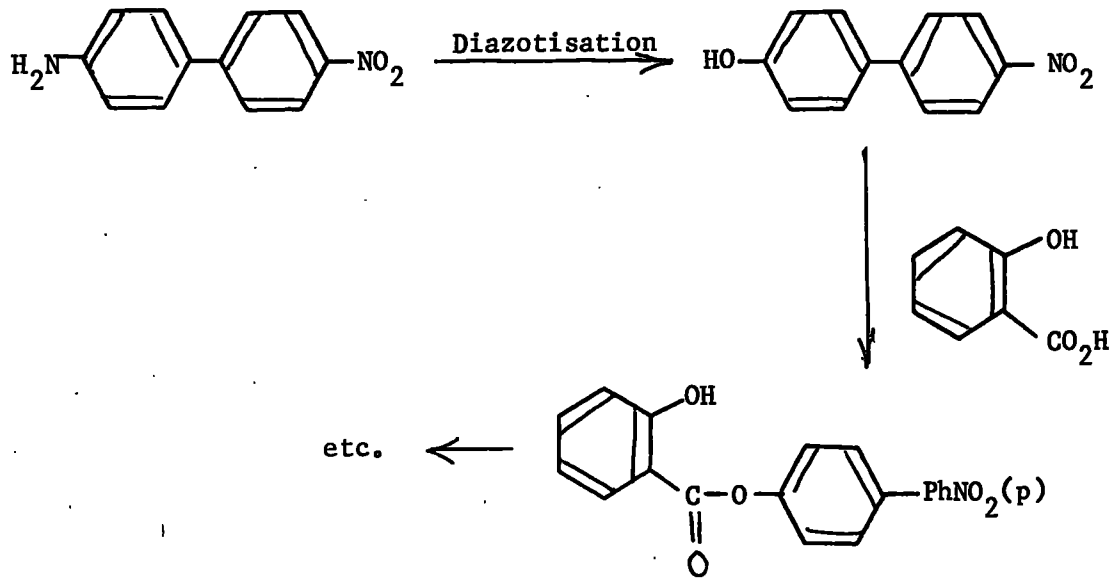
II

have been prepared.

Compound I was prepared by the Smiles rearrangement using an amine of the formula:



The preparation of compoundII is a further extension of the Smiles rearrangement involving the migration of a para-nitrodiphenyl group and involves the following synthesis:



(see Chapter VIII, p. for experimental details).

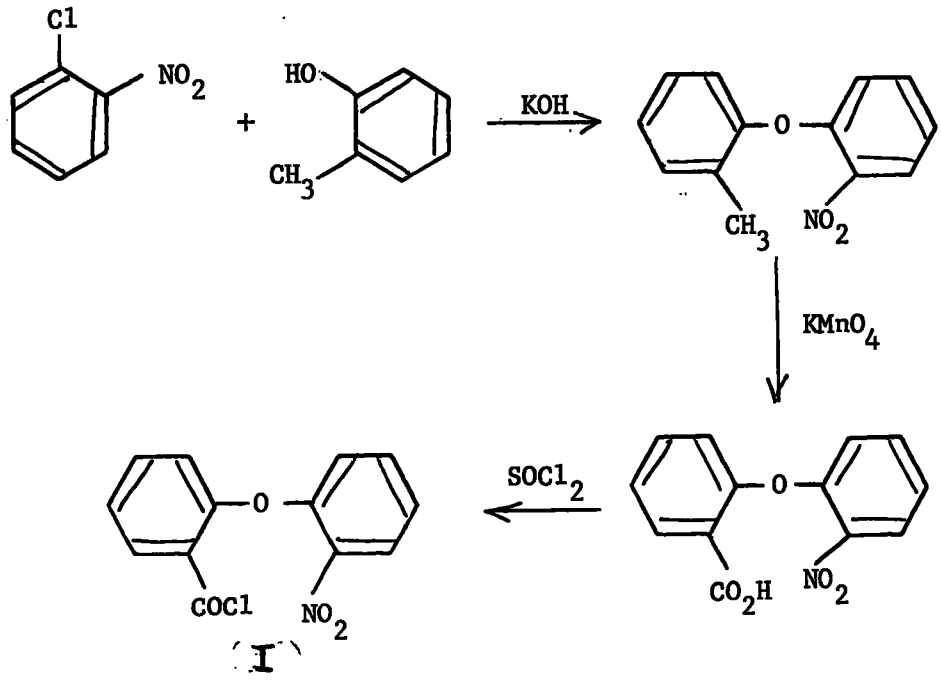
The diazotisation stage gave very low yields of the 4-nitro-4'-hydroxydiphenyl.[24] The hydroxy-derivative was prepared with more success by the nitration of the benzoate of 4-hydroxydiphenyl.[25,26] (See Chapter VIII, p.153 for experimental details).

3.3 Preparation of 2-nitrodiphenylamines

The application of the Smiles rearrangement to the preparation of 2-nitrodiphenylamines presented some difficulties.

The first stage, the attempted preparation of orthonitrophenyl salicylate, gave rise to a resin from which no product could be isolated. A literature search failed to find a reference to the compound.

A method of circumventing this difficulty was found.[27] The potassium salt of o-cresol was treated with o-chloro-nitrobenzene to form 2-methyl-2'-nitrodiphenyl ether. Oxidation of this compound with potassium permanganate formed the corresponding acid, which on treatment with thionyl chloride formed the acid chloride I.



I

(See Chapter VIII, p.155 for experimental details).

The acid chloride was readily converted into the following 2-nitrodiphenylamines by the Smiles rearrangement:

Substituent	Colour	Recryst. solvent	I.R. spectrum	M.pt.
3'Cl	Orange needles	alcohol	Peak at 3400	91°
3'F	Orange needles	acetone	"	73-74°
3'CH_3	Orange needles	alcohol	"	90-91°
3'CH_3O	Yellow needles	pet-ether	"	119-121°
3'CF_3	Orange plates	alcohol	"	69-70°
3'NO_2	Orange needles	acetone	"	158°
4'F	Orange needles	alcohol	"	83-84°
4'phenylazo	Orange needles	alcohol	"	128-129°
4'$COCH_3$	Brown needles	alcohol	"	137-139°

Attempts to prepare pure samples of the 3'CO_2H, 4'(4nitrophenyl), and 4' nitro derivatives failed. In all cases difficulty was met in the recrystallisation procedure.

A literature search failed to find reference to the following diphenylamines.

2 nitro-3'-methyldiphenylamine, orange needles, m.p. 90-91° (Kofler) Found: C,67·3; H,5·4; N,12·28. $C_{13}H_{12}N_2O_2$ requires C,68·4; H,5·3; N,12·10.

2 nitro-3'-methoxydiphenylamine, yellow needles, m.p. 119-120° (Kofler). Found: C,59·4; H,4·8; N,11·14. $C_{13}H_{12}N_2O_3$ requires C,60·0; H,5·0; N,11·47.

2 nitro-3'-benzotrifluorodiphenylamine, orange plates, m.p. 69° (Kofler). Found: C,54•6; H,3•4; N,9•89. $C_{13}H_9N_2O_2F_3$ requires C,55•3; H,3•2; N,9•93.

2 nitro-4'-phenylazodiphenylamine, orange needles, m.p. 128°-129° (Kofler). Found: C,67•2; H,4•5; N,17•8. $C_{18}H_{14}N_4O_2$ requires C,67•9; H,4•4; N,17•60.

2 nitro-4'-acetodiphenylamine, reddish-brown needles, m.p. 137-139° (Kofler). Found: C,65•0; H,4•55; N,10•72. $C_{14}H_{12}N_2O_3$ requires C,65•7; H,4•7; N,10,94.

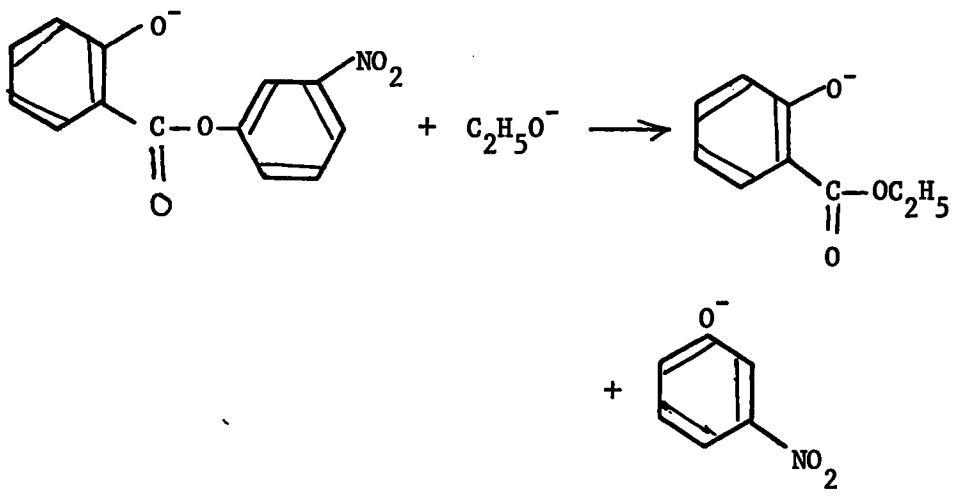
3.4 Attempted preparation of 3-nitrodiphenylamine by the Smiles rearrangement

The preparation of 3-nitrophenylsalicylate was successful, m.p. 97-98°. The attempted rearrangement of the salicylate with aqueous sodium hydroxide to the 3-nitro-2'-carboxydiphenyl ether was a failure resulting in the formation of salicylic acid.

The use of sodium ethoxide in ethanol led to the formation of ethyl salicylate and no rearrangement was observed.

An attempt was made to isolate the solid sodium derivative of meta-nitrophenyl salicylate by removal of the alcohol solvent under vacuum with the application of a minimum amount of heat. An orange solid residue remained of the sodium derivative smelling strongly of ethyl salicylate.

The presence of ethyl salicylate indicates that the excess ethoxide ions present readily attack the nitrophenyl ester, displacing meta-nitrophenol.



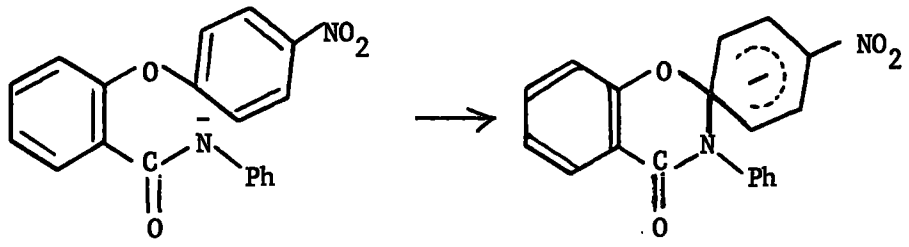
It was concluded that the meta-nitrophenyl group does not migrate and that hydrolysis occurs instead.

Attempts were made to isolate the potassium and calcium derivatives of the meta-nitrophenyl salicylates from alcoholic solutions but decomposition of the ester was observed again in both cases.

3.5 Preparation of azodiphenylamines by the Smiles rearrangement

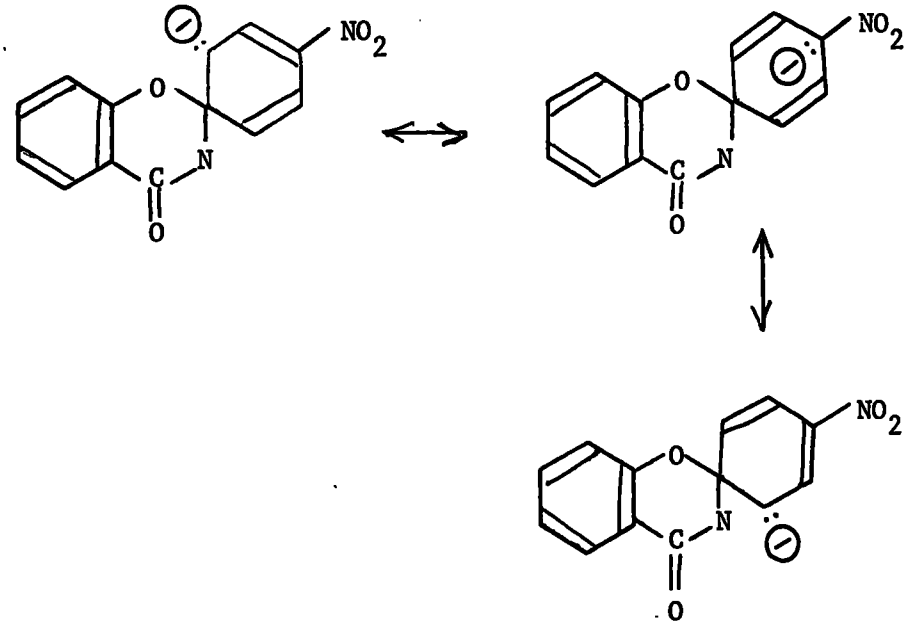
In all of the successful cases of the Smiles rearrangement using orthocarboxyamides we have had a $-NO_2$ group conjugated with the ruptured C-O bond. It would appear that for the success of the Smiles

rearrangement dispersal of the charge in the intermediate carbanion is necessary and this is most effectively accomplished by a nitro group conjugated with the reaction site.

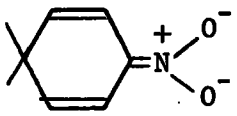


(I)

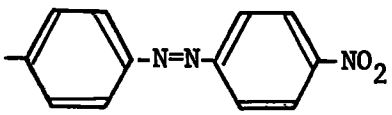
The following canonical forms can be written for I

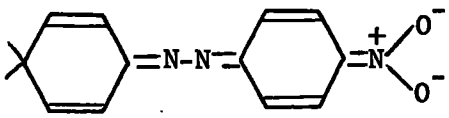


The NO_2 group is able to disperse the charge further.

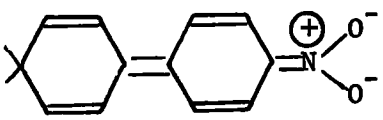


In the case of the 4-nitrophenylazodiphenylamine:





and for 4-nitrophenyldiphenylamino:



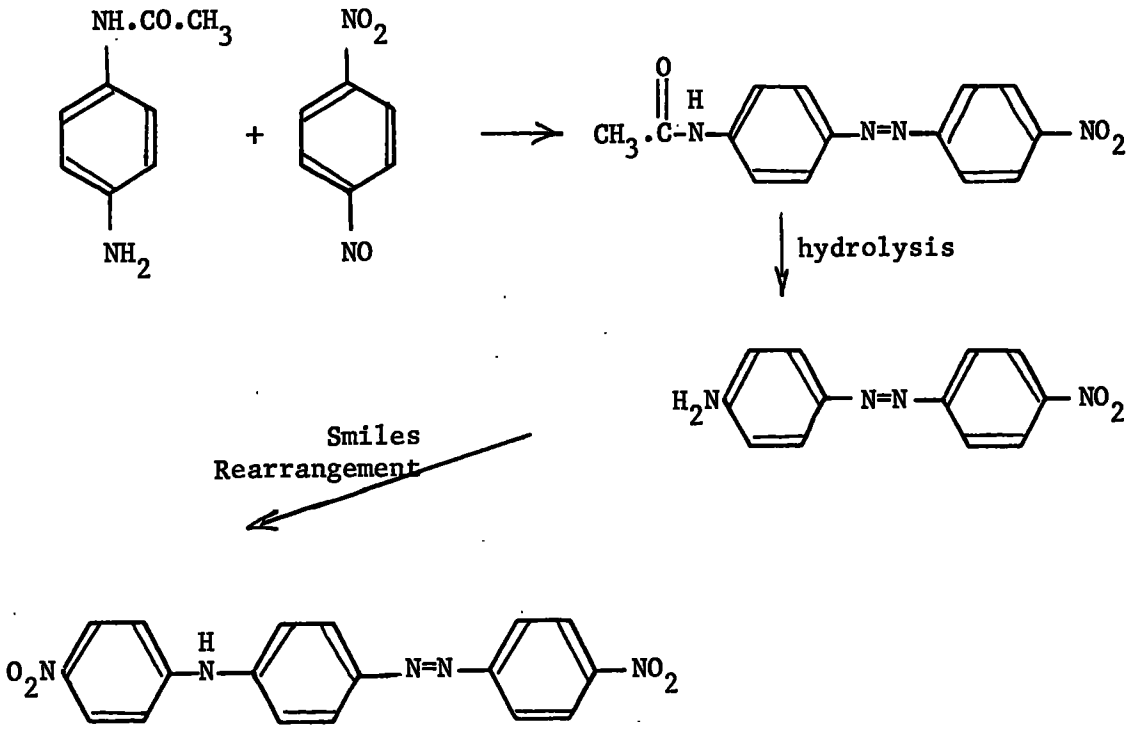
Meta-substituents do not give the same dispersal of charge.

3.5.1 Preparation of 4-nitro-4'-phenylazodiphenylamine

The Smiles rearrangement was used to prepare this compound.

3.5.2 Preparation of 4-nitro-4'(4-nitrophenylazo)diphenylamine

The preparation of 4-nitro-4'-(4-nitrophenylazo)diphenylamine was accomplished as follows:



The product was a brown powder which was not very soluble in most organic solvents and was difficult to crystallise. Hot saturated pyridine solutions deposited a brown powder. This had an indefinite melting point and thin layer chromatography indicated the presence of at least two compounds. This substance was not used in acidity measurements.

3.6 Preparation of 4-anilino-4'-nitroazobenzene (see Chapter VIII, p.156)

This was prepared by coupling diazotised p-nitroaniline with diphenylamine in aqueous alcoholic solution in the presence of sodium acetate. Recrystallised from alcohol, m.p.115°.

3.7 Preparation of 4-anilino-2'-nitroazobenzene

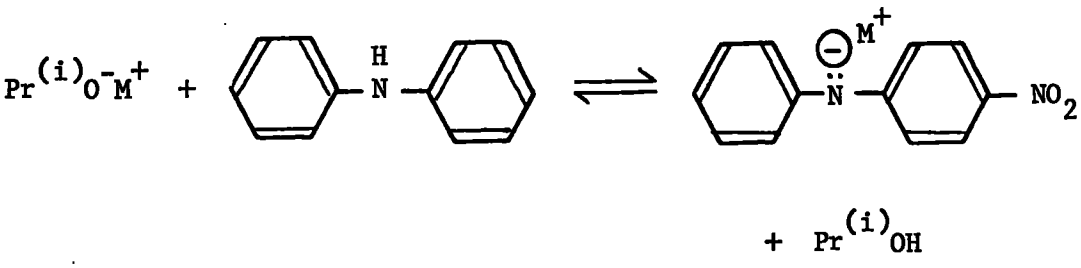
This was prepared by coupling diazotised o-nitroaniline with diphenylamine. Recrystallised from alcohol, m.p.134°.

CHAPTER IV

RELATIVE ACIDITIES OF SUBSTITUTED DIPHENYLAMINES

4.1 The Relative Acidity of 4-nitrodiphenylamine

The reaction between 4-nitrodiphenylamine and sodium or potassium isopropoxides in isopropyl alcohol has been shown to involve the following equilibrium:[28]



The ultra-violet visible spectrum of the anion is sufficiently different from that of 4-nitrodiphenylamine to enable the equilibrium to be examined spectrophotometrically.

There is disagreement between various workers[29] on the value of the equilibrium constant, K, and also on the value of the molar extinction coefficient (ε) of the anion:

	K(mole^{-1}l)	ε_{ion}
Hine and Hine[31]	236	12,100
Schaal et al.[32]	74	24,500
Wheatley[33]	272	11,050

Because of these discrepancies, the equilibrium was re-examined.

4.2 Stearns-Wheland Equation

Most of the compounds investigated are so weakly acidic that it is impossible to force the equilibrium of the reaction:

$$HA + B^- \rightleftharpoons A^- + HB$$

completely to the right. The extinction coefficient of the ion therefore cannot be determined directly in isopropyl alcohol. Stearns and Wheland[30] determined the extinction coefficient of the anion by an extrapolation procedure. Assuming that the equilibrium constant,

$$K = \frac{[\text{Anion}]}{[\text{4-nitrodiphenylamine}][Pr^{(i)}O^-]} \quad ;$$

equation (1) was derived, relating the apparent extinction coefficient, ε' of the anion, the true extinction coefficient, ε, the concentration of base, and the equilibrium constant.

$$\frac{1}{\varepsilon'} = \frac{1}{\varepsilon} + \frac{1}{[Pr^{(i)}O^-]} \cdot \frac{1}{\varepsilon K} \qquad (1)$$

If absorbance values are measured at a particular wavelength, in solutions of varying base strength and the resulting values of $\frac{1}{\varepsilon'}$ are plotted against $\frac{1}{[B^-]}$, a straight line is obtained, the intercept of which is equal to the reciprocal of the true extinction coefficient, ε, at the given wavelength. From the slope of the line, knowing ε

we can calculate K. The stronger the acid the smaller will be the slope of the line obtained by plotting $\frac{1}{\varepsilon'}$ against $\frac{1}{[B^-]}$.

The Stearns-Wheland equation is only valid when measurements are made at the wavelength of absorption of the ion and when the molecule does not absorb at this wavelength.

Hine and Hine[31] modified the Stearns and Wheland method to allow for overlap, but this gave only a small change in the extinction coefficient of the anion.

Schaal et al[32] worked at higher propoxide concentrations than Hine and Hine. Both the extrapolated value of the extinction coefficient and the value of K obtained differed greatly from the values obtained by Hine and Hine.

Wheatley[33] examined the Stearns and Wheland method, and came to the conclusion that the method was unsatisfactory since a considerable extrapolation into concentrated solution was necessary and the results obtained indicated that the graph was not a straight line, and the position of the intercept was in doubt.

4.3 Determination of Molar Extinction Coefficient of 4-nitrodiphenylamine anions

In view of the discrepancies previously observed an attempt was made to determine the extinction coefficient of the anion of 4-nitrodiphenylamine and substituted 4-nitrodiphenylamines. 4-nitrodiphenylamine and the more acidic 3'-chloro-4-nitrodiphenylamine were

Graph 1

$[^{(t)}BuO^-]_3$ x 10^3	3.14	31.4	62.8	94.2	125.6
Abs.	0.83	0.889	0.894	0.896	0.896

3'-Cl-4- NO_2 D.P.A.

$[^{(t)}BuO^-]_3$ x 10^3	22.2	44.4	66.6	88.8	111.0
Abs.	0.575	0.585	0.585	0.585	0.585

4-NO_2 D.P.A.

Absorbance.

1.0
0.8
0.6
0.4
0.2
0

20 40 60 80 100 120

$[PrO^-]$ x 10^{-3} (moles/litre)

treated with varying concentrations of the stronger base, potassium t-butoxide in t-butyl alcohol. A plot of the absorbance of the anion against concentration of the base indicated that the conversion to the anion was virtually complete at moderate base concentrations, λ_{max} being identical with that in isopropyl alcohol (see Graph 1). By this means an extinction coefficient of 28,480 was obtained for 4-nitrodiphenylamine. The more acidic 4-nitro-3'-chlorodiphenylamine gave a molecular extinction coefficient of 30,700.

A comparison of the molar extinction coefficients of phenols and their anions indicates that these values are more reasonable than those found by previous workers.

Substance	ε max for molecule	ε max for anion
phenol	1,660	2,300
p-nitrophenol	10,600	19,000
p-hydroxocetophenone	16,800	30;000
p-hydroxbenzaldehyde	14,000	25,000
4-nitrodiphenylamine	19,725	28,480
3'-chloro-4-nitrodiphenyl-amine	22,900	30,700

The validity of using t-butyl alcohol as solvent for the determination of the extinction coefficient of the ionic form for

nitrodiphenylamines was tested by determining the value of the extinction coefficient of the ionic form for 4,3'-dinitrophenylamine using isopropoxide and tertiary butoxide as the base. The values of ε_{max} and λ_{max} obtained for the two systems showed close agreement, i.e. ε_{max} using isopropoxide was 34,830 at 505 mμ and using tertiary butoxide was 34,910 at 507 mμ.

4.4 Verification of existence of simple acid-base reversible reactions

To verify that the reaction between the nitrodiphenylamines and the base is a simple acid-base reversible reaction and does not involve the formation of Meisenheimer compounds, 4,3'-dinitrodiphenylamine was dissolved in potassium t-butoxide and reprecipitated by addition of acid. The dinitrodiphenylamine was obtained unchanged.

The existence of an isosbestic point gives further evidence in favour of a simple acid-base equilibrium (see Graph 2 and Table I for results). On considering the typical spectral curves for 3'-methoxy-4-nitrodiphenylamine it is obvious that a simple equilibrium exists.

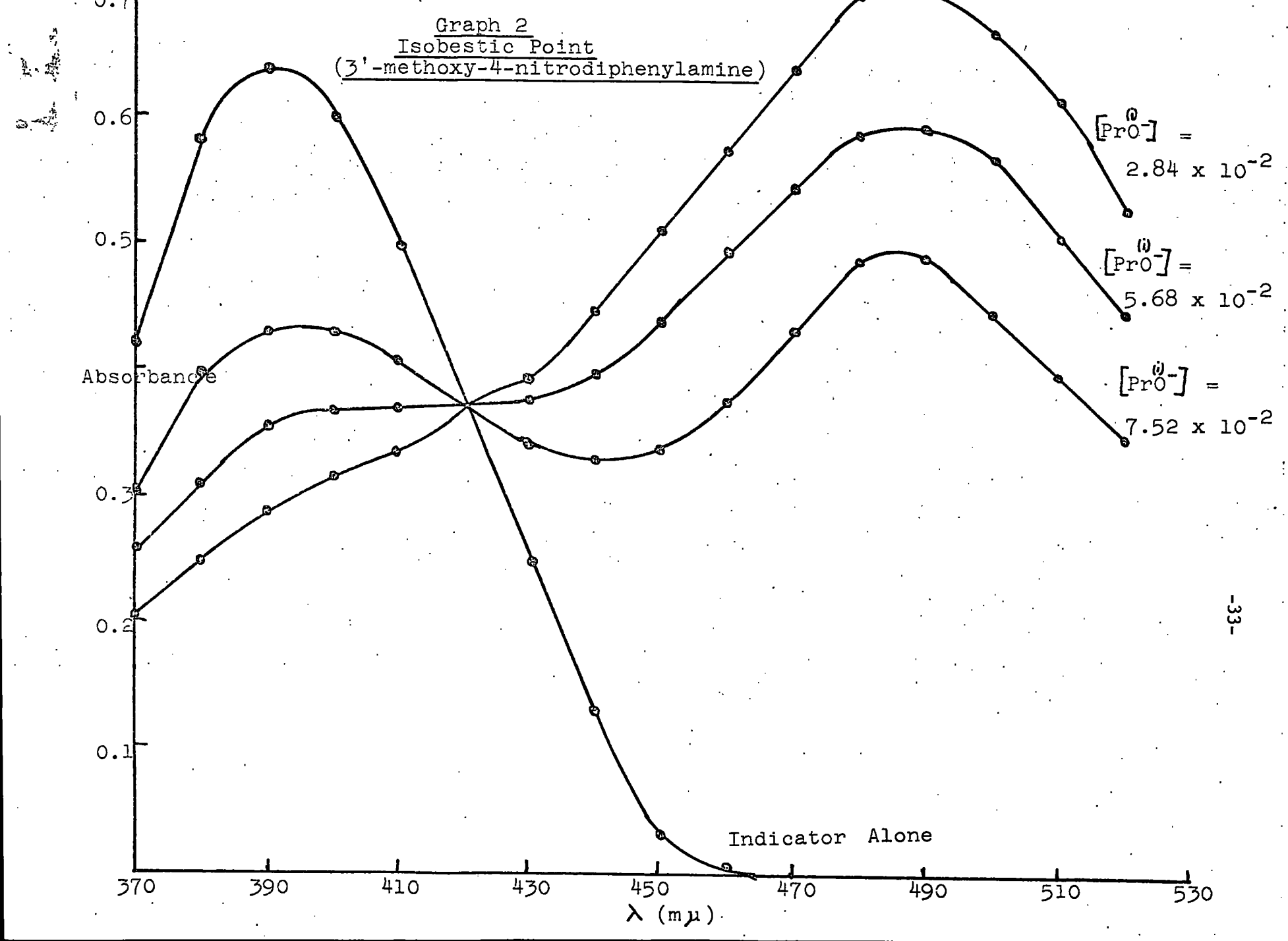

Graph 2
Isobestic Point
(3'-methoxy-4-nitrodiphenylamine)
[PrO⊖] = 2.84 x 10⁻²
[PrO⊖] = 5.68 x 10⁻²
[PrO⊖] = 7.52 x 10⁻²
Absorbance
Indicator Alone
0.6
0.5
0.3
0.2
0.1
370
390
410
430
450
470
490
510
530
λ (mμ)

TABLE I

Isosbestic Point

[HA] added = $2 \cdot 94 \times 10^{-5}$ moles/litre

$[PrO^-]$ added (moles/litre) / λ (mμ)	Absorbance			
	Indicator alone	$2 \cdot 84 \times 10^{-2}$	$5 \cdot 68 \times 10^{-2}$	$7 \cdot 52 \times 10^{-2}$
370	0•42	0•2	0•26	0•3
380	0•58	0•25	0•31	0•4
390	0•635	0•29	0•36	0•43
400	0•6	0•32	0•37	0•43
410	0•5	0•335	0•375	0•41
420	0•38	0•36	0•375	0•37
430	0•25	0•39	0•375	0•335
440	0•13	0•45	0•4	0•325
450	0•03	0•52	0•44	0•34
460	0•01	0•59	0•5	0•38
470	0•0	0•65	0•55	0•44
480	0•0	0•70	0•585	0•49
490	0•0	0•70	0•585	0•49
500	0•0	0•68	0•57	0•45
510	0•0	0•62	0•51	0•4
520	0•0	0•53	0•45	0•35

CHAPTER V

DETERMINATION OF EQULIBRIUM CONSTANT FOR THE REACTION BETWEEN 4-NITRODIPHENYLAMINES AND POTASSIUM ISOPROPOXIDE

5.1 Solvent Purification

Analar isopropyl and tertiary butyl alcohols were dried by refluxing over calcium turnings for six hours followed by fractionation in a stream of nitrogen, the receiver being protected by a guard tube containing soda-asbestos and anhydrone. The alcohols were stored under nitrogen in the glove box.

The solutions were prepared and manipulated in a glove box under an atmosphere of dry, carbon dioxide-free nitrogen and weighings were made on an analytical five-figure balance (Oertling, Model 141).

5.2 Spectrophotometric Measurements

Measurements were obtained, at a temperature of $30 \pm 0{\cdot}02^{\circ}$ on Unicam S.P.500 and S.P.700 spectrophotometers which were fitted with thermostatted cell holders.

5.3 Determination of Extinction Coefficients

5.3.1 Molecular Forms

The value of Σ_{max} and λ_{max} for the molecular form was obtained by measuring absorbances in isopropyl alcohol over a range of concentrations and wavelengths.

A rigorous check was made with every indicator studied to make sure that the molecular form spectra curve made no contribution to the maxima of the ionic form.

5.3.2 Ionic Forms

The extinction coefficient and wavelength at maximum absorption for the ionic form were determined in tertiary butyl alcohol containing potassium t-butoxide. The solution was checked for complete ionisation using various concentrations of potassium t-butoxide. (For results see Table II).

5.4 Verification of Beer's Law

The assumption that the absorbance values are a measure of anion concentration was confirmed by the addition of varying amounts of a solution of the nitrodiphenylamines to equal concentrations of isopropoxide. (See Graph 3 and Table III for results).

The absorbance was shown to be proportional to the concentration of the diphenylamines in every case examined. Absorbance measurements can therefore be used to determine the anion concentration in solution.

5.5 Determination of Acidity Constants of Substituted 4-nitro-diphenylamines

Varying amounts of a solution of potassium isopropoxide were added to known concentrations of the indicator solution in isopropyl

Table II

Extinction Coefficients of Substituted 4 NO_2 Diphenylamines

Substance	Molecular Form		Ionic Form	
	λmax	εmax	λmax	εmax
3'Me	395.0	20,720	485	27,837
3'H	395.0	19,725	485	28,540
3'MeO	392.5	21,900	485	32,300
3'F	395.0	21,900	500	31,800
3'Cl	395.0	22,900	505	32,300
3'NO_2	380.0	23,000	510	34,810
4'E+O	395.0	20,650	480	27,740
4'MeO	395.0	18,900	485	26,300
4'Me	395.0	21,800	475	28,870
4'F	390.0	20,300	485	28,160
4'Cl	385.0	20,800	490	31,130
2'F	380.0	18,600	485	33,600
2'Me	385.0	26,200	475	29,360
2'MeO	385.0	19,200	475	27,240
2'Cl	380	19,000	485	32,730
4'phenyl	390	23,700	490	30,890
4'-(4-nitrophenyl)-diphenylamine	345	18,320	435	24,170
4'-(4-nitrophenyl)	405	18,500	505	33,710
4'phenylazo	420	40,830	580	34,930
4'(4-nitrophenylazo)-diphenylamine	485.4	33,480	650	75,650

Table III

Verification of Beer's Law

Concentration of Indicator = 2.44×10^{-5} moles/litre

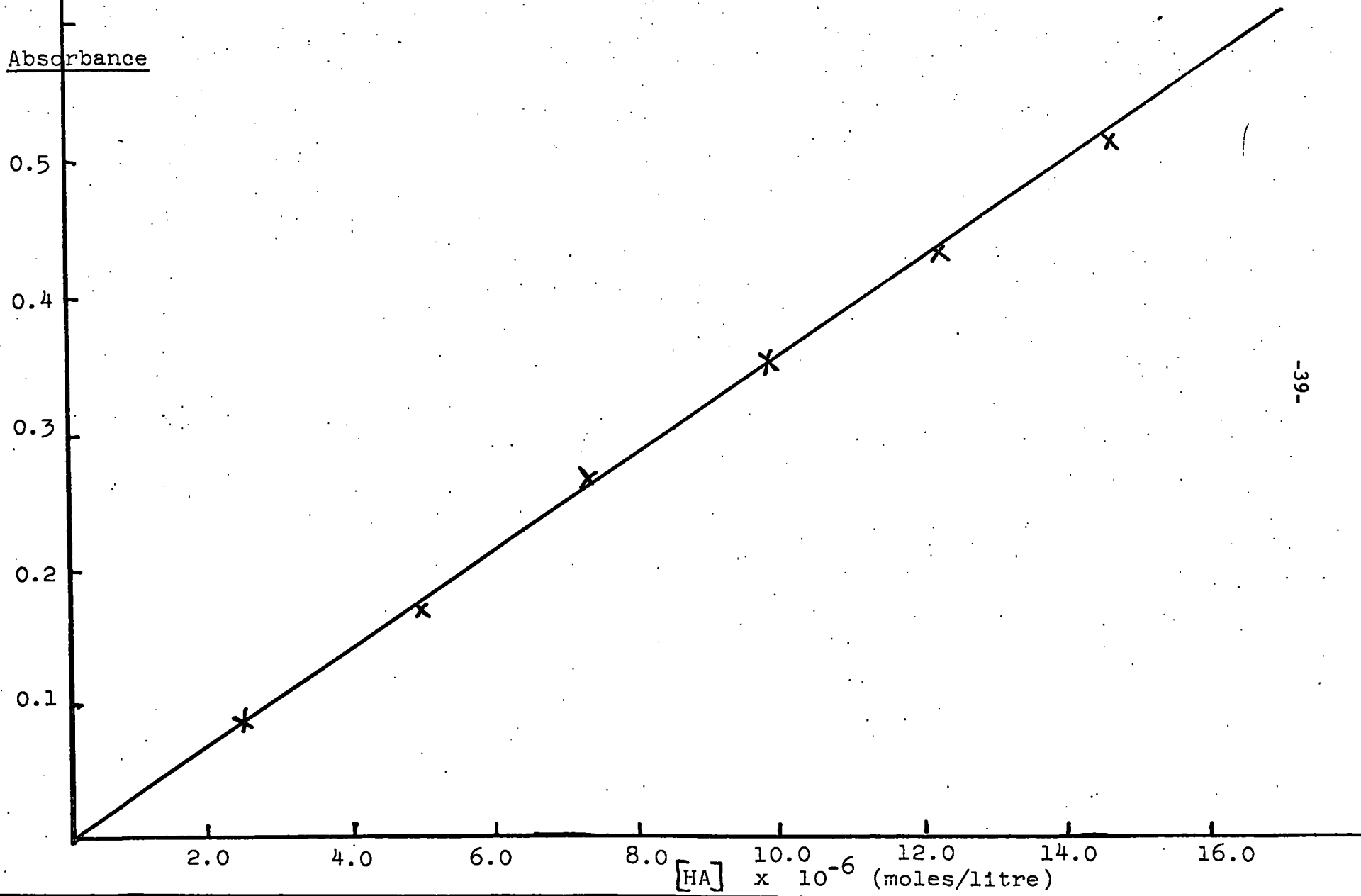
Concentration of propoxide solution = 4.98×10^{-2} moles/litre

Indicator Concentration (moles/litre)	Isopropoxide Concentration (moles/litre)	Absorbance
2.44×10^{-6}	4.98×10^{-2}	0.086
4.88×10^{-6}	4.98×10^{-2}	0.17
7.32×10^{-6}	4.98×10^{-2}	0.255
9.76×10^{-6}	4.98×10^{-2}	0.35
1.22×10^{-5}	4.98×10^{-2}	0.43
1.46×10^{-5}	4.98×10^{-2}	0.51
2.44×10^{-5}	4.98×10^{-2}	0.85

A plot of absorbance versus indicator concentration was a straight line.

Graph 3

Verification of Beers Law



alcohol. The concentration of the indicator solutions used were of the order of 5×10^{-4} moles/litre.

The absorbance of the ionic form present in solution was determined spectrophotometrically for each sample of varying concentration and a value for the respective acidity constants calculated as shown below:

$$HA + Pr^{(i)}O^- \rightleftharpoons A^- + Pr^{(i)}OH$$

$$K = \frac{[A^-]}{[HA][Pr^{(i)}O^-]}$$

where $$[A^-] = \frac{\text{Absorbance at } \lambda_{max} \text{ of ionic form}}{\Sigma_{max} \text{ of ionic form}}$$

$$[HA]_{\text{at equilibrium}} = [HA]_{\text{added}} - [A^-]$$

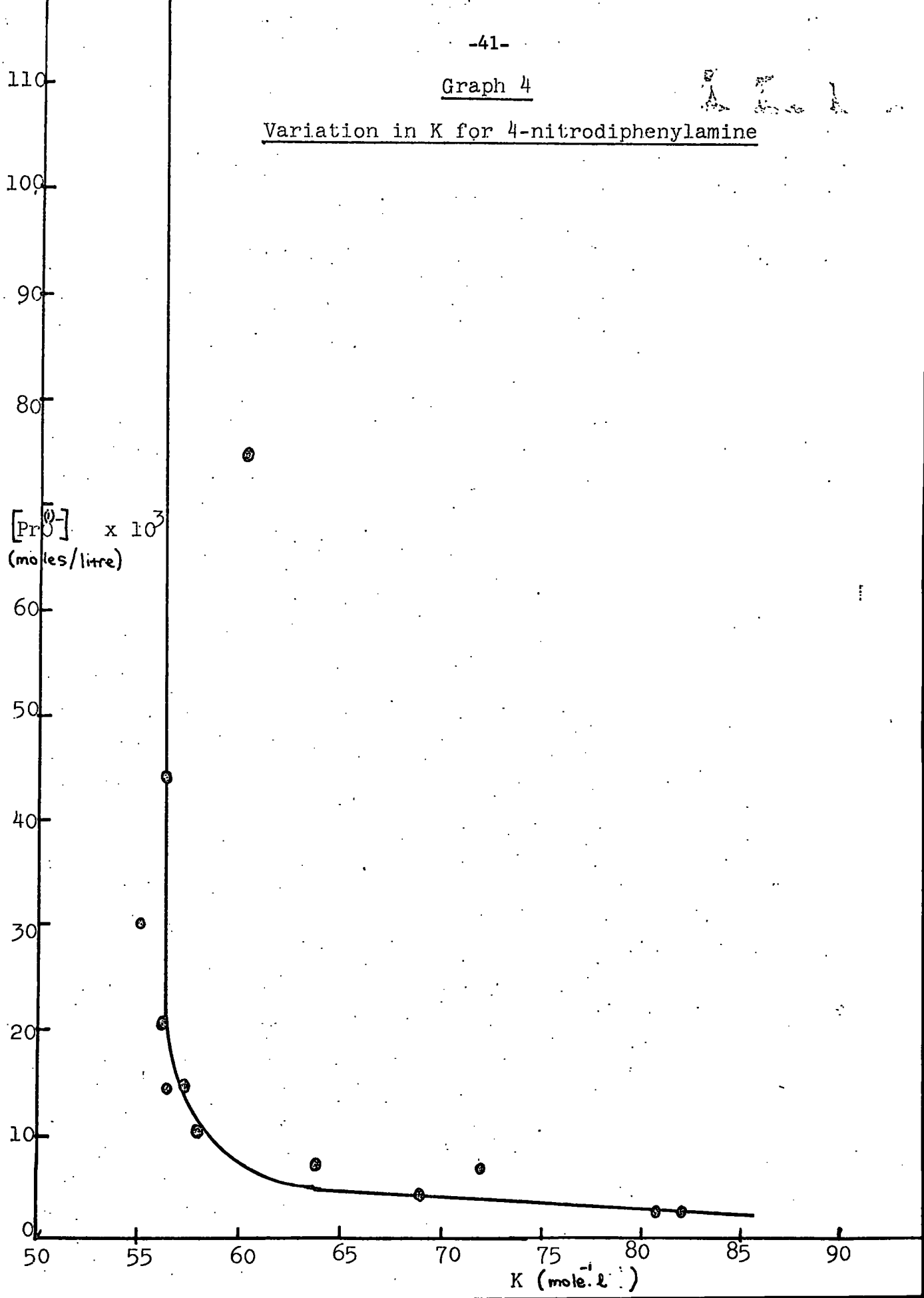
$$[Pr^{(i)}O^-]_{\text{at equilibrium}} = [Pr^{(i)}O^-]_{\text{added}} - [A^-]$$

5.6 Observed Variation of the Apparent Equilibrium Constant with Base Concentration

A graph of K vs. $[Pr^{(i)}O^-]$ was plotted for each indicator. The shape of the curve given below is typical for the variation of the

Graph 4

Variation in K for 4-nitrodiphenylamine



apparent equilibrium constants for all the diphenylamines studied with base concentration. (See Graph 4 and Tables IV-XXIII for results on page 41 and pages 59-78).

The variation in K with $[Pr^{(i)}O^-]$ has led to erroneous values for Σ_{max}. for the ionic form when determined by the Stearns and Wheland extrapolation method. The value of the equilibrium constant increases rapidly in dilute propoxide solution below a concentration of 10^{-2} moles/litre approximately. Above this concentration K is approximately constant or slowly decreases.

5.7 Suggested Explanation for variation of K

5.7.1 Ion-pair Formation

A possible explanation of the variation of K with base concentration is ion-pair formation in solution.

In very dilute solution there will be extensive dissociation to propoxide ion. In solutions with a concentration of more than 10^{-2} molar, it is likely that mainly ion-pairs will be present. One would expect the free propoxide ions to more effective bases than the ion-pairs.[34]

Experiments by Kraus and Fuoss[35] are regarded as establishing the soundness of Bjerrum's[36] concept of electrostatic ion-pairs.

The shape of the curves in which the apparent equilibrium constant increases rapidly at dilute concentrations is difficult to

explain by variation of ion activity. Ion-pair formation seems to be a more reasonable explanation of the phenomenon.

We thus have in solution the following three equilibria:

(i) $$K^+Pr^{(i)}O^- \rightleftharpoons K^+ + Pr^{(i)}O^-$$

for which in dilute solution $K_1 = \dfrac{[K^+][PrO^-]}{[K^+Pr^{(i)}O^-]}$

(ii) $$Pr^{(i)}O^- + HA \rightleftharpoons Pr^{(i)}OH + A^-$$

for which $$K_2 = \frac{[A^-]}{[Pr^{(i)}O^-][HA]}$$

(iii) $$K^+A^- \rightleftharpoons K^+ + A^-$$

for which $$K_3 = \frac{[K^+][A^-]}{[K^+A^-]}$$

The problem is to find values of K_1, K_2 and K_3 which:

(a) are in reasonable agreement with the results found in solvents of similar dielectric constant by electrical conductivity methods.[37]

(b) give reasonably constant values for K_1, K_2 and K_3 over a wide range of base concentration.

(c) give consistent results for a number of substituted diphenylamines, i.e. using the same value for K_1, the values of K_3 do not

differ to a large extent for the various nitrodiphenylamines.

(d) the value of K_2 obtained should be in agreement with the extrapolated value from the curves previously obtained (see Graph 4).

5.7.2 Computation Technique

The equations (i), (ii) and (iii) may be obtained in a form suitable for computer programming.

Let B = concentration of potassium isopropoxide at equilibrium

C = $[A^-] + [M^+A^-]$

D = $[HA]_{\text{at equilibrium}}$

E = K_1

F = K_3

Y = $[Pr^{(i)}O^-]$

X = $[M^+]$

Z = $[A^-]$

From electrical neutrality:

$$X = Y + Z$$

$$E = \frac{X.Y}{B-Y}; \qquad F = \frac{X.Z}{C-Z}$$

$$\frac{E}{X} = \frac{B}{Y} - 1; \qquad \frac{X}{F} = \frac{C}{Z} - 1$$

$$\frac{B}{Y} = \frac{X + E}{E}; \qquad \frac{C}{Z} = \frac{X + F}{F}$$

$$Y = \frac{B.E}{X + E} \; ; \qquad Z = \frac{C.F}{X + F}$$

$$Y + Z = X = \frac{B.E}{X + E} + \frac{C.E}{X + F}$$

$$X = \frac{B.E.F. + B.E.X. + C.E.F. + C.F.X}{(X + E)(X + F)}$$

$$X^3 + (E + F)X^2 + E.F.X = (B + C)E.F + (BE + CF)X$$

$$X^3 + (E + F)X^2 + (E.F.-B.E + C.F)X - (B-C)E.F = 0$$

$$Y = \frac{B.E}{X + E} \; ; \qquad Z = \frac{C.F}{X + F} \; ; \qquad K_2 = \frac{Z}{DY}$$

A computer programme was worked out to calculate values of K_2 for given values of B, C, D, E and F (See Appendix I). B, C and D are obtained directly from the experimental observations since:

B = concentration of potassium isopropoxide added - C

$$C = \frac{\text{absorbance due to ionic form at } \lambda_{max}}{\Sigma_{max} \text{ for ionic form}}$$

D = Initial concentration of nitrodiphenylamine - C

Values of K_1 and K_3 are not known. Values of these constants were then selected and values of K_2 computed.

5.7.3 Selection of values of K_1 and K_3 used for computing K_2

Values of the ion-pair dissociation constant of a number of substances in various non-aqueous solvents have been obtained by electrical conductivity methods.[37] Bjerrum[38] had deduced an equation relating the ion-pair dissociation constant to the dielectric constant of the medium, the distance of closest approach of the ions, the ionic charges and the absolute temperature. Reasonable agreement has been obtained between the calculated and the theoretical values of the dissociation constants.[39]

According to the Bjerrum equation:

$$K^{-1} = 4 \pi Na^2(d-a)\exp.(Z_+|Z_-|e^2)/\Sigma akT$$

where N = Avogadro number

a = closest distance of approach of ions in an ion pair

e = proton charge

Σ = dielectric constant (18·3 for isopropyl alcohol)

k = Boltzman constant

T = absolute temperature

K = ion-pair dissociation constant for a uni-valent salt

For a given electrolyte;

$$-\log K = pK \propto \frac{1}{\Sigma.T.}$$

The value of the dissociation constant of potassium picrate in acetone (dielectric constant of 20) at 25^{o} is $3 \cdot 47 \times 10^{-3}$ mole^{-1} 1.[37]

pK for potassium picrate in acetone (ε = 20•7) at 25^{o}

$$= -\log 3 \cdot 47 \times 10^{-3}$$

$$= \underline{2 \cdot 46}$$

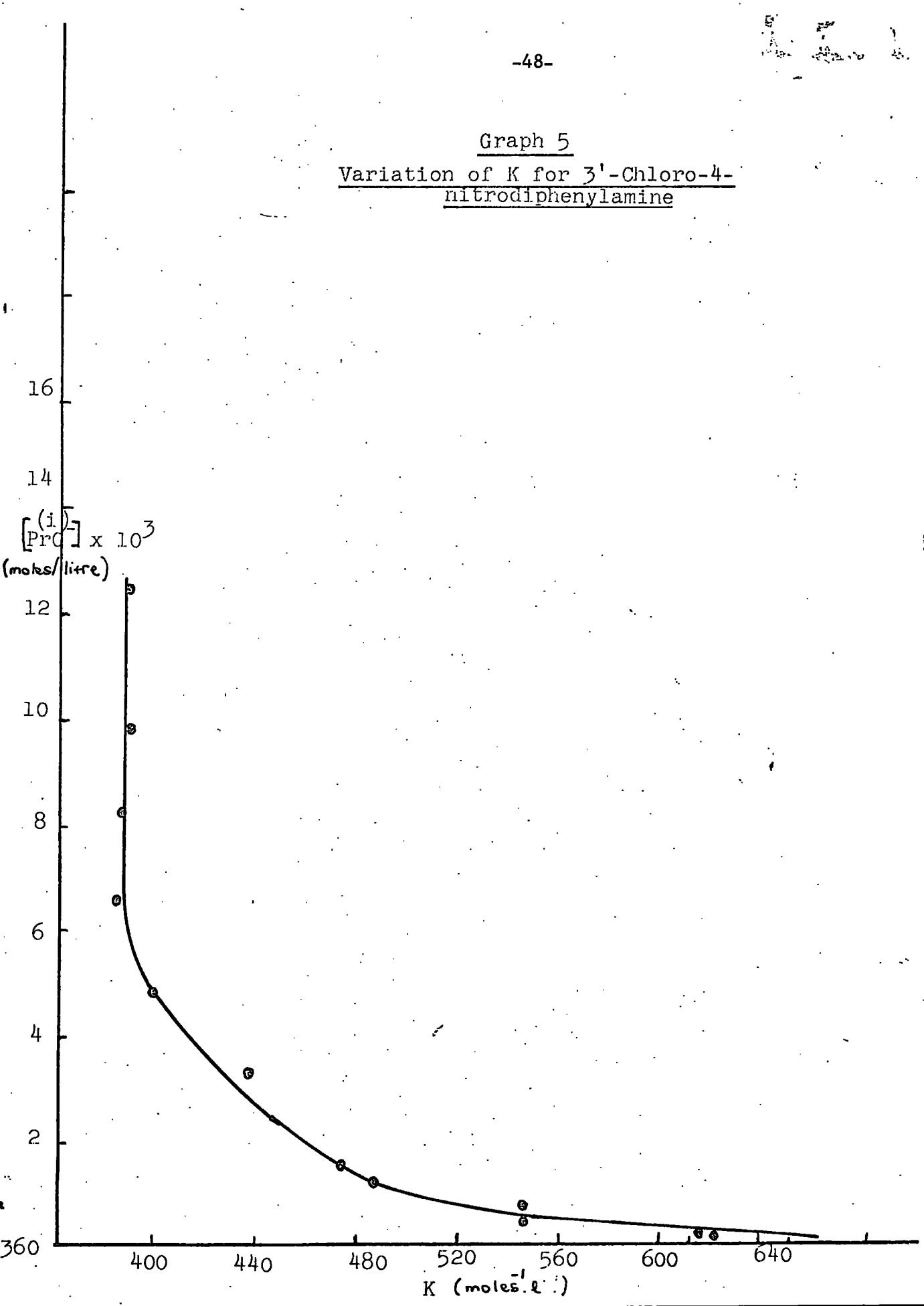
Therefore pK for potassium picrate in isopropyl alcohol (ε = 18•1) at 30^{o} is 2•69, i.e. K = 2×10^{-3} mole^{-1} 1. approximately.

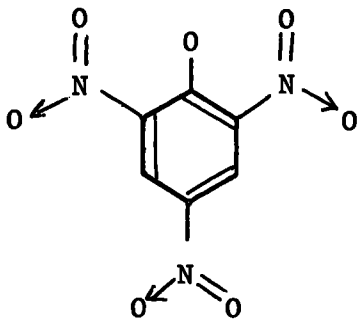
For the purpose of computing values of K_2 we may assume that K_3, the ion-pair dissociation constant of the potassium salt of a substituted diphenylamine is of this order. A range of values of K_3 was therefore selected about a mean value of 2×10^{-3} mole 1^{-1}.

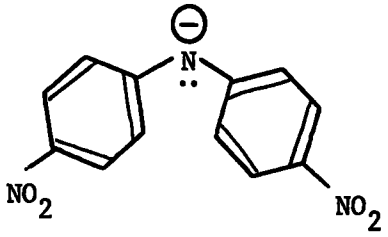
There is some justification for the assumption that the ion-pair dissociation constants are similar in the same solvents since the main factor in the case of potassium picrate is the distance of closest approach of the potassium ion and the negatively charged oxygen. In the case of the potassium salt of the nitrodiphenylamine we are concerned with the approach of the potassium ion to the negatively charged nitrogen.

Graph 5

Variation of K for 3'-Chloro-4-nitrodiphenylamine







It would be unreasonable to consider thr whole ion in estimating the distance of closest approach. The additional phenyl group in the diphenylamine anion will of course hinder the approach by the potassium ion, but so will the ortho nitro groups in the picrate ion.

Now suppose we consider 3'-chloro-4-nitrodiphenylamine (see Graph 5). Extrapolation of the graph gives a value for K_2 in the region of 700 $mole^{-1}l$.

Taking values of K_2 and K_3 of 700 $mole^{-1}l$ and 2×10^{-3} mole l^{-1} respectively a value of approximately $7{\cdot}7 \times 10^{-4}$ mole l^{-1} is obtained for K_1 at various base concentrations (see Appendix II for calculation).

It would appear that K_1 is less than K_3. Values of K_1 were selected to go with the values of K_3 such that K_3 was equal to and several times greater than K_1.

The experimental results of the reaction of 3'-chloro-4-nitro-diphenylamine were then computerised using values of K_1 from 2×10^{-4}

to 5×10^{-3} and K_3 from 2×10^{-4} to $1{\cdot}5 \times 10^{-2}$ mole l^{-1}.

Results for 3'-chloro-4-nitrodiphenylamine

Graphs were drawn of the computed values of K_2 against base concentration for various values of K_1 and K_3. The graphs were of the form shown (see Graph 6). It will be noted that for a value of $K_1 = 7 \times 10^{-4}$ mole l^{-1} and various values of K_3 the computed values of K_2, converge at low base concentrations. When K_3 equals $1{\cdot}8 \times 10^{-3}$ mole l^{-1}, the values of K_2 are approximately constant at all base concentrations:

$$K_1 = 7 \times 10^{-4} \text{ mole } l^{-1}, \quad K_3 = 1{\cdot}8 \times 10^{-3} \text{ mole } l^{-1}$$

$[Pr^{(i)}O^-] \times 10^4$ (mole/litre)	3·3	8·3	16·6	49·8	66·4	83·0	124·5
K_2 (Mean = 707·3)	710·5	709·4	720·0	683·3	680·0	702·2	746
% Variation from Mean	+0·45	+0·28	+1·8	-3·4	-3·72	+0·72	+5·5

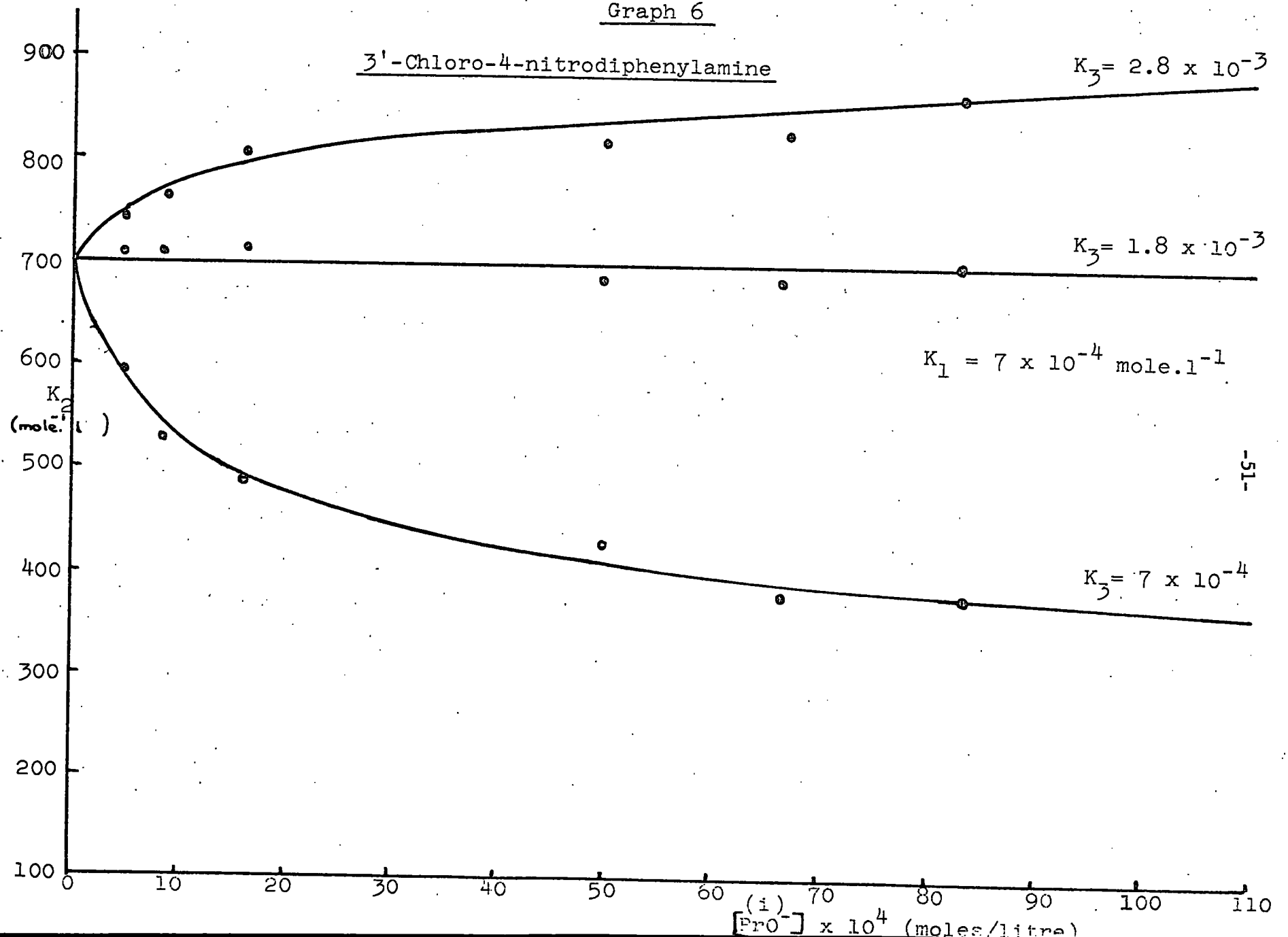
The effect of increasing K_3 may be seen from the following results:

$$K_1 = 7 \times 10^{-4} \text{ mole } l^{-1}; \quad K_3 = 2{\cdot}8 \times 10^{-3} \text{ mole } l^{-1}$$

$[Pr^{(i)}O^-] \times 10^4$ (mole/litre)	3·32	8·3	16·6	49·8	66·4	83·0	124·5
K_2	742·0	768·0	808·3	818·6	829·5	869·0	946·0

Graph 6

3'-Chloro-4-nitrodiphenylamine



The effect of reducing K_3 may be seen from the following results:

$$K_1 = 7 \times 10^{-4} \text{mole } 1^{-1}; \quad K_3 = 7 \times 10^{-4} \text{ mole } 1^{-1}$$

$[Pr^{(i)}O^-] \times 10^4$ (mole/litre)	3•32	8•3	16•6	49•8	66•4	83•0	124•5
K_2	597•6	531•2	488•1	432•3	379•2	380•9	386•2

When a lower value of K_1, the dissociation constant of potassium isopropoxide, is taken it is not possible to obtain values for K_2 as consistent as those obtained when K_1 was taken as 7×10^{-4} mole 1^{-1}.

$$K_1 = 2 \times 10^{-4} \text{ mole } 1^{-1}; \quad K_3 = 4 \times 10^{-4} \text{ mole } 1^{-1}$$

$[Pr^{(i)}O^-] \times 10^4$	3•32	8•3	16•6	49•8	66•4	83•0	124•5
K_2 (Mean = 711•7)	780•6	767•0	755•6	669•9	654•3	666•1	690•3
% Variation from Mean	+9•7	+7•8	+6•2	-5•9	-8•1	-6•45	-3•0

The upper limit of the value of the ion-pair dissociation constant K_1, is indicated by calculations of the ionic radius using Bjerrum's equation.

As K_1 increases the ratio of K_3/K_1 required to give approximately constant values of K_2 over a wide range of base concentrations also increases.

K_1	K_3	K_3/K_1
2×10^{-4}	4×10^{-4}	2•0
7×10^{-4}	$1•8 \times 10^{-3}$	2•6
1×10^{-3}	$3•2 \times 10^{-3}$	3•2
2×10^{-3}	9×10^{-3}	4•5

Applying the simplified version of Bjerrum's equation:

$$K_3^{-1} = \frac{4}{3} \pi a^3 N \exp. \frac{e^2}{a \Sigma k T}$$

when $K_3 = 9 \times 10^{-3}$

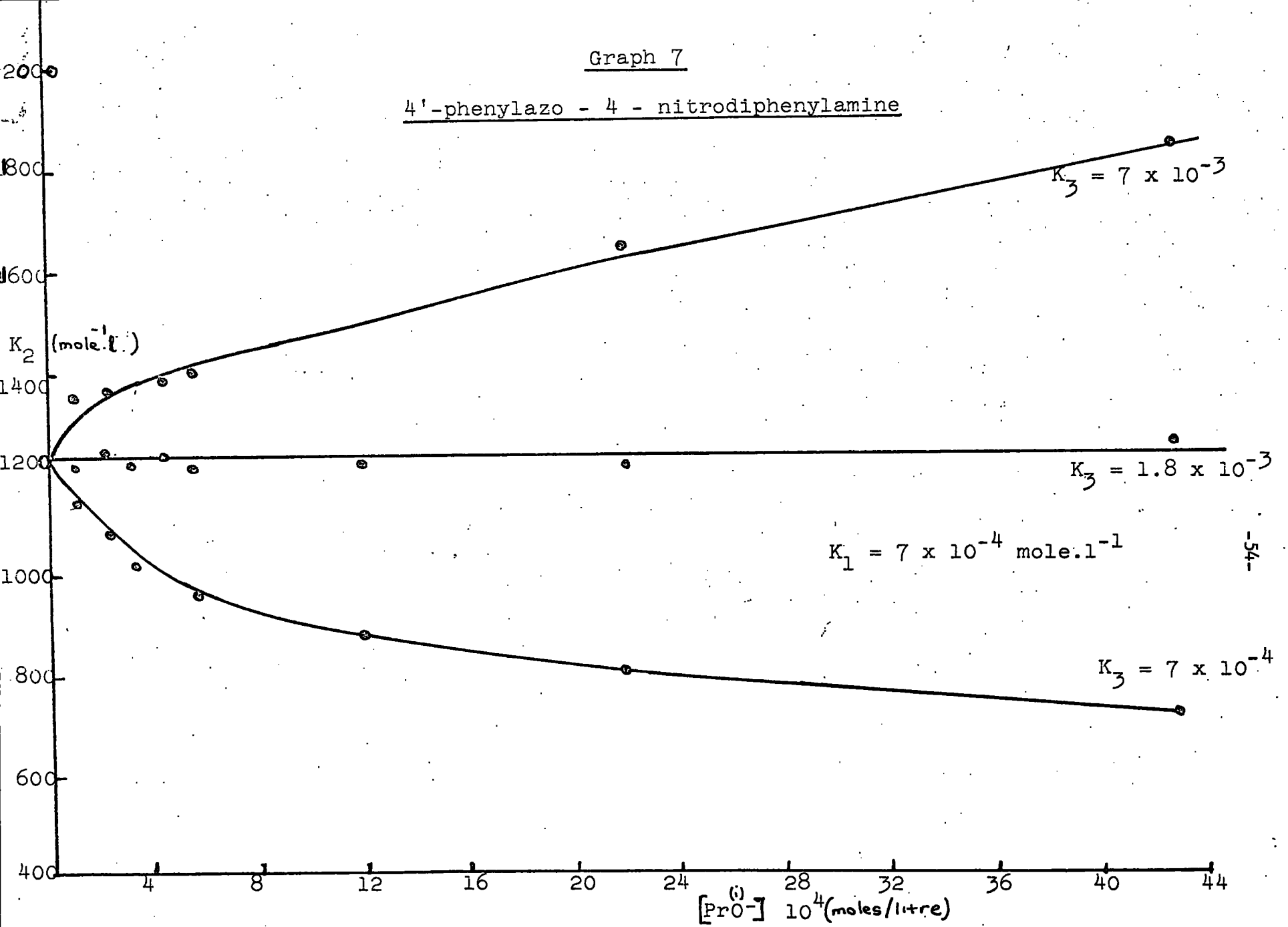
$$\underline{a = 5•6\text{Å}}$$

Since the crystallographic radius of a potassium ion is 1•33Å, this would give 4•27Å for the radius of the diphenylamine anion which is a rather large value.

These results indicate that ion-pair formation could successfully account for the apparent variation in the apparent acidity constant with base concentration. Although precise values of the apparent dissociation constants cannot be obtained the range at which these values occur can be fixed to quite narrow limits and agree with the values found by conductivity methods.

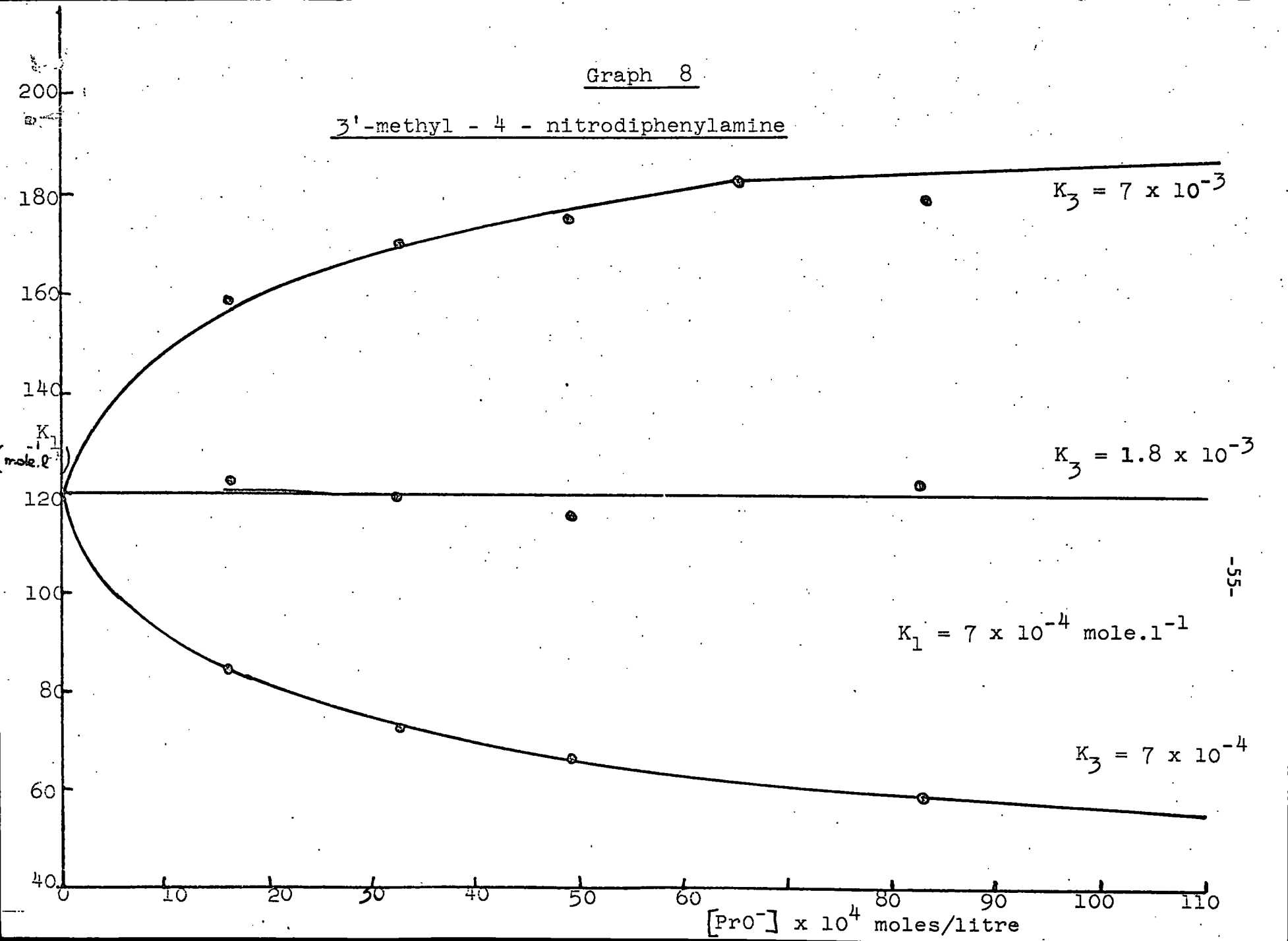
Graph 7

4'-phenylazo - 4 - nitrodiphenylamine



Graph 8

3'-methyl - 4 - nitrodiphenylamine



The curves obtained can be readily extrapolated to give reasonably accurate values of the acidity constants at infinite dilution.

The acidity constants of the other diphenylamines were obtained using the same technique. In each case the curves were of a similar pattern to those shown for 3'-Cl, 3'-Me and 4' phenylazo-4-nitro-diphenylamines in Graphs 6, 7 and 8, pp.54 - 55. The graphs converge at low base concentrations and values for the acidity constants at infinite dilution can readily be obtained by extrapolation (see Tables XXIV-LXI for results, pp.79 -117).

A value for the ion-pair dissociation constant for the potassium isopropoxide of between 7×10^{-4} mole l^{-1} and 1×10^{-3} mole l^{-1} gives values of K_2 that are inclose agreement with those values for the apparent acidity constants obtained by extrapolation to infinite dilution of the results illustrated by Graph 5, page 48.

The value of K_3 for all of the diphenylamines studied is approximately $1{\cdot}8 \times 10^{-3}$ mole l^{-1} when K_1 is taken as 7×10^{-4} mole l^{-1}. In view of the small differences in the structure of the diphenylamines the ion-pair dissociation constants of the potassium salts would be expected to be of the same order.

The results obtained for the relative acidities are of the order expected taking into account the known inductive and resonance values.

Values of K_2 at infinite dilution of substituted 4-nitrodiphenylamines ($mole^{-1}$ 1)

3'-Me	120	4'-MeO	98	4'-(4-nitrophenyl) diphenylamine	145
3'-H	170	4'-Me	100	4'-phenylazo	1230
3'-MeO	146	4'-F	365	4'-(4-nitrophenylazo) diphenylamine	90
3'-F	450	4'-Cl	700	2'-F	630
3'-Cl	700	4'-phenyl	265	2'-Me	180
3'-NO_2	4500	4'-(4-nitrophenyl)	710	2'-MeO	80
				2'-Cl	1500

The computer technique was repeated using a value for K_1 of 1x 10^{-3} $mole^{-1}$ 1 and values for K_3 of 1 x 10^{-3}, 3 x 10^{-3}, 6 x 10^{-3}, 1 x 10^{-2} mole 1^{-1} respectively. The extrapolated values for K_2 at infinite dilution were the same as those obtained previously when using a value for K_1 of 7 x 10^{-4} mole 1^{-1} and values of 7 x 10^{-4}, 1·8 x 10^{-3}, 7 x 10^{-3}, and 1·5 x 10^{-2} mole 1^{-1} for K_3.

5.7.4 The reaction of lithium, sodium and potassium isopropoxide in isopropyl alcohol with 4-nitrodiphenylamine

The value of the equilibrium constant for the reaction between isopropoxide and the diphenylamine in isopropyl alcohol is dependent on the metal ion present. The results are shown below:

Values of the equilibrium constant

Metal ion	Concentration of isopropoxide (moles/litre)			
	10^{-3}	10^{-2}	$2{\cdot}0 \times 10^{-2}$	5×10^{-2}
Lithium	66·0	26·1	22·3	-
Sodium	81·94	58·0	53·1	49·0
Potassium	110·0	60·0	56·2	56·0

These results are in agreement with the ion-pair theory. Ion-pair formation should be more pronounced in the case of lithium isopropoxide. The lithium isopropoxide ion-pair should be less effective as a base than the sodium or potassium compound. The relative reactivities of lithium, sodium and potassium ethoxides in a Dieckmann reaction has been interpreted in terms of ion-pair formation.

Results Showing Variation In K for Substituted 4-nitrodiphenylamines

Table IV

4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 485 m μ	K
4.44×10^{-5}	1.5×10^{-3}	0.17	57.0
4.44×10^{-5}	3.0×10^{-3}	0.25	56.2
2.22×10^{-5}	1.5×10^{-2}	0.286	54.75
4.44×10^{-5}	1.5×10^{-2}	0.58	103.3
2.22×10^{-5}	3.0×10^{-2}	0.385	82.0
2.22×10^{-5}	4.5×10^{-2}	0.455	81.94
2.22×10^{-5}	7.5×10^{-2}	0.52	69.0
2.22×10^{-5}	11.25×10^{-2}	0.55	81.5
2.22×10^{-5}	3.0×10^{-3}	0.125	63.7
4.44×10^{-5}	4.5×10^{-3}	0.3	72.0
4.44×10^{-5}	4.5×10^{-3}	0.17	56.0
4.44×10^{-5}	7.5×10^{-3}	0.41	60.0
2.22×10^{-5}	7.5×10^{-3}	0.215	57.1

Table V

3'methyl-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 485 mμ	K
5.337×10^{-5}	1.66×10^{-3}	0.18	83.07
5.337×10^{-5}	3.32×10^{-3}	0.29	73.07
5.337×10^{-5}	4.98×10^{-3}	0.37	66.7
5.337×10^{-5}	8.30×10^{-3}	0.485	58.37
5.337×10^{-5}	1.245×10^{-2}	0.60	54.45
4.44×10^{-5}	2.84×10^{-2}	0.71	52.0
4.44×10^{-5}	5.68×10^{-2}	0.92	51.51
4.44×10^{-5}	7.1×10^{-2}	0.99	56.9

Table VI

3'-methoxy - 4 - nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 485 m μ	K
5.88×10^{-5}	7.1×10^{-3}	0.65	79.87
5.88×10^{-5}	1.42×10^{-2}	0.88	70.57
5.88×10^{-5}	2.13×10^{-2}	1.06	67.5
2.94×10^{-5}	2.84×10^{-2}	0.59	67.42
2.94×10^{-5}	5.68×10^{-2}	0.71	65.89

Table VII

3'-fluoro-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 500 m μ	K
2.24×10^{-5}	1.5×10^{-3}	0.23	318.3
2.24×10^{-5}	3.0×10^{-3}	0.32	272.0
2.24×10^{-5}	4.5×10^{-3}	0.375	248.0
2.24×10^{-5}	6.0×10^{-3}	0.415	233.0
2.24×10^{-5}	8.7×10^{-3}	0.465	216.0
2.24×10^{-5}	13.05×10^{-3}	0.52	207.5

Table VIII

3'-chloro-4-nitrodiphenylamine

@ 505 mμ

5.46×10^{-5}	1.66×10^{-4}	0.16	619.0
5.46×10^{-5}	3.32×10^{-4}	0.292	613.0
5.46×10^{-5}	4.98×10^{-4}	0.38	542.0
5.46×10^{-5}	8.3×10^{-4}	0.54	542.0
5.46×10^{-5}	1.25×10^{-3}	0.63	485.0
2.73×10^{-5}	1.66×10^{-3}	0.39	471.6
2.73×10^{-5}	3.32×10^{-3}	0.52	434.3
2.73×10^{-5}	4.98×10^{-3}	0.59	397.3
2.73×10^{-5}	6.64×10^{-3}	0.63	380.1
2.73×10^{-5}	8.3×10^{-3}	0.67	381.8
2.73×10^{-5}	9.96×10^{-3}	0.7	387.3
2.73×10^{-5}	1.25×10^{-2}	0.73	386.3

Table IX

3' Nitro-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 510 m μ	K
1.75×10^{-5}	1.74×10^{-4}	0.25	4160
1.75×10^{-5}	3.48×10^{-4}	0.35	3980
1.75×10^{-5}	5.22×10^{-4}	0.39	3460
1.75×10^{-5}	6.96×10^{-4}	0.435	3560
1.75×10^{-5}	8.7×10^{-4}	0.45	3220
1.75×10^{-5}	1.74×10^{-3}	0.435	1467
1.75×10^{-5}	3.48×10^{-3}	0.575	4800
1.75×10^{-5}	5.22×10^{-3}	0.59	5600

Table X

4'-ethoxy-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO^-] added (moles/litre)	Absorbance of Ionic Form @ 480 m μ	K
3.969×10^{-5}	1.74×10^{-3}	0.15	90.67
3.969×10^{-5}	8.48×10^{-3}	0.21	67.7
3.969×10^{-5}	5.22×10^{-3}	0.25	56.27
3.969×10^{-5}	6.96×10^{-3}	0.29	51.64
3.969×10^{-5}	8.70×10^{-3}	0.33	49.4
3.969×10^{-5}	1.31×10^{-2}	0.425	48.2
3.969×10^{-5}	1.74×10^{-2}	0.49	46.1
3.969×10^{-5}	3.48×10^{-2}	0.66	42.9
3.969×10^{-5}	4.35×10^{-2}	0.69	39.0
3.969×10^{-5}	5.22×10^{-2}	0.75	40.9
3.969×10^{-5}	8.7×10^{-2}	0.83	39.0
3.969×10^{-5}	1.31×10^{-1}	0.93	41.7

Table XI

4'-methoxy-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 485 mμ	K
4.024×10^{-5}	1.74×10^{-2}	0.46	44.2
4.024×10^{-5}	3.48×10^{-2}	0.64	43.9
4.024×10^{-5}	5.22×10^{-2}	0.74	44.4
4.024×10^{-5}	8.7×10^{-2}	0.85	46.7
4.024×10^{-5}	13.05×10^{-2}	0.92	50.8

Table XII

4'-methyl-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 475 m u	K
2.109×10^{-5}	2.4×10^{-3}	0.1	78.2
2.109×10^{-5}	4.8×10^{-3}	0.14	59.2
2.109×10^{-5}	7.2×10^{-3}	0.18	55.2
2.109×10^{-5}	9.6×10^{-3}	0.21	51.0
2.109×10^{-5}	12.0×10^{-3}	0.24	51.6
2.109×10^{-5}	1.8×10^{-2}	0.28	44.1
2.109×10^{-5}	2.4×10^{-2}	0.32	42.7
2.109×10^{-5}	6.0×10^{-2}	0.45	39.6
2.109×10^{-5}	7.2×10^{-2}	0.475	41.8
2.109×10^{-5}	9.6×10^{-2}	0.515	45.0
2.109×10^{-5}	1.2×10^{-1}	0.53	43
2.109×10^{-5}	1.8×10^{-1}	0.57	50.1

Table XIII

4'-fluoro-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 485 mμ	K
2.743×10^{-5}	1.84×10^{-3}	0.23	231.5
2.743×10^{-5}	3.68×10^{-3}	0.315	189.0
2.743×10^{-5}	4.6×10^{-3}	0.35	180.0
2.743×10^{-5}	5.52×10^{-3}	0.38	176.0
2.743×10^{-5}	7.36×10^{-3}	0.435	170.0
2.743×10^{-5}	9.2×10^{-3}	0.46	160.3
2.743×10^{-5}	1.38×10^{-2}	0.53	159.0
2.743×10^{-5}	1.84×10^{-2}	0.595	182.5
2.743×10^{-5}	3.68×10^{-2}	0.685	213.3
2.743×10^{-5}	5.52×10^{-2}	0.745	495.0

Table XIV

4'-chloro-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 490 m μ	K
1.988×10^{-5}	1.84×10^{-3}	0.25	368.4
1.988×10^{-5}	3.68×10^{-3}	0.33	311.5
1.988×10^{-5}	5.52×10^{-3}	0.37	270.0
1.988×10^{-5}	7.36×10^{-3}	0.41	267.2
1.988×10^{-5}	9.2×10^{-3}	0.44	268.1
1.988×10^{-5}	13.8×10^{-3}	0.49	275.0

Table XV

4'-phenyl-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 490 m μ	K
	2.17×10^{-3}	0.12	138.5
	4.34×10^{-3}	0.165	107.2
	8.68×10^{-3}	0.24	98.9
	10.85×10^{-3}	0.265	87.8
	16.35×10^{-3}	0.32	84.4

Table XVI

4'-(4-nitrophenyl)-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 505 mμ	K
1.635×10^{-5}	2.17×10^{-3}	0.24	357.8
1.635×10^{-5}	4.34×10^{-3}	0.32	281.0
1.635×10^{-5}	6.51×10^{-3}	0.36	288.0
1.635×10^{-5}	8.68×10^{-3}	0.394	290.0
1.635×10^{-5}	10.85×10^{-3}	0.425	302.0
1.635×10^{-5}	16.35×10^{-3}	0.458	304.0

Table XVII

4'-(4-nitrophenyl)-diphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 435 m μ	K
2.032×10^{-5}	1.84×10^{-3}	0.053	85.43
2.032×10^{-5}	3.68×10^{-3}	0.09	60.9
2.032×10^{-5}	5.52×10^{-3}	0.11	52.3
2.032×10^{-5}	7.36×10^{-3}	0.13	49.5
2.032×10^{-5}	9.2×10^{-3}	0.142	44.2
2.032×10^{-5}	13.8×10^{-3}	0.18	40.0
2.032×10^{-5}	18.4×10^{-3}	0.21	39.5

Table XVIII

4'-phenylazo-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO^-] added (moles/litre)	Absorbance of Ionic Form @ 580 m μ	K
3.378×10^{-5}	2.17×10^{-3}	0.75	807.6
3.378×10^{-5}	4.34×10^{-3}	0.90	738.4
1.689×10^{-5}	2.17×10^{-3}	0.375	802.4
1.689×10^{-5}	4.34×10^{-3}	0.45	735.3
1.689×10^{-5}	6.51×10^{-3}	0.50	1292.0
1.689×10^{-5}	8.68×10^{-3}	0.532	1038.0
1.689×10^{-5}	10.85×10^{-3}	0.545	1089.0

Table XIX

4'(4-nitrophenylazo)-diphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 650 m μ	K
1.613×10^{-5}	2.17×10^{-3}	0.1	41.12
1.613×10^{-5}	4.34×10^{-3}	0.14	29.85
1.613×10^{-5}	6.51×10^{-3}	0.185	27.46
1.613×10^{-5}	8.68×10^{-3}	0.21	23.96
1.613×10^{-5}	10.85×10^{-3}	0.24	22.56
1.613×10^{-5}	16.2×10^{-3}	0.282	19.0

Table XX

2'-fluoro-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 485 mμ	K
2.25×10^{-5}	1.84×10^{-3}	0.35	472.5
2.25×10^{-5}	3.68×10^{-3}	0.44	381.4
2.25×10^{-5}	5.52×10^{-3}	0.505	366.9
2.25×10^{-5}	7.36×10^{-3}	0.548	360.6
2.25×10^{-5}	9.20×10^{-3}	0.58	360.8
2.25×10^{-5}	13.8×10^{-3}	0.625	350.0
2.25×10^{-5}	15.64×10^{-3}	0.646	360.0

Table XXI

2'-methyl-4-nitrodiphenylamine

[HA] added (moles/litre)	[PrO$^-$] added (moles/litre)	Absorbance of Ionic Form @ 475 m μ	K
2.22×10^{-5}	1.84×10^{-3}	0.12	123.0
2.22×10^{-5}	3.68×10^{-3}	0.182	105.7
2.22×10^{-5}	5.52×10^{-3}	0.24	105.9
2.22×10^{-5}	7.36×10^{-3}	0.27	96.54
2.22×10^{-5}	9.2×10^{-3}	0.30	93.1
2.22×10^{-5}	13.8×10^{-3}	0.37	95.5
2.22×10^{-5}	18.4×10^{-3}	0.41	93.0
2.22×10^{-5}	36.8×10^{-3}	0.51	98.0
2.22×10^{-5}	55.2×10^{-3}	0.56	111.4

Table XXII

2'-methoxy-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 475 m μ	K
2.033×10^{-5}	1.84×10^{-3}	0.053	57.53
2.033×10^{-5}	3.68×10^{-3}	0.09	52.72
2.033×10^{-5}	5.52×10^{-3}	0.11	44.96
2.033×10^{-5}	7.36×10^{-3}	0.13	41.67
2.033×10^{-5}	9.20×10^{-3}	0.142	37.47
2.033×10^{-5}	1.38×10^{-2}	0.182	35.47
2.033×10^{-5}	1.84×10^{-2}	0.215	34.48
2.033×10^{-5}	3.68×10^{-2}	0.30	32.11
2.033×10^{-5}	5.52×10^{-2}	0.37	35.4
2.033×10^{-5}	7.36×10^{-2}	0.39	32.5
2.033×10^{-5}	9.2×10^{-2}	0.43	37.8

Table XXIII

2'-chloro-4-nitrodiphenylamine

$[HA]$ added (moles/litre)	$[PrO^-]$ added (moles/litre)	Absorbance of Ionic Form @ 485 m μ	K
2.231×10^{-5}	3.68×10^{-4}	0.24	1354.0
2.231×10^{-5}	5.52×10^{-4}	0.285	1180.0
2.231×10^{-5}	7.36×10^{-4}	0.33	1138.0
2.231×10^{-5}	9.2×10^{-4}	0.375	1107.0
2.231×10^{-5}	1.84×10^{-3}	0.46	1025.0
2.231×10^{-5}	3.68×10^{-3}	0.57	1014.0

4-nitrodiphenylamine

Table XXIV

$[PrO^-]_{left} \times 10^{-4}$ (moles/litre)	$[Anion]_{total} \times 10^{-5}$ (moles/litre)	$[HA] \times 10^{5}$ (moles/litre)
0.566	0.8165	78.42
1.392	2.284	96.77
3.109	1.307	28.39
4.688	1.721	27.98
6.274	2.056	27.64
16.09	1.086	6.834
32.24	1.644	6.276
48.39	2.074	5.846
64.56	2.404	5.516
233.3	2.218	1.742
466.7	2.751	1.209

Table XXV

$[PrO^-]$ left x 10^4	$K_1 = 7 \times 10^{-4}$ mole $l.^{-1}$			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
0.566	183.9	193.4	198.3	199.2
1.392	169.6	188.5	199.3	201.4
3.109	148.1	175.8	192.9	196.5
4.688	131.2	163.4	184.9	189.8
6.274	118.6	153.2	178.1	183.7
16.09	98.8	145.4	187.3	197.9
32.24	81.25	132.3	188.4	204.4
48.39	73.3	126.3	191.9	212.4
64.56	67.5	120.7	192.7	216.5
233.3	54.6	112.3	224.8	275.9
466.7	50.85	110.7	249.8	325.4

3'-methyl-4-nitrodiphenylamine

Table XXVI

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
5.53	1.73	28.83
4.413	1.47	29.09
3.302	1.18	29.38
2.2	0.90	29.66
16.6	0.6468	4.69
33.2	1.042	4.295
49.8	1.329	4.008
83.0	1.742	3.595
124.5	2.156	3.181
284.0	2.69	1.745
568.0	3.306	1.13
710.0	3.556	0.88

Table XXVII

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
5.53	108.5	137.9	158.4	162.8
4.413	114.5	141.5	159.3	163.1
3.302	121.6	145.2	159.9	163.0
2.2	137.9	157.9	169.7	172.1
16.6	83.1	122.8	158.7	167.8
33.2	73.1	119.4	170.7	185.4
49.8	66.6	115.1	175.6	194.5
83.0	58.4	107.7	179.4	204.5
124.5	54.4	105.2	188.3	220.6
284.0	54.3	113.7	235.6	293.9
568.0	51.5	113.7	264.9	351.4
710.0	56.9	127.4	307.7	416.7

3'-methoxy-4-nitrodiphenylamine

Table XXVIII

$[ProO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.065	0.75	53.11
2.715	1.65	52.21
4.38	1.78	25.15
5.494	2.06	24.87
70.79	2.125	3.755
141.71	2.876	3.0
212.6	3.465	2.415
284.0	1.934	1.01
568.0	2.32	0.62

Table XXIX

$[PrO^-]_{left}$ x 10^4	$K_1 = 7 \times 10^{-4}$ mole.l.$^{-1}$			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.065	132.6	143.7	149.6	150.7
2.715	128.3	146.2	152.1	159.1
4.38	130.4	140.2	156.2	168.2
5.494	115.3	150.1	160	166.5
70.79	79.9	144.6	234.4	264.8
141.71	67.6	132.6	242.9	287.2
212.6	67.5	137.7	271.4	330.7
284.0	67.4	141.2	292.6	364.8
568.0	65.9	145.4	338.8	449.3

3'-fluoro-4-nitrodiphenylamine

Table XXX

$[ProO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
3.24	1.8	10.08
4.353	2.07	9.81
5.47	2.3	9.58
15.0	0.7233	1.5152
17.32	0.7861	1.4529
30.0	1.007	1.2315
45.0	1.18	1.0585
60.0	1.305	0.9335
75.0	1.384	0.8545
87.0	1.462	0.777
112.5	1.541	0.6975
130.5	1.635	0.604
174.0	1.698	0.541
348.0	1.95	0.289
522.0	2.075	0.164

Table XXXI

$[PrO^-]$ left x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
3.24	551.1	658.2	725.5	740.1
4.353	484.7	599.1	674.9	691.6
5.47	438.9	558.1	641.3	659.3
15.0	318.2	463.5	591.4	623.1
17.32	312.3	464.6	603.9	639.7
30.0	272.5	439.1	617.9	668.1
45.0	247.7	422.3	633.6	698.3
60.0	232.9	412.6	649.7	726.7
75.0	215.9	393.4	643.7	729.2
87.0	216.3	401.1	673.5	770.2
112.5	196.4	375.3	659.4	766.8
130.5	207.4	402.9	727.1	854.0
174.0	180.4	360.9	685.7	822.6
348.0	193.9	412.9	886.3	1124.4
522.0	242.4	531.9	1222.6	1608.1

3'-chloro-4-nitrodiphenylamine

Table XXXII

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
3.32	0.904	4.56
8.133	1.071	3.79
16.48	1.22	1.51
49.62	1.81	0.919
66.2	1.92	0.81
82.8	2.074	0.656
124.0	2.26	0.47

Table XXXIII

$[PrO^-]$ left x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}		
	K_2		
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 2.8 \times 10^{-3}$
3.32	597.6	710.5	742.0
8.133	531.2	709.4	768.0
16.48	488.1	720.0	808.3
49.62	432.3	683.3	818.6
66.2	379.2	680.0	829.5
82.8	380.9	702.2	869.0
124.0	386.2	746.0	946.0

3'-nitro-4-nitrodiphenylamine

Table XXXIV

$[ProO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.668	0.7182	1.0349
3.38	1.006	0.747
5.108	1.12	0.633
6.835	1.249	0.504
8.70	1.293	0.46
34.6	1.652	0.133
55.2	1.695	0.058

Table XXXV

$[PrO^-]$ left x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.668	4159.4	4646.6	4924.2	4978.5
3.38	3984.4	4766.6	5254.3	5360.7
5.108	3463.9	4349.9	4952.4	5086.4
6.835	3625.7	4730.5	5530.7	5713.1
8.70	3230.1	4356.9	5219.9	5421.7
34.6	3589.9	5904.1	8498.5	9251.9
55.2	5294.4	9275.6	1440.5	1604.7

4'-methoxy-4-nitrodiphenylamine

Table XXXVI

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
22.56	2.414	13.39
45.26	3.384	12.42
174.0	1.749	2.275
348.0	2.433	1.591
522.0	2.813	1.211
870.0	3.231	0.793
1305.0	3.497	0.527

Table XXXVII

$[Pro^-]$ left $\times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
22.56	79.9	123.7	167.3	178.9
45.26	60.1	102.8	154.8	170.8
174.0	44.1	88.4	167.9	201.5
348.0	43.9	93.6	200.9	254.9
522.0	44.5	97.7	224.5	295.3
870.0	46.8	106.1	264.4	364.9
1305.0	50.8	117.7	311.0	446.4

4'-methyl-4-nitrodiphenylamine

Table XXXVIII

$[ProO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.088	0.52	55.93
2.216	0.64	27.56
3.334	0.855	27.37
4.456	1.04	27.19
5.578	1.215	27.01
24.0	0.3334	1.7756
48.0	0.4667	1.6423
72.0	0.6001	1.51
96.0	0.6834	1.40
120.0	0.8067	1.3023
180.0	0.9335	1.176
240.0	1.067	1.042
600.0	1.484	0.625
720.0	1.583	0.526
960.0	1.717	0.392
1200.0	1.767	0.342
1800.0	1.90	0.21

Table XXXIX

$[PrO^-]$ left x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.088	88.5	92.6	96.4	97.1
2.216	104.8	119.9	128.8	130.6
3.334	93.7	111.8	123.2	125.6
4.456	85.84	105.9	119.3	122.1
5.578	80.6	102.4	117.6	120.9
24.0	78.2	121.9	165.9	177.7
48.0	59.2	101.7	154.2	170.4
72.0	55.1	100.0	162.3	183.5
96.0	50.8	95.4	162.8	187.4
120.0	51.6	99.3	176.5	206.1
180.0	44.1	88.5	169.2	203.4
240.0	42.7	88.0	177.0	217.7
600.0	39.6	87.7	206.1	274.5
720.0	41.7	93.7	226.7	307.2
960.0	45.6	103.9	262.8	366.1
1200.0	43.1	99.3	259.1	368.9
1800.0	50.3	118.0	325.6	482.1

4'-fluoro-4-nitrodiphenylamine

Table XXXX

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.967	3.13	47.65
4.405	1.55	11.14
5.52	1.8	10.89
18.32	0.8168	1.926
36.7	1.119	1.624
45.88	1.243	1.50
55.06	1.35	1.393
73.45	1.545	1.198
91.84	1.634	1.11
137.8	1.882	0.861
183.8	2.113	0.63
367.8	2.433	0.31

Table XXXXI

$[PrO^-]$ left $\times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.967	333.9	382.8	411.7	417.9
4.405	315.9	390.1	439.4	450.2
5.52	299.4	380.6	437.2	449.4
18.32	231.5	347.1	454.9	482.6
36.7	187.7	311.0	451.0	492.9
45.88	180.6	308.7	464.8	512.6
55.06	176.0	308.3	478.3	532.7
73.45	175.6	319.0	520.0	588.8
91.84	160.1	298.9	506.8	581.6
137.8	158.6	309.9	564.7	666.0
183.8	182.5	367.2	704.5	848.7
367.8	213.4	456.4	989.0	1261.0

4'-chloro-4-nitrodiphenylamine

Table XXXXII

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
0.987	1.526	24.0
2.017	2.634	22.9
4.33	2.313	10.46
5.437	2.634	10.14
18.4	0.803	1.185
36.64	1.059	0.929
55.0	1.189	0.80
73.47	1.317	0.671
91.86	1.414	0.574
137.8	1.574	0.414

Table XXXXIII

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
0.987	644.2	697.9	727.5	733.1
2.017	570.3	653.4	703.1	712.9
4.33	510.7	631.2	711.6	728.6
5.437	477.7	607.5	698.6	718.3
18.4	368.3	552.7	724.5	768.6
36.64	311.1	515.6	748.3	816.6
55.0	270.2	473.1	733.9	817.3
734.7	267.1	485.4	791.2	895.6
91.86	268.2	500.6	845.5	973.6
137.8	275.9	539	982.1	1157.9

4'-pheryl-4-nitrodiphenylamine

Table XXXXIV

$[(i)\text{-PrO}]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
21.7	0.3885	1.293
43.4	0.534	1.148
65.0	0.7452	0.937
86.8	0.7767	0.905
108.5	0.8576	0.824
163.5	0.971	0.711

Table XXXXV

$[PrO^-]_{left}$ x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
21.7	138.5	212.7	285.2	304.3
43.4	107.2	181.7	270.9	297.9
65.0	122.4	218.9	349.2	392.3
86.8	98.9	183.3	307.5	351.5
108.5	95.9	182.5	318.5	369.4
163.5	83.5	166.1	311.9	372.3

4'-(4-nitropheryl)-4-nitrodiphenylamine

Table XXXXVI

$[PrO^-]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.03	1.113	15.94
2.09	1.899	15.15
3.168	2.522	14.53
4.39	1.691	6.834
5.52	1.809	6.716
21.63	0.712	0.92
43.3	0.8658	0.646
65.0	1.068	0.564
86.63	1.168	0.464
108.37	1.261	0.371
163.36	1.359	0.305

Table XXXXVII

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.03	677.9	734.5	764.7	771.4
2.09	599.7	686.7	738.7	749.0
3.168	547.9	654.7	722.5	736.4
4.39	563.6	696.3	784.7	803.4
5.52	487.9	620.2	712.4	732.4
21.63	357.8	549.7	736.8	786.2
43.3	309.5	525.0	782.4	860.2
65.0	291.3	521.2	831.7	934.7
86.63	290.6	538.6	903.5	1032.9
108.37	313.6	596.8	1041.4	1207.9
163.36	272.8	542.4	1018.6	1215.8

4'-(4-nitrophenyl)-diphenylamine

Table XXXXVIII

$\left[{}^{(i)}PrO^{-} \right]_{left} \times 10^{4}$ (moles/litre)	$\left[Anion \right]_{total} \times 10^{5}$ (moles/litre)	$\left[HA \right] \times 10^{5}$ (moles/litre)
18.4	0.2762	1.757
36.8	0.3724	1.661
55.2	0.4552	1.578
73.6	0.5379	1.475
92.0	0.5876	1.445
138.0	0.7447	1.288
184.0	0.8690	1.164

Table XXXXIX

$[PrO^-]_{left}$ x 10^4 (moles/litre)	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
18.4	85.4	128.1	167.8	177.9
36.8	60.9	100.9	146.5	159.8
55.2	52.3	91.5	141.9	158.0
73.6	49.5	90.0	146.7	165.9
92.0	44.2	82.5	139.8	160.4
138.0	41.9	81.9	149.1	175.8
184.0	40.6	81.6	156.6	188.6

4'-phenylazo-4-nitrodiphenylamine

Table L

$[(i)\text{-PrO}]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
1.051	0.8876	6.97
2.131	1.489	6.37
3.225	1.946	5.91
4.322	2.376	5.48
5.43	2.691	5.17
5.4	1.6	1.778
21.6	1.071	0.618
43.27	1.285	0.404
64.95	1.443	0.246
86.65	1.52	0.169
108.3	1.557	0.132

Table LI

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.051	1211.7	1230.0	1366.8	1377.2
2.131	1096.9	1255.9	1349.7	1368.5
3.225	1021.0	1219.4	1345.2	1370.9
4.322	1003.2	1239.8	1397.9	1431.2
5.43	958.6	1218.9	1401.7	1441.2
5.4	1666.5	2110.9	2417.5	2485.9
21.6	802.3	1233.7	1653.2	1764
43.27	735.0	1246.4	1858.6	1764.0
64.95	903.1	1615.6	2578.9	2898.5
86.65	1037.9	1924.3	3229.1	3691.9
108.3	1089.0	2072	3617.0	4195.0

4'(4-nitrophenylazo)-diphenylamine

Table LII

$[(i)\text{-PrO}]_{left}$ x 10^4 (moles/litre)	$[Anion]_{total}$ x 10^5 (moles/litre)	$[HA]$ x 10^5 (moles/litre)
1.1	0.35	37.4
2.207	0.675	37.03
3.329	0.91	36.79
4.446	1.15	36.56
5.577	1.225	36.48
21.7	0.1322	1.481
43.4	0.185	1.428
65.08	0.2444	1.369
86.77	0.2776	1.335
108.5	0.3173	1.296
162.0	0.3727	1.24

Table LIII

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole.l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.1	85.1	92.1	95.9	96.6
2.207	82.6	94.5	101.4	107.8
3.329	74.3	88.7	97.7	99.6
4.446	70.7	87.4	98.4	100.7
5.577	60.2	76.5	87.7	90.2
21.7	41.1	63.2	84.6	90.3
43.4	29.8	50.6	75.4	82.9
65.08	27.4	49.1	78.3	87.9
86.77	23.9	44.4	74.5	85.1
108.5	22.6	42.9	74.9	86.8
162.0	18.6	36.8	69.1	82.4

2'-fluoro-4-nitrodiphenylamine

Table LIV

$[(i)\text{-PrO}]_{left}$ x 10^4 (moles/litre)	$[Anion]_{total}$ x 10^5 (moles/litre)	$[HA]$ x 10^5 (moles/litre)
1.01	1.324	15.42
2.064	2.161	14.58
3.134	2.858	13.88
5.498	2.024	6.35
18.3	1.042	1.205
36.67	1.31	0.937
55.05	1.503	0.744
73.44	1.622	0.625
91.53	1.712	0.551
137.8	1.861	0.386
156.2	1.923	0.324

Table LV

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
1.01	850.1	921.1	960.0	967.4
2.064	718.1	822.8	884.5	896.8
3.134	657.0	788.1	866.4	883.9
5.498	579.7	736.8	846.4	870.9
18.3	472.5	708.8	928.7	985.6
36.67	381.25	631.9	917.6	1001.6
55.05	366.9	642.7	997.6	1110.7
73.44	353.4	642.1	1046.8	1185.0
91.83	338.35	631.6	1070.8	1228.8
137.8	349.9	683.6	1245.6	1469.1
156.2	379.9	752.2	1401.8	1668.3

2'-methyl-4-nitrodiphenylamine

Table LVI

$[(i)\text{-PrO}]_{left} \times 10^4$ (moles/litre)	$[Anion]_{total} \times 10^5$ (moles/litre)	$[HA] \times 10^5$ (moles/litre)
2.012	2.68	58.88
3.21	2.1	28.7
4.27	2.52	28.26
5.41	2.9	27.88
18.4	0.4087	1.806
36.74	0.6198	1.596
55.12	0.8174	1.399
73.5	0.9196	1.296
91.88	1.022	1.194
137.87	1.26	0.956
183.9	1.396	0.82
367.8	1.737	0.479
551.8	1.907	0.310

Table LVII

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
2.012	226.2	259.2	278.9	282.8
3.21	227.9	272.2	300.3	306.1
4.27	208.8	257.8	290.5	297.7
5.41	192.3	244.5	281.1	289.3
18.4	122.9	184.5	241.7	256.4
36.74	105.7	175.2	254.2	277.3
55.12	106.0	185.6	287.9	320.6
73.5	96.5	175.4	285.8	323.4
91.88	93.2	173.9	294.7	338.1
137.87	95.6	186.7	340.3	401.2
183.9	92.6	186.3	357.4	430.4
367.8	98.59	210.8	456.9	582.5
551.8	111.5	245.6	569.6	753.1

2'-methoxy-4-nitrodiphenylamine

Table LVIII

$[(i)\text{-PrO}]_{left}$ x 10^4 (moles/litre)	$[Anion]_{total}$ x 10^5 (moles/litre)	$[HA]$ x 10^5 (moles/litre)
18.4	0.1945	1.838
36.8	0.3304	1.703
55.2	0.4038	1.629
73.6	0.4772	1.556
92.0	0.5213	1.512
138.0	0.6682	1.365
184.0	0.789	1.244
368.0	1.101	0.932
552.0	1.358	0.695
736.0	1.432	0.601
920.0	1.579	0.454

Table LIX

$[PrO^-]_{left}$ x 10^4	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
18.4	57.5	86.2	112.9	119.7
36.8	52.7	87.3	126.6	138.1
55.2	44.9	78.6	121.9	135.7
73.6	41.7	75.7	123.3	139.6
92.0	37.5	69.9	118.5	135.9
138.0	35.5	69.3	126.2	148.8
184.0	34.4	69.4	133.1	160.2
368.0	32.1	68.7	148.8	189.6
552.0	35.4	77.9	180.8	239.1
736.0	32.4	72.6	176.4	239.5
920.0	37.8	85.9	215.9	299.5

2'-chloro-4-nitrodiphenylamine

Table LX

$[(i)\text{-PrO}^-]_{left}$ x 10^4 (moles/litre)	$[Anion]_{total}$ x 10^5 (moles/litre)	$[HA]$ x 10^5 (moles/litre)
3.61	0.733	1.5
5.43	0.8708	1.36
7.26	1.008	1.22
9.09	1.146	1.08
18.26	1.406	0.82
36.63	1.742	0.49
53.4	1.833	0.397

Table LXI

$[PrO^-]_{left} \times 10^4$	$K_1 = 7 \times 10^{-4}$ mole. l^{-1}			
	K_2			
	$K_3 = 7 \times 10^{-4}$	$K_3 = 1.8 \times 10^{-3}$	$K_3 = 7 \times 10^{-3}$	$K_3 = 1.5 \times 10^{-2}$
3.61	1354.2	1629.9	1805.2	1841.6
5.43	1179.1	1491.5	1706.5	1752.9
7.26	1138.0	1495.7	1758.0	1818.1
9.09	1167.3	1583.4	1905.5	1979.7
18.26	939.0	1408.5	1846.4	1959.7
36.63	970.5	1608.9	2337.8	2550.7
53.4	864.6	1508.4	2330.0	2591.1

CHAPTER VI

LINEAR FREE ENERGY RELATIONSHIPS

6.1 Linear Free Energy Relationships

The effects of substituents on the rates of chemical reactions and on the acid-base equilibria of aromatic compound can be expressed as the sum of the independent polar, resonance and steric contributions. The general form of these correlations is based on a linear relationship between the logarithms of the rate or equilibrium constant for one reaction (A) and those for another (B) subjected to the same conditions.

i.e. $$\log K_B = m \log K_A + C$$

where K_B and K_A are corresponding rate or equilibrium constants, m is the slope and C the intercept of the straight line obtained.

At constant temperature, the logarithm of a rate constant is proportional to the standard free energy of activation ($\Delta G^{\ddagger}$), and that of an equilibrium constant to the standard free energy change of reaction (ΔG^{o}).[40]

i.e. $$\Delta G^{o} = -RT \log_e K$$

The expression is termed a linear free energy relationship. Hammett[41] and Burkhardt[42] discovered linear relationships involving log K for a number of systems. This work led to the formulation of the Hammett Equation.[43,44]

6.2 The Hammett Equation

Hammett observed that a linear free energy relationship existed for meta- and para-substituted benzene derivatives. This empirical observation can be expressed by the equation;

$$\log\left(\frac{K}{K_o}\right) = \sigma\rho$$

where K is the equilibrium constant for a meta- or para-substituted compound and K_o is the corresponding value for the unsubstituted benzene derivative. The equation does not apply to the influence of ortho-substituents, which may exert steric effects.

6.2.1 Substituent Constant

The substituent constant, σ, measures the ability of a group to withdraw or donate electrons by resonance and inductive interactions, a positive value denoting net electron withdrawal at reaction centre and a negative value denoting net electron donation. The σ value is independent of the nature of the reaction and dependent only on the substituent and its position.

6.2.2 Reaction Constant

The reaction constant, ρ, depends on the nature of the reaction and is a measure of the overall susceptibility of the equilibrium to changes in electron density.

Hammett chose the ionisation of benzoic acids in water at 25° as a standard process, for which ρ was defined as 1·00. Values of σ for many substituents were then calculated as $\log\left(\frac{K}{K_o}\right)$. Jaffe[45] has recalculated and added to the list of σ values given by Hammett and his values are given in Table I.

TABLE I

Some Common σ Values

Substituent	σm	$\sigma \rho$
H	0	0
Me	-0·07	-0·17
MeO	0·12	-0·27
F	0·34	0·06
Cl	0·37	0·23
Br	0·39	0·23
CN	0·56	0·66
NO_2	0·71	0·78

In the case of any particular series of compounds for which data on a reasonable number of meta- and para-substituted derivatives are available, ρ is obtained from the slope of the best line through the values of $\log\left(\frac{K}{K_o}\right)$ plotted against σ. Further, if for any substituent σ is unknown from benzoic acid data then this value may

be obtained by substitution in the Hammett equation. More useful is the fact that the equilibrium constant of a particular derivative can be predicted since this will correspond with the σ value of the substituent.

6.2.3 Enhanced σ values

Discrepancies occur when this treatment is applied to meta- and para-nitrophenols. The ionisation of para-nitrobenzoic acid gave σ = 0•778 for p-NO_2, but this value proved inapplicable to the reactions of phenol and aniline. In these a value of 1•27 is required. This exalted value[46] is attributed to conjugation of para-NO_2 (-M effect) with OH or NH_2 (+M effect) so that para-NO_2 was effectively more electron attracting than it was in para-NO_2-benzoic acid. Hammett[47] suspected that this duality of substituent constants might be more widespread than indicated by the evidence then available.

These enhanced σ-values are denoted by σ^-_ρ. Biggs[48] has recently reported σ^- values for several more substituents based on the ionisation constant of para-substituted anilinium ions and phenols. The σ^- values are presumed to be applicable to those reaction series in which direct conjugation between the substituent and reaction site group, with a lone-pair of electrons, can occur. Since the effect of meta-groups is not so pronounced alternative σ^-_m values have not been calculated. Some σ^- values which have been determined are:

TABLE II

Substituent	σ^-
p-NO_2	+1·27
p-CN	+1·00
p-CH_3CO	+0·87
p-COOH	+0·73
p-COOEt	+0·68

Enhanced σ^+ values also occur when there is direct conjugation between the -COOH group of the benzoic acids and powerful (+M) substituents in the para position. The enhanced σ^+ values are illustrated further by the solvolysis of tertiary cumyl chlorides,[49] which proceeds via the carbonium ion, ArC^+Me_2. The values differed from ordinary σ^- values to the greatest extent in the case of para-substituents of the +M type, e.g. halogen and methoxy, in which the +M effect was enhanced by conjugation in the carbonium ion. The new parameters have been applied to a number of electron-demanding reactions with reasonable success.

6.3 Limitations of Hammett Equation

Because of the apparent failure of the Hammett equation, especially for para-substituents, it became necessary to examine the generality of the simple equation and various attempts have been made

to correlate non-linearity of logK with σ. The original restriction on the equation of applying only to meta- and para-substituents clearly indicates that the variable correlated only derives from the polar effect of the substituent, steric effects and resonance interactions being absent. Hammett himself realised the difficulties and suggested the enhanced σ^+ and σ^- values to correlate the data for direct conjugation due to para-substituents. This placed additional restriction on the equation that the σ value for a substituent depended upon the nature of the parent group.

6.4 Primary and Secondary σ values

6.4.1 Normal Primary σ values

Wepster[50] strongly criticised the 'duality of substituent constants'. In his view 'mesomeric para interaction' inevitably depends on both the mesomeric effect of the para-substituent and the reaction centre. Hence it will vary from reaction to reaction and thus a sliding scale of σ-values would be expected rather than a single exalted constant, i.e. σ^+ for +M substituents, or an analogous σ^- for -M substituents. He suggested a limited set of eight σ-values defined by the relative ionisation constants of meta-substituted benzoic acids together with two para-substituted derivatives for use only when direct resonance interactions were completely absent. These values are called normal primary sigma values, i.e. σ^n.[51]

TABLE III

Primary σ^n values

Substituent	σ^n	Substituent	σ^n
H	0·000	m-I	0·352
m-Me	-0·690	m-CH_3CO	0·376
m-F	0·337	m-NO_2	0·710
m-Cl	0·373	p-CH_3CO	0·502
m-Br	0·391	p-NO_2	0·778

6.4.2 Secondary σ values

Only these values were used in evaluating ρ. For other substituents, σ-values relevant to particular reactions were then calculated and secondary σ^n values for such substituents were suggested.

6.5 Separation of substituent effects

Taft's and Lewis'[51,52,53] approach was through a quantitative separation of substituent effects into inductive and resonance contributions. An assumption was made that the (I) effect is transmitted equally in both meta- and para-positions and then the difference in influence of a certain substituent on the para- and meta-positions can be taken as a measure of its (R) effect. These ideas can be expressed by:

$$\sigma_p^o = \sigma_I + \sigma_R^o$$

and $$\sigma_m^o = \sigma_I + \alpha\sigma_R^o \qquad \text{where } \alpha = \frac{R_m}{R_p}$$

The factor α allows for the lower effectiveness of conjugative interactions from meta- as compared to para-positions.

Since the contributions are separated the following Hammett type equations can be written for all meta- and para-substituents:

$$\log\left(\frac{K}{K_o}\right)_m = I_m + R_m$$

and

$$\log\left(\frac{K}{K_o}\right)_p = I_p + R_p$$

However $$I_m = I_p = I$$

and $$R_m = \alpha R_p = \alpha R$$

hence

$$I = \left(\frac{1}{1 - \alpha}\right)\left\{\log\left(\frac{K}{K_o}\right)_m - \alpha \log\left(\frac{K}{K_o}\right)_p\right\}$$

This equation may be used to calculate the inductive effects of all substituents for which meta- and para-reaction data is available. Consequently a linear inductive energy relationship was developed:

$$I = \sigma_I \rho_I$$

Similarly for resonance contributions:

$$R = \sigma_R \rho_I$$

Values for σ_I are obtained from studies of aliphatic and alicyclic reactions, where resonance contributions will be zero. Unenhanced σ_R^o values are obtained by consideration of meta- and para-substituents which exhibit no direct conjugation interaction with the reaction centre. The σ^o values can then be derived from the expression

$$\sigma^o = \sigma_I + \alpha\sigma_R^o$$

TABLE IV

σ^o values

Substituent	σ_m^o	σ_p^o
CH_3	-0·07	-0·15
CH_3O	0·13	-0·12
F	0·35	0·17
Cl	0·37	0·27
Br	0·38	0·26
CN	0·62	0·69
NO_2	0·79	0·82

The σ^o values are the same as the σ^n values for meta-substituents but there are discrepancies for the para-substituents. Taft suggests that the σ_p^n values are overcompensated.

Taft has observed that variations in σ^o values occur with solvent change and also that highly polarising side-chains modify the values.

However, σ^{o} values, are a considerable improvement on the original σ values, and are probably more reliable than σ^{n} values, especially for para-substituents.

6.6 Elimination of Polar Effects

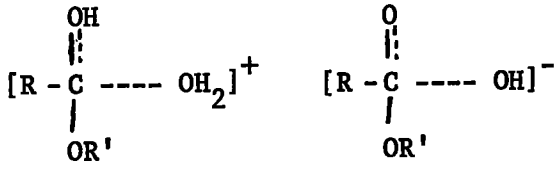
Norman[54] and his co-workers reported the results of a study of rates of saponification of a number of substituted ethyl phenyl acetates. They argued that the σ^{n} values did not eliminate the polar effect of the substituent on the resonance interaction of the reaction site with the benzene ring. A new scale of substituent constant, denoted as σ_{G}, was established from their rate data.

6.7 Ortho-substitution

No true σ constants can be obtained for ortho-substituents because of complicating steric effects. Taft has attempted to evaluate polar effects in aliphatic compounds by elimination of steric effects and has applied the method to ortho-substituted benzene derivatives.

Taft examined the difference between the substituent effects on base-catalysed and acid-catalysed esterification and ester hydrolysis. He concluded that base-catalysed ester reactions showed a very substantial response to substituent polar effects whereas the acid-catalysed reactions are relatively insensitive.

On examination of the postulated transition-state configuration:



A B

It is reasonable to assume that differences in steric effects and conjugative effects between the initial and transition states will be closely similar for otherwise identical acid (A) and base-catalysed (B) reactions.

i.e. $$\log\left(\frac{K}{K_o}\right)_B = P + S + R \qquad (1)$$

$$\log\left(\frac{K}{K_o}\right)_A = S + R \qquad (2)$$

The combinations of equations 1 and 2 enabled Taft to separate the polar effect[55] and he utilised this fact to define a σ^* value for substituent polar effects relative to Me- in aliphatic and ortho-substituted benzene derivatives:

$$\log\left(\frac{K}{K_o}\right)_B - \log\left(\frac{K}{K_o}\right)_A = P = \sigma^*\rho^*$$

In an attempt to place the σ^* values on the same scale as the Hammett σ values, the ρ^* values for alkyl ester hydrolysis was set to

equal 2·48 although based on the Me-group as standard. Taft, from correlations of 37 aliphatic and four ortho-substituted benzene reactions produced the equation:[56,57]

$$\log\left(\frac{K}{K_o}\right) = \sigma^* \rho^*$$

which is a linear free energy relationship for separating polar effects.

σ^* is the polar substitution constant and ρ^* is the susceptibility of a given reaction series to polar substituents. This equation does not include any steric or resonance terms and hence assumes that especially steric factors are similar in a particular reaction series and approximate to the steric effect of a Me-group. Hence it may be expected that larger, more bulky substituents lead to failure of the equation.

TABLE V

σ_o^* values

Substituent	σ_o^*	Substituent	σ_o^*
o-Me	-0·17	o-Br	0·21
o-MeO	-0·39	o-I	0·21
o-F	0·24	o-NO_2	0·80
o-Cl	0·20		

A number of reaction series have been studied where steric interactions between ortho-substituents and the reaction centre has been assumed to be negligible. The phenylpropiolic acid series[58,59,60] were utilised because the acetylenic bond is linear and should eliminate steric effects of ortho-substituents more than any other group capable of joining the -COOH group to the benzene ring.

Taft's procedure may be criticised. It is assumed that steric effects are the same in both basic and acidic reactions. The argument used by Taft to justify this assumption neglects possible differences in the role of the solvent, due to opposite charges of the transition states. This could lead to incomplete elimination of the steric effect. Chapman and Shorter[61] have adduced some evidence for this.

6.8 Conclusion

The development of linear free energy equations has stimulated the study of the effects of structure on reactivity of organic molecules. Considerable progress has been made in the elucidation of many interlocking factors involved in this problem. The ever increasing number of interdependent factors present a formidable obstacle. Nearly a dozen sets of substituent constants have been proposed and it has been suggested that there is a close similarity of some of the values. It has been recommended[62] that only the σ_I, σ, σ^- and σ^+ symbolism should be retained.

CHAPTER VII

HAMMETT PLOTS AND DISCUSSION

7.1 Hammett Plot for 3'- and 4'-substituted 4-nitrodiphenylamines

A plot of Hammett σ values[63] against $\log\left(\frac{K}{K_o}\right)$ for the 3'- and 4'-substituted 4-nitrodiphenylamines was used to obtain a value of ρ (see Graph 9 and Table LXII, p.133). The value of ρ obtained from the graph was 1·6.

The following statistical information was obtained:

1. Best straight line:

$$\log\left(\frac{K}{K_o}\right) = 0{\cdot}0203 + 1{\cdot}624\sigma \qquad (1)$$

2. Correlation coefficient (r) = 0·96

Jaffe[64] regarded r = 0·99-1·00 as excellent; 0·95-0·99 as satisfactory; 0·90-0·95 as fair; and below 0·90 as poor.

7.2 The ρ value

We have obtained a ρ value of 1·6 for the effect of substituents in the ring not containing the nitro group on the acidity of 4-nitrodiphenylamines. This value may be compared with the ρ value of phenols, anilinium ions and diphenylamine.

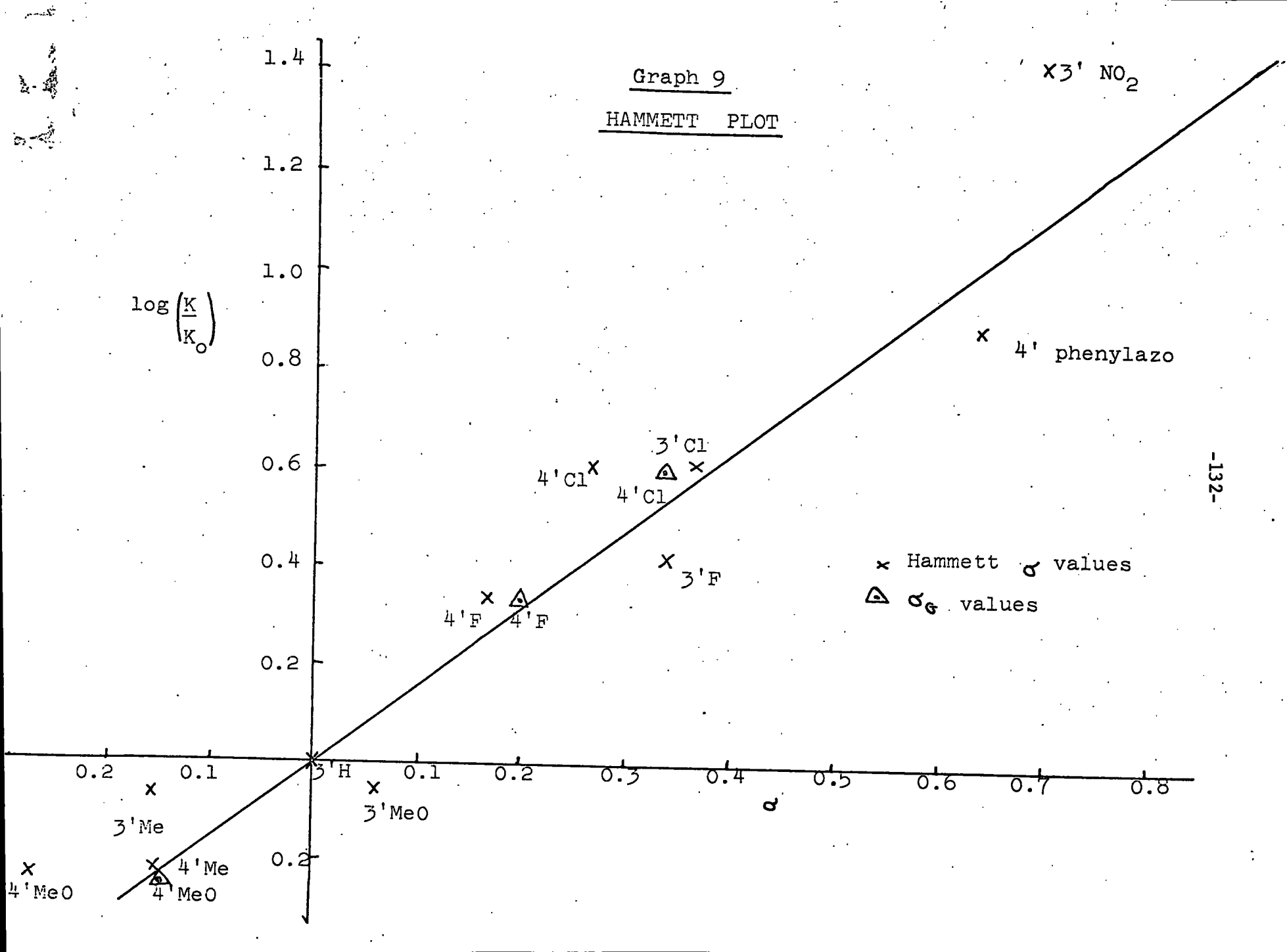

Graph 9
HAMMETT PLOT
1.4
1.2
1.0
0.8
0.6
0.4
0.2
0.2
log (K/K_o)
3' NO2
4' phenylazo
3'Cl
4'Cl
4'Cl
3'F
4'F
4'F
Hammett σ values
σ_G values
0.2
0.1
3'H
0.1
0.2
0.3
0.4
0.5
0.6
0.7
0.8
σ
3'Me
3'MeO
4'Me
4'MeO
4'MeO
-132-

TABLE LXII

Substituent	log K/K_o	σ constant
3'-CH_3	-0•512	-0•07
3'-H	0•0	0•0
3'-CH_3O	-0•066	0•06
3'-F	+0•4228	0•34
3'-Cl	+0•5825	0•37
3'-NO_2	+1•4228	0•70
4'-CH_3O	-0•2392	-0•27
4'-CH_3	-0•2304	-0•15
4'-F	+0•332	0•17
4'-Cl	+0•615	0•27
4'-phenylazo	+0•88	0•64
4'-phenyl	+0•1928	no reference in literature
4'-(4-nitrophenyl)	0•62	
4'-(4-nitrophenyl)D.P.A.	-0•069	
4'-(4-nitrophenylazo)D.P.A.	-0•276	

Reaction Parameters and Correlation Data for Acid Dissociation

Reaction Series	n	ρ	r
ArOH; H_2O; 25°	7	2·26 ± 0·07	0·997
ArOH; 49% EtOH; 21°	6	2·69 ± 0·24	0·984
$Ar\overset{+}{N}H_3$; H_2O; 25°	7	2·94 ± 0·06	0·999
$Ar\overset{+}{N}H_3$; 30% EtOH; 25°	5	3·19 ± 0·17	0·995
$Ar\overset{+}{N}(CH_3)_2H$; H_2O; 20°	3	3·56 ± 0·00	1·000
C_6H_5.NH.Ar; D.M.S.O.; H_2O	6	4·07	0·991
4-nitrodiphenylamines	11	1·624	0·96

The value of 1·6 for ρ is thus lower than the values for the ionisation of phenols and aromatic amines. Dolman and Stewart[65] have remarked that in the case of diphenylamines, an electron withdrawing substituent has a smaller effect on the acidity if there is an electron withdrawing substituent in the other ring.

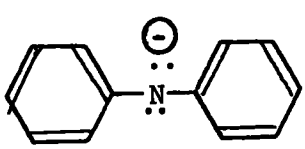
They quote the following results to demonstrate this:

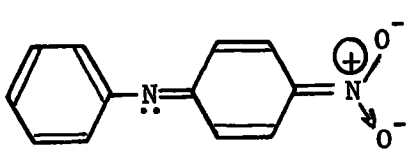
The pK_{HA} values of some nitrosubstituted diphenylamines

Substituent	Observed pK_{HA}	Calculated pK_{HA}
None	22•44	
2-nitro	17•91	
3-nitro	19•53	
4-nitro	15•67	
2,4-dinitro	13•84	11•14
3,4'-dinitro	14•66	12•76
4,4'-dinitro	14•08	8•9
2,4,6-trinitro	10•38	6•61
2,4,4'-trinitro	12•35	4•37

The effect of nitro groups on the acidity of diphenylamines is not additive, and the effect is most marked when the nitro groups are in both rings. Dolman and Stewart attribute this to the inability of both rings to attain simultaneously maximum overlap with the nitrogen atom.

Delocalisation of electrons effectively increase the electronegativity of the nitrogen relative to the diphenylamine anion and would be expected to reduce the effect of electron withdrawing substituents in the other ring:





This is probably one of the reasons why ρ is small compared with for diphenylamine. If one considers 4-nitrodiphenylamine as the standard and calculate the value of ρ for 4-nitro-3'-trifluoromethyl-diphenylamine and 4,3'-dinitrodiphenylamine using the formula:

$$\log\left(\frac{K}{K_o}\right) = \sigma\rho$$

$$\rho = 1{\cdot}42 \text{ and } 1{\cdot}65 \text{ respectively.}$$

Of course an accurate value cannot be obtained from two results but the values indicate the greatly reduced value of ρ when 4-nitro-diphenylamine is considered as the standard instead of diphenylamine.

These results also indicate the fact that the ρ values are only applicable over a limited range of acidities. It must be remembered however, that the ρ values for the diphenylamine was determined in aqueous dimethylsulphoxide whereas the ρ values in our case were determined in isopropyl alcohol.

The σ_G values for the 4'-substituted-4-nitrodiphenylamines gave the best correlation to the straight line defined by equation 1 (see Graph 9).

The σ_G values were derived from an examination of the rates of hydrolysis of substituted phenylacetic esters. In these compounds, no resonance interaction can occur between the substituent and the functional centre because of the insulation provided by the

intervening methylene group. The close correlation of the σ_G values would indicate that there is almost no resonance between groups which donate electrons and the nitrogen atom. This would again suggest that an electron withdrawing substituent has a smaller effect on the acidity if there is an electron withdrawing substituent in the other ring.

Comparison of corresponding σ values

Substituent	(a) σ_G	(b) Hammett σ	(c) Taft and Lewis σ^o	(d) σ^+	(e) σ^-	(f) σ
4'-CH_3O	-1•5	-0•27	-0•12	-0•78	-0•2	-0•17
4'-F	+0•20	+0•06	+0•17	-0•07	-0•02	+0•03
4'-Cl	+0•34	+0•23	+0•27	-0•11	-	+0•25

(a) Values from R.O.C. Norman, G.K. Radda, D.A. Brimacombe, P.D. Ralph, and E.M. Smith, J. Chem. Soc., 1961, 3247.

(b) Values from D.H. McDaniel and H.C. Brown, J. Org. Chem., 23, 420 (1958).

(c) R.W. Taft, Jr., J. Phys. Chem., 64, 1805 (1960).

(d) H.C. Brown and Y. Okamoto, J. Am. Chem. Soc., 80, 4979 (1958).

(e) A.I. Biggs and R.A. Robinson, J. Chem. Soc., 1961, 388.

(f) J.J. Hine, J. Am. Chem. Soc., 82, 4877 (1960).

7.3 Hammett Plot for 2'-substituted-4-nitrodiphenylamines

Various workers[66,67] have been unsuccessful in their attempts of a direct application of the Hammett equation to ortho-substituted

benzene derivatives partly because of steric effects. It has been shown however that substituted benzene reaction series in which the substituent and reaction site are not adjacent can be correlated by the Hammett equation using σ_p substituent constants. The Taft[68] σ_o^* values are almost identical with the σ_p values.

Charton[69,70] compared the effects of ortho- and para-substituents in phenyl propiolic acid and found that the transmission of a substituent in the ortho position was 0·75 times its effect in the para position.

Bowden[71] has recently studied a limited number of ortho-substituted benzoic acids in a wide variety of solvents. He found with ortho substituents which were not sterically demanding that the results could be correlated by a linear free energy relationship using σ_p values. The ortho substituents used were only those of moderate steric bulk, e.g. H, Me, F, Cl, Br, I, OMe. The hydroxyl and nitro-substituents did not correlate well presumably because of H-bonding in the case of the OH-group and the steric effect of the NO_2 group causing reduced conjugation. A value of 2·1 for ρ was observed.

Bowden's approach to the acidities of ortho-substituted benzoic acids may be subjected to some criticism since the ρ value for the ionisation of substituted benzoic acid is fixed at 1·00. Therefore the ionisation of the ortho substituted acid should perhaps have

been correlated by keeping a value of 1·00 for ρ and having special ortho-substitution σ values.

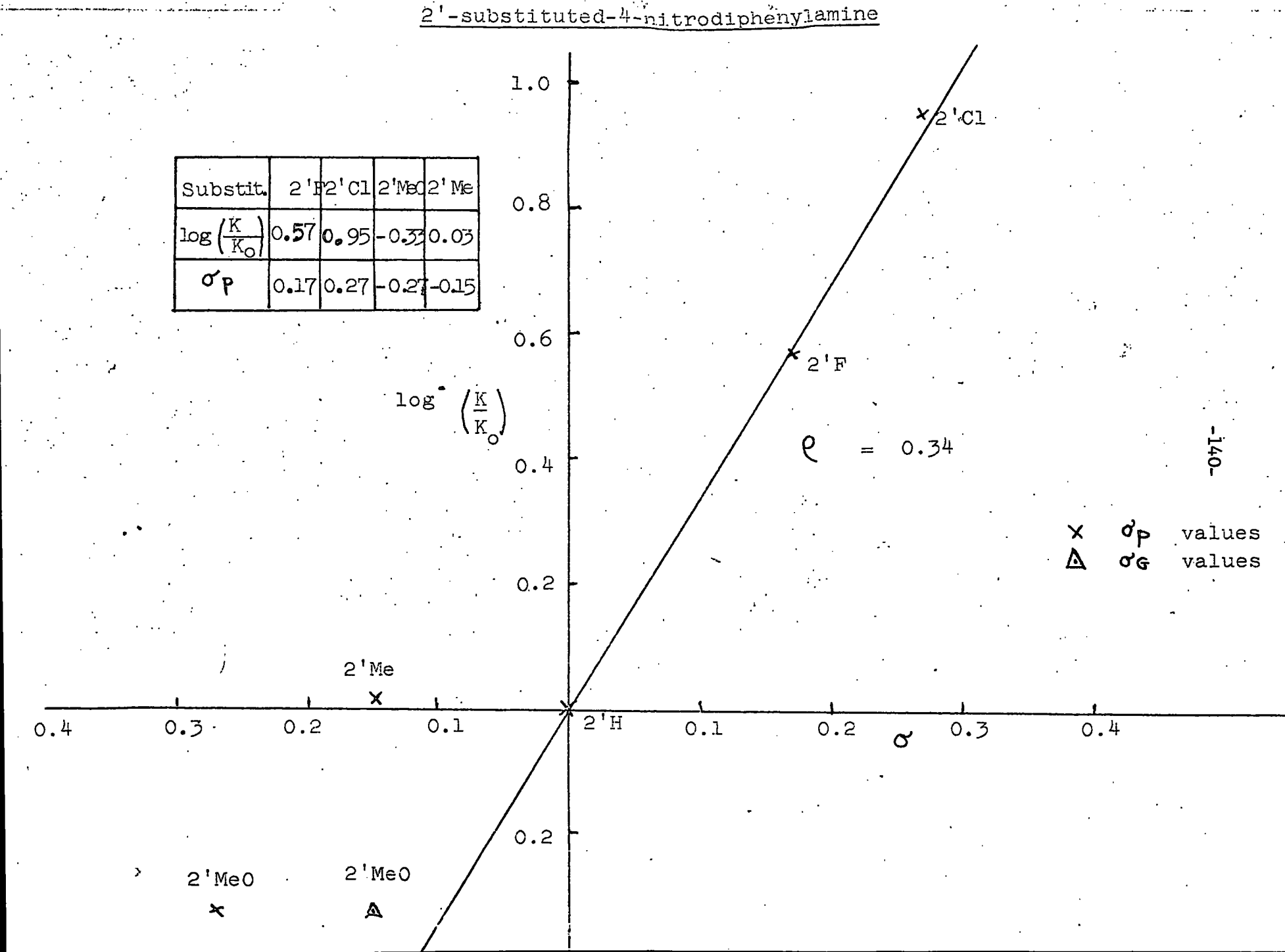
A possible justification of Bowden's approach is that in comparing reaction constants for the meta/para-substituted benzoic acids[65,71] with those of the ortho-substituted acids, it is noted that in the former system the values vary considerably with changes in the medium and in the latter the values are insensitive to medium changes. It is suggested that this is due to transmission by the field effect passing almost entirely through the molecular cavity for ortho-substituents. The transmission of polar effects in the para-substituted benzoic acids is explained by resonance and inductive effect considerations.

The assumption by Bowden that the ionisation of ortho-substituted benzoic acids can be treat as a seperate reaction series with a different ρ value may therefore be a valid one.

The assumption that the reaction constant is the same for ortho-substituted compounds as for meta- or para-compounds apparently suggests that the polar effects of substituents operate equally from the ortho- and para-positions. As a general rule this seems unlikely. Further, when Taft's 'polar free energy' equation[72] $\log(K/K_o) = \sigma^* \rho^*$ is applied to certain reaction series within which steric effects are apparently constant, ρ^* is not always found equal to the ordinary ρ-value, e.g. for the ionisation of ortho-substituted benzoic acids

2'-substituted-4-nitrodiphenylamine

Substit.	2'F	2'Cl	2'MeO	2'Me
$\log\left(\frac{K}{K_o}\right)$	0.57	0.95	-0.33	0.03
σ_p	0.17	0.27	-0.27	-0.15



in water ρ° = 1·79, compared with ρ = 1·00.

This brings to light a general difficulty in dealing with polar effects of ortho-substituents. A related matter is the use of a common ρ value for meta- and para-substituents. If ρ_o is distinctive, should there not also be ρ_m and ρ_p? This has been investigated by Jaffe[73] and by Ehrenson,[74] and developments may be expected.[75]

In view of Bowden's success in correlating ortho-benzoic acids with ortho-substituents of relatively small size we attempted to correlate our limited number of results. The results tend to indicate that the 2'-Cl and 2'-F-4-nitrodiphenylamines using σ_p values and the 2'-MeO-4-nitrodiphenylamine using a σ_G value will give a value for ρ of 3·4 with a reasonable correlation (see Graph 10). The 2'-methyl-4-nitrodiphenylamine showed poor correlation.

The ρ value for meta- and para-substituents is approximately half of the value for the 2'-substituted 4-nitrodiphenylamine series. The results are therefore in agreement with those of Bowden.

7.4 Transmission of Electronic Effects

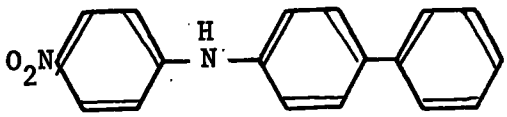
Considerable discussion has been made about the mechanism of transmission of substituent effects in recent reviews.[76] The contribution of the direct field effect, inductive effect through the molecular framework and the resonance effect are under dispute. Methods for the precise calculation of substituent constants are not possible although approaches in this direction have been made.

Measurement of the transmission of substituent effects through molecules has been done by a number of workers.[77] Most workers use the ρ values as an indication of the electronic transmission. The ratio of the ρ values before the interpolation of a group to the ρ value after the interpolation is considered as a measure of the transmission of the substituent effect. This ratio is termed the fall-off factor or attenuation factor.

Sager and Richie[78] use σ^* values i.e. measure the fall-off factor of X by comparing the σ^* values of -Y and -XY.

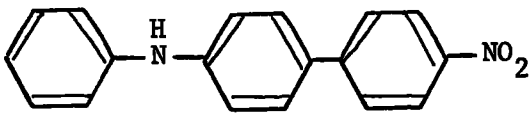
Calculation of Fall-Off Factor for Phenyl group

The relative acidities of the following compounds may be used:



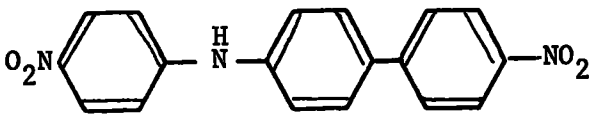
$K'_2 = 265$

(A)



$K''_2 = 145$

(B)



$K'''_2 = 710$

(C)

$$\log \frac{K_2'''}{K_2'} = \sigma_{NO_2}\rho'$$

$$0{\cdot}428 = \sigma_{NO_2}\rho'$$

Also $$\log \frac{K_2'''}{K_2''} = \sigma_{NO_2}\rho''$$

$$0{\cdot}700 = \sigma_{NO_2}\rho''$$

$$\frac{\rho''}{\rho'} = \frac{0{\cdot}700}{0{\cdot}428} = \underline{1{\cdot}64}$$

ρ' is a measure of the effect of the nitro group operating through two phenyl groups and ρ'' through one phenyl group. The fall-off factor for a phenyl group is therefore 1·64.

The fall-off factor for a $-CH_2$ group is quoted in the range 2-3.[79] Substituent effects are therefore more easily transmitted through benzene rings than $-CH_2$ groups.

Results have been obtained by other workers[80] which indicate a larger fall-off factor for the benzene ring.

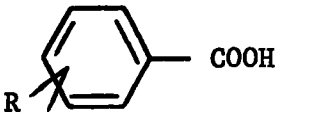
For acid dissociation of the following series the ρ values obtained are:

$R.CH_2.COOH \quad \rho = 1{\cdot}72$

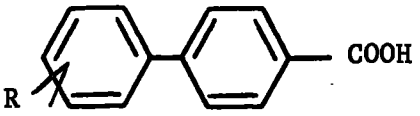
$\rho = 0{\cdot}56$

giving a fall-off factor of 3·1.

Also the following results[81] have been obtained in 50% butyl cellosolve.



ρ = 1·415

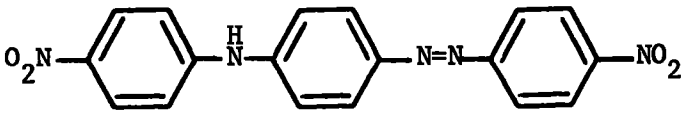


ρ = 0·482

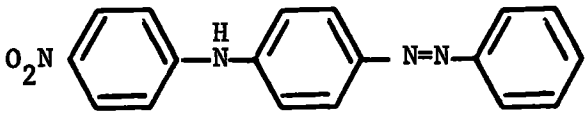
giving a fall-off factor of 2·98.

In these cases direct conjugation with the reaction site is not possible. This would explain the discrepancy between the above workers and our value for the fall-off factor. Transmission through a cross-conjugated ring is more effective.

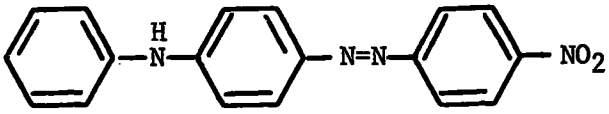
In the case of the nitroazodiphenylamines, we were unable to obtain pure 4-nitro-4'-(4-nitrophenylazo)-diphenylamine,



From the acidities of the 4-nitro-4'phenylazodiphenylamine and 4-(4'-nitrophenylazo)-diphenylamine it is clear that the transmission through an azo group is much smaller than through a benzene ring, i.e. fall-off factor is greater.



K_2 = 1290



K_2 = 90

In the second case where the nitro group must operate through a phenylazo group in addition to the benzene ring the acidity is reduced to a much greater extent than when the nitro group operates through two phenyl groups.

CHAPTER VIII

EXPERIMENTAL DETAILS FOR THE PREPARATION OF SUBSTITUTED DIPHENYLAMINES

8.1 Ullmann Reaction

8.1.1 Preparation of 4-nitrodiphenylamine

4-bromonitrobenzene (10 g.), aniline (10 g.), potassium carbonate (8 g.) and copper powder (0•1 g.) were heated to 190-200° for 8 hours. The contents were steam distilled to remove excess 4-bromonitrobenzene and aniline. The water was decanted and the residue washed with dilute hydrochloric acid. The product was treated with charcoal and recrystallised from alcohol. Orange crystals (alcohol). M.p.114°. Yield 0•2 g.

8.1.2 Preparation of 4'-methyl-2-nitrodiphenylamine

o-bromonitrobenzene (4 g.), p-toluidine (3•6 g.) and ethanol (2•0 ml.) were heated in a sealed tube at 180°C for six hours. The contents of the tube were then rinsed into a small distillation flask with ethanol, and excess of solvent removed. The dark material remaining was washed several times with dilute hydrochloric acid, then extracted with four 25 ml. portions of a hot benzene-ligroin solution. This was then evaporated to low volume, and allowed to cool. The orange-red precipitate was then filtered off and recrystallised from aqueous methanol solution as orange-red crystals (M.p. 68-70°). Yield 1•3 g.

8.2 Modified Ullmann Reaction

8.2.1 Preparation of 2-methyl-4-nitrodiphenylamine

o-Toluidine (1·5M) was condensed with 2-Cl-5-NO_2-benzene sodium sulphonate in glycol solution and using chalk (3 equivalents) as acid-binding agent for 10 hours at 190°. On cooling the mixture was acidified with dilute hydrochloric acid, boiled, filtered hot and the sulphonic acid separated from the filtrate. The diphenylamine-2-sulphonic acid, recrystallised from hot water, was not desulphonated by 50% w/w H_2SO_4 or by concentrated hydrochloric acid under reflux. To effect the desulphonation it was necessary to treat the free acid with an equivalent amount of sodium carbonate, dissolved in a minimum amount of water and crystallise the sodium salt. The sodium salt was desulphonated with 50% w/w H_2SO_4 after about 30 mins. The free diphenylamine was precipitated on addition to water. It was purified by repeated extraction with ligroin, orange-yellow plates, m.p.115°.

8.2.2 Preparation of 3'-methoxy-4-nitrodiphenylamine

Condensation between m-anisidine and p-chloronitrobenzene at 210° for 18-20 hours under a nitrogen atmosphere and using N-CH_3-2-pyrrolidone as solvent was affected. After steam distillation acidification and filtration, the diphenylamine was extracted from the residue with ligroin and finally crystallised from ligroin-benzene, yellow crystals, m.p.112°.

8.2.3. Preparation of 3-nitrodiphenylamine

Aniline (9•2 g.), 2-chloro-4-nitrobenzoic acid (10 g.), anhydrous sodium carbonate (10•4 g.) and butyl alcohol (33 ml.) were refluxed for four hours above the temperature of the constant boiling mixture of the alcohol and water. After steam distillation the diphenylamine carboxylic acid was precipitated by addition of mineral acid. Careful heating of this compound just above its melting point was accompanied by excessive charring and a 20% yield was recorded, m.p.232°.

8.3 Chapman Rearrangement

8.3.1 Preparation of 4-nitrodiphenylamine

C-phenylbenzimidoyl chloride was prepared by treating the benzanilide, previously dried at 110°, with PCl_5 on a water bath for about 15 minutes. After distilling off $POCl_3$ (b.p. 107°) at 20 mm pressure, the pure imidoyl chloride was distilled at 166-8°/8 mm.

The crystalline mass, formed by addition of dry Na-pNO_2-phenate (1•25M) to the imidoyl chloride, was extracted with methylene chloride. The residue was filtered off and the solvent removed at room temperature to leave the free imidate which crystallised from ethanol as yellow crystals, m.p.77°.

The benzoyl derivative of the diphenylamine was obtained by extraction with ethanol and activated charcoal, filtration,

crystallisation and finally recrystallisation from ethanol to give yellow crystals, m.p. 147°.

The hydrolysis of the benzoyl derivative with 50% aqueous-ethanolic potassium hydroxide, was complete after 30 mins. when the mixture was concentrated and poured onto water to precipitate the diphenylamine. After filtration and washing, the product was purified by vacuum sublimation. Bright yellow needles (m.p.114°).

8.3.2 Preparation of 3'-chloro-4-nitrodiphenylamine

The imidate was obtained from Na-pNO_2-phenate and benzo-3Cl-anilide iminochloride. Yellow crystals, m.p.103° from ethanol. The rearrangement was effected at 220° after 1 hour and subsequent hydrolysis of the benzoyl derivative gave the diphenylamine. Yellow crystals, m.p.143° from ethanol.

8.4 Smiles Rearrangement

8.4.1 Preparation of 4-nitrodiphenylamine

Stage I. Preparation of 4-nitrophenyl salicylate

Salicylic acid (100 g.), p-nitrophenol (100 g.), phosphorus pentachloride (52 g.) and xylene (500 ml.) were refluxed for 45 minutes when the evolution of hydrogen chloride ceased. The xylene was removed by steam distillation and the remaining residue was triturated with a saturated solution of sodium carbonate. The product was filtered, washed with water and dried in an oven. The

salicylate was purified by recrystallisation from benzene. Yield 122 g; m.p. 150-153°.

Stage II. Rearrangement of the salicylate to the 4'-nitro-2-carboxydiphenyl ether

The ester (17 g.) and 1M-NaOH (82 ml.) were refluxed for 75 mins. when all the solid ester dissolved. The solution was cooled and on addition of dilute hydrochloric acid, the ether separated as a brown oil which slowly crystallised on standing. After filtration the crude ether was dissolved in hot sodium carbonate solution and recrystallised by addition of concentrated hydrochloric acid.

The purified ether was washed with water, dried in a vacuum oven, and stored in a desiccator until needed. Yield 11·3 g., m.p. 160°.

Stage III. Preparation of 2-p nitrophenoxybenzoyl chloride

4'-nitro-2-carboxydiphenyl ether (10 g.) was warmed with excess thionyl chloride until the evolution of sulphur dioxide ceased. The excess thionyl chloride was removed under vacuum. An oil, was formed which separated as colourless crystals on standing.

Stage IV. Preparation of 2—p nitrophenoxybenzanilide

Aniline (1·5 g.) was added, in 50% excess, to a solution of the acid chloride (20 g.) in pyridine and left to react for 30 minutes. The mixture was then poured onto water. A brown oil

separated on addition of dilute hydrochloric acid which solidified on standing. After filtration the anilide was purified by recrystallisation from benzene, m.p.197-198°.

Stage V. Rearrangement of the anilide and hydrolysis to form the diphenylamine

Sodium hydroxide solution (100 ml. of 0·2M) was added to a solution of the anilide in a 4:1 mixture of acetone and water (150 ml.). The reaction mixture was stirred for 1 hour, pouted into water, and the rearranged product was precipitated by the addition of concentrated hydrochloric acid. The product was recrystallised from alcohol, m.p.233°.

The diphenylamine was obtained by hydrolysis on refluxing with a mixture of methanol (30 ml.) and aqueous potassium hydroxide (10 ml.) for 1 hour. The diphenylamine was recrystallised from alcohol, m.p. 114°.

8.4.2 Preparation of 4-nitro-4'-formyldiphenylamine

2-(4-nitrophenoxy-4'-formylbenzanilide was prepared by reaction of 2-p nitrophenoxybenzoyl chloride (9·1 g.) with p-amino benzaldehyde (4 g.). The p-amino benzaldehyde was prepared from p-nitrotoluene.[25]

Fresh crystalline sodium sulphide nonahydrate (30 g.), flowers of sulphur (15 g.) and sodium hydroxide (27 g.) were added to distilled

water (600 ml.). The mixture was heated on a steam-bath for 15-20 minutes with occasional stirring and then poured into a 2 litre flask containing a hot solution of p-nitrotoluene (50 g.) in 95% ethanol (300 ml.). The solution was refluxed for 3 hours.

The resulting deep red solution was rapidly steam distilled until about 1•5-2L of condensate were collected.

The residue had a volume of 500-600 ml. The solution was rapidly chilled in an ice-bath with stirring to induce crystallisation. After two hours in the ice-bath the crystals were collected by filtration and washed free of sodium hydroxide with 500 ml. of ice-cold water. The crystals were stored in a vacuum dessicator over caustic potash pellets. Yield 20 g., m.p.68-70°.

8.5 Preparation of 4-amino-4'-nitrodiphenyl

Suspended 44'-dinitrodiphenyl (10 g.) in 50% ethanol (600 ml.) with vigorous stirring and the mixture was boiled under reflux. A solution of sodium sulphide nonahydrate (16 g.) and sulphur (4•2 g.) in water (60 ml.) was added over 15 minutes and the mixture was refluxed for a further 30 minutes. After cooling the product was filtered and recrystallised from acetone, m.p.198°.

8.6 Preparation of 4-nitro-4'-hydroxydiphenyl[24]

4-nitro-4'-aminodiphenyl (6 g.) was dissolved in boiling dilute hydrochloric acid (500 ml. of 1%), the clear solution was cooled

rapidly to 10° and the sodium nitrite (2·4 g.) was added. After standing for 1 hour with occasional shaking the solution was filtered, dilute sulphuric acid added and the bulky precipitate of the diazonium sulphate was decomposed by steam. The precipitate obtained was filtered and extracted with boiling dilute aqueous potassium hydroxide. The extract was acidified with concentrated hydrochloric acid and the crude nitrophenol was precipitated, filtered and boiled with alcohol (100 ml.) leaving any dinitrophenol undissolved. The filtered alcohol extract was evaporated to dryness and the residue was recrystallised from benzene, melting point 198-200°. A very small yield was recorded.

8.7 Preparation of 4-diphenylyl benzoate

4-hydroxydiphenyl (30 g.) was suspended in cold sodium hydroxide (250 ml. of N solution) with vigorous stirring. The benzoyl chloride (28·52 g.) was added slowly to the suspension in 15% excess. When all the chloride was added the mixture was stirred for 1 hour and then filtered. The product was washed with a small quantity of alcohol to remove the last traces of benzoyl chloride. Recrystallised from alcohol, m.p.148°.

8.8 Nitration of 4-diphenyl benzoate[26]

To a solution of the ester (40 g.) in glacial acetic acid (310 ml.) at 85°, fuming nitric acid (100 ml.) was added, with stirring, at such a rate that the temperature was kept at 85-90° throughout. Under

these conditions nitration proceeded smoothly, and, as the last few mls. of nitric acid were added, the 4'-nitro-4-diphenyl benzoate began to separate from solution. After the mixture had cooled slowly to room temperature, the solid deposited was collected and washed in turn with water and methanol.

At this stage the product was contaminated with some 2'-nitro ester, but this was readily removed by a single crystallisation from acetic acid (500 ml.) followed by digestion of the resulting solid with boiling acetic acid (200 ml.). When the solution cooled pure 4'-nitro-4-diphenylyl benzoate (21 g.) was obtained, m.p.209-210°.

8.9 Preparation of 4-hydroxy-4'-nitrodiphenyl

A suspension of the 4'-nitroester (30 g.) in ethanol (150 ml.) was heated under reflux and hydrolysed by careful addition of a solution of potassium hydroxide (20 g. in 50 ml. of water). The immediate red colouration showed that hydrolysis was rapid, but, to ensure that it was complete, the mixture was heated for 15 minutes. On cooling, the potassium salt of 4-hydroxy-4'-nitrodiphenyl separated as deep blue lustrous plates (24 g.). These were dissolved in a minimum volume of hot water and acidified, 4-hydroxy-4'-nitrodiphenyl being precipitated as a bright yellow solid (18 g.), m.p. 200-201°.

8.10 Preparation of 2-nitrodiphenylamine

Preparation of the Acid Chloride

Stage I. o-nitrochlorobenzene (50 g.), o-cresol (38 g.), potassium hydroxide (16·5 g.) were heated for 2 hours at 130-140°. The product was extracted with ether and washed with 10% potassium hydroxide. The ether was removed under water vacuum.

Stage II. The product from Stage I (24 g.) in 200 ml. of pyridine was treat portion-wise with potassium permanganate (75 g. in 375 ml. of hot water) at 90° for 1 hour. The reaction mixture was filtered while hot and the product was concentrated under water vacuum. The residue was washed with ether and acidified. The product was recrystallised from ethanol. Yield 17·5 g., m.p.154°.

Stage III. The product from Stage II was treated with thionyl chloride (50% excess) under reflux until the evolution of sulphur dioxide ceased. The excess thionyl chloride was removed by heating on an oil bath at 100°C under water vacuum with an air bleed. The product was purified by recrystallisation from benzene.

The acid chloride was readily converted into 2-nitrodiphenylamine by the Smiles rearrangement.

Treatment of Acid Chloride

Preparation of anilide. The acid chloride (3 g.) was dissolved in 'Analar' pyridine (10 ml.) and the amine (50% excess) was added. The reaction mixture was heated to 80°C in a water-bath and this

temperature was maintained for 30 minutes. The resultant product was poured into water (100 ml.) and on acidification with concentrated hydrochloric acid (30 ml.), a precipitate was formed which was filtered and washed with water.

Rearrangement of the anilide. The anilide was added to acetone (40 ml.) and N-NaOH (10 ml.). The mixture was shaken until the anilide dissolved and left to stand for 30 minutes. Concentrated hydrochloric acid (2 ml.) was added and the bulk of the acetone was removed by immersing the flask in a bath of warm water and blowing air over the surface of the solvent. At this stage oils were formed which solidified on standing.

Hydrolysis. The rearranged anilide was refluxed for 1 hour with alcohol (15 ml.) and a saturated solution of aqueous potassium hydroxide (5 ml.). The reaction mixture was poured into water and acidified with concentrated hydrochloric acid (10 ml.). Filtered and purified by recrystallisation.

8.11 Preparation of 4-anilino-4'-nitroazobenzene

p-nitroaniline (4 g.) was diazotised and added to an excess of an aqueous alcoholic solution of diphenylamine (3·1 g.) containing sodium acetate (1·5 g.). A precipitate of 4-anilino-4'-nitroaxobenzene was obtained. The product was filtered and recrystallised from alcohol, m.p.128°.

APPENDIX I

COMPUTER PROGRAMME AND RESULTS

```
0   'PROGRAM' (BRM6)
0   'INPUT' 0 = CRO
0   'OUTPUT' 0 = LPO
0   'BEGIN'
1   'REAL' A,A1,A2,YO,YN,INCR,X,Y,Z,Q:
1   'INTEGER' I,J,M,N,H:
2   'REAL' 'ARRAY' B,C,D[1:100], E,F[1:50]:
3   N: = READ:
5   'FOR' J: = 1 'STEP' 1 'UNTIL'N'DO'
6   'BEGIN'
6   E[J]: = READ/10↑4:  E = K1
8   F[J]: = READ/10↑3:  F = K3
9   'END'
10  L2:M: = READ:
11  'FOR' I: = 1 'STEP'1' UNTIL 'M'DO'
12  'BEGIN'
12  B[I]: = READ/10↑4:  B = [PrO⁻]left
14  C[I]: = READ/10↑5:  C = [Anion]total
15  D[I]: = READ/10↑5:  D = [HA]
16  'END'
```

```
17   'FOR'I: = 1 'STEP' 1 'UNTIL'M'DO'
18   'BEGIN'
18   NEWLINE(5):
20   SPACE(20);
21   WRITE TEXT ('('B=')'):
22   PRINT (B[I],0,6);
23   SPACE(10);
24   WRITE TEXT ('('C=')');
25   PRINT (C[I],0,6);
26   SPACE(10);
27   WRITE TEXT ('('D=')');
28.  PRINT (D[I],0,6);
29   NEWLINE (2);
30   SPACE (10);
31   NEW LINE (2);
32   'FOR' J: = 1'STEP'1'UNTIL'N'DO'
33   'BEGIN'
33   A: = (B[I] + C[I])*E[J]*F[J];
35   A1: = E[J]*F[J]-B[I]*E[J]-C[I]*F[J];
36   A2: = E[J]+[J];
37   X: = 0;
38   YN: = -A
39   INCR: = 0,01;
```

```
40   H: = 1;
41   START:YO: = YN;
42   X: = X + H*INCR;
43   YN: = X↑3 + A2*X↑2 + A1*X-A;
44   'IF' YO*YN>O'THEN''GOTO'START;
45   INCR: = INCR/10;
46   H: =-H;
47   'IF'INCR>O.OOOOOO 1'THEN' 'GOTO' START;
48   Y: = B[I]*E[J]/(X + E[J]);
49   Z: = C[I]*F[J]/(X + F[J]);
50   Q: = Z/(D[I]*Y);
51   NEWLINE(1);
52   PRINT (E[J],O,6);
53   SPACE (5);
54   PRINT (F[J],O,6);
55   SPACE (5);
56   PRINT (X,O,6);
57   SPACE (5);
58   PRINT (Y,O,6);
59   SPACE (5);
60   PRINT (Z,O,6);
61   SPACE (5);
```

```
62    PRINT (Q,0,6);
63    NEWLINE (1);
64    'END';
65    'END';
66    'GO TO' L2;
67    'END'
```

APPENDIX II

CALCULATION OF K_1 for 3'-CHLORO-4-NITRODIPHENYLAMINE

Taking $K_3 = 2 \times 10^{-3}$ mole l^{-1} and $K_2 = 700$ mole^{-1}l. (by extrapolation)

Now $$K_3 = \frac{[M^+][A^-]}{[M^+A^-]} = 2 \times 10^{-3} \qquad \text{(i)}$$

and $$K_2 = \frac{[A^-]}{[HA][PrO^-]} = 700 \qquad \text{(ii)}$$

Since

$$[PrO^-] = [M^+]$$

Then

$$\frac{[A^-]}{[M^+]} = 700 \times [HA]$$

$$\therefore \quad [A^-] = 700.[HA].[M^+]$$

Substituting for $[A^-]$ in (i)

$$2 \times 10^{-3} = \frac{[M^+]^2.700.[HA]}{[M^+A^-]} \qquad \text{(iii)}$$

Since

$$[Anion]_{total} = [M^+A] + [A^-]$$

$$[M^+A^-] = [Anion]_{total} - [A^-]$$

Substituting in (iii) for $[M^+A^-]$

$$2 \times 10^{-3} = \frac{[M^+]^2 . 700 . [HA]}{[Anion]_{total} - [A^-]}$$

Substituting for $[A^-]$

$$2 \times 10^{-3} = \frac{[M^+]^2 . 700 . [HA]}{[Anion]_{total} - (700 . [HA] . [M^+])} \qquad \text{(iv)}$$

Consider:

$$[Pr^{(i)}O^-]_{left} = 33{\cdot}0 \times 10^{-4} \text{ moles/litre}$$

$$[Anion]_{total} = 1{\cdot}61 \times 10^{-5} \text{ moles/litre}$$

$$[HA] = 1{\cdot}121 \times 10^{-5} \text{ moles/litre}$$

Substituting in equation (iv)

$$2 \times 10^{-3} = \frac{[M^+]^2 \times 700 \times 1{\cdot}121 \times 10^{-5}}{1{\cdot}61 \times 10^{-5} - (700 \times 1{\cdot}121 \times 10^{-5} \times [M^+])}$$

$$7{\cdot}847 \times 10^{-3}[M^+]^2 + 15{\cdot}69 \times 10^{-6} . [M^+] - 3{\cdot}22 \times 10^{-8} = 0$$

Solving for $[M^+]$

$$[M^+] = \underline{1{\cdot}259 \times 10^{-5} \text{moles/litre}}$$

Now since $[M^+Pr^{(i)}O^-] = [Pr^{(i)}O^-]_{left} - [M^+]$ and

$$[Pr^{(i)}O^-] = [M^+]$$

$$[M^+Pr^{(i)}O^-] = 3{\cdot}3 \times 10^{-3} - 1{\cdot}259 \times 10^{-3}$$

$$= \underline{2{\cdot}041 \times 10^{-3} \text{ moles/litre}}$$

Then $$K_1 = \frac{[M^+]^2}{[M^+Pr^{(i)}O^-]} = \frac{1{\cdot}259^2 \times 10^{-6}}{2{\cdot}041 \times 10^{-3}}$$

$$= \underline{\underline{7{\cdot}74 \times 10^{-4} \text{ mole } 1^{-1}}}$$

REFERENCES

1. The Acridines, Adrien Albert, Ch.4.
2. Fanta, Chem. Revs., 64, 6 1964 and subsequent references.
3. Jourdan, Ber., 1885, 18, 1444.
4. Ullmann, Ber., 1907, 355, 342.
5. Ullmann, Kipper, Ber., 38, 2120, 1905.
6. Albert and Gledhill, Ber., 64, 169, 1945.
7. Ullmann and Dahmen, Ber., 1908, 41, 3746.
8. Fanta, Chem. Revs., 64, 6, 1964.
9. Goldberg and Sissoef, Ber., 1907, 40, 4541.
10. J.C.S., 1928, 355.
11. Chapman, J.C.S., 1927, 1743 and Hall, J.C.S., 1948, 1603.
12. Organic Reactions, 1965, Vol.14, p.1.
13. Chapman, J.C.S., 1929, 569.
14. Mumm, Hesse and Volquartz, Ber., 1915, 48, 379.
15. Chapman, J.C.S., 1927, 1743.
16. Wheatley, The Acidity and Basicity of Aromatic Media, 1965.
17. Wiseberg and Rowland, J. Amer. Chem. Soc., 77, 2205, 1955.
18. Patai, 1967, Chemistry of Ether Linkages and subsequent references.
19. Warren and Smiles, J.C.S., 914 (1931) and subsequent papers.
20. Bunnett and Zahler, Chem. Revs., 49, 273 (1951), also Bunnett Quart.Revs., London, 12, 1 (1958).

21. Levy, Rains and Smiles, J.C.S., 3264 (1931).

22. Clement and Smiles, J.C.S., 1016 (1937).

23. Okamoto and Bunnett, J.A.C.S., 78, 5357 (1956); J.A.C.S. 78, 5363 (1956).

24. Bell and Kenyon, J.C.S., 1926, 3028.

25. Organic Synthesis, Vol.31, p.6.

26. Finar, p.647.

27. Chem. Abstracts, 50, 24799.

28. J.C.S.(B), 1966, p.498; J.C.S.(B), 1967, p.23.

29. Wheatley, The Acidity and Basicity of Aromatic Media, 1965, p.38.

30. Stearns and Wheland, J. Amer. Chem. Soc., 69, 2025, 1947.

31. Hine and Hine, J. Amer. Chem. Soc., 74, 5266, 1952.

32. Veimesse-Jacquinat, Schaal and Rumpf., Bull Soc. Chim., 1960, 230.

33. Wheatley - The Acidity and Basicity of Aromatic Media, 1965, p.40.

34. A. Brandstrom, Arkiv for Kemi II, 1957, p.527 and 567.

35. Fuoss and Kraus, J. Amer. Chem. Soc., 55 (1933) 1019; Fuoss, ibid, 80 (1958) 5059; Krauss and Fuoss, J. Amer. Chem. Soc., 55 (1933) 21; Robinson and Stokes, Electrolyte Solutions, p.392.

36. Bjerrum, danste vidensk. Selsk, 7 (1926) No.9; 'Selected Papers', p.108, Einar Munksgaard Copenhagen (1949).

37. Renolds and Kraus, J. Amer. Chem. Soc., 1948, 70, 1709; Gover and Sears, J. Phys. Chem., 1956, 60, 330; Shedlovsky and Goffredi, J. Phys. Chem., 1967, 71, 2176.

38. Bjerrum, Kgl. danske Videnskab, Mat-fys. Medd., 1926, 7, No.9.

39. Prue, Ionic Equilibria (1966) p.109.

40. Barrow, Physical Chemistry, International Student Edn., pp.162 and 370. New York, McGraw-Hill, 1961.

41. Hammett, Chem. Revs., 1935, 17, 125.

42. Burkhardt, Ford and Singleton, J.C.S., 1936, 17.

43. Hammett, J. Amer. Chem. Soc., 1937, 59, 96.

44. Hammett, Physical Organic Chem., Ch.7, New York, McGraw-Hill, 1940.

45. Jaffe, Chem. Revs., 53, 191, 1953.

46. Branch and Calvin: Theory of Organic Chem., Ch.2, London, Bell, 1953.

47. Hammett, Physical Organic Chem., Ch.7, New York, McGraw Hill, 1940.

48. Biggs and Robinson, J.C.S., 1961, 388.

49. Brown and Okamoto, J. Amer. Chem. Soc., 80, 4979 (1958).

50. von Bekkum, Verkade and Wepster, Red. Trav. Chim., Poys-Bas, 1959, 78, 815.

51. Taft and Lewis, J. Amer. Chem. Soc., 80, 2436, 1958.

52. Taft and Lewis, J. Amer. Chem. Soc., 81, 5343, 1959.

53. Taft and Lewis, Tetrahedron, 5, 210, 1959.

54. Norman, Radda, Brimacombe, Ralph and Smith, J.C.S., 1961, 3247.

55. Taft, J. Amer. Chem. Soc., 74, 3120, 1952.

56. Taft, J. Amer. Chem. Soc., 75, 4231, 1953.

57. Taft, Steric Effects in Organic Chem., Ch.13, Wiley, NewYork, 1956.

58. Newman and Merrill, J. Amer. Chem. Soc., 77, 5552, 1955.

59. Roberts and Carboni, J. Amer. Chem. Soc., 77, 5554, 1955.

60. Solomon and Filler, J. Amer. Chem. Soc., 85, 3492, 1963.

61. Chapman, Shorter and Toynne, J.C.S., 1961, 2543; Chapman, Shorter and Utley, J.C.S., 1963, 1291; Bowden and and Chapman, J.C.S., 1963, 5239 and 1964, 3370.

62. An examination of Structure-Reactivity Relationships, Ritchie and Sager; Progress in Physical-Organic Chem., Cohen Streitweiser and Taft, Vol.2.

63. Clark and Perrin, Quart. Revs., 1964, 18, 295. Progress in Physical-Organic Chem., Cohen Streitweiser and Taft, Vol.2, p.323. Linear Free Energy Relationships, J. Shorter (Chem. in Britain).

64. Jaffe, Chem. Rev., 1953, 53, 191.

65. Dolman and Stewart, J. Can. Chem. Soc.

66. Charton, Ca. J. Chem., 38, 2493 (1960).

67. Mammalis and Rydan, J.C.S., 1049 (1955).

68. Taft, Steric Effects in Organic Chem. Ed. M.S. Newman, John Wiley and Sons Inc., New York, 1957, p.556.

69. Charton, Can. J. of Chem., 1960-38, 2493 (1960).

70. Charton, J. Organic Chem., 1961, 26, 735.

71. Bowden and Manser, Can. J. of Chem., 1967, 46, 2941.

72. Taft, Steric Effects in Organic Chemistry, ed. Newman, Ch.13, 1956.

73. Roberts and Jaffe, J. Amer. Chem. Soc., 1959, 81, 1635.

74. Ehrenson, Progress in Physical Organic Chemistry, Vol.2, p.195, New York, 1964.

75. Communication at Second Conference of Linear Free Energy Relationships, Irvine, California, 1968.

76. Ritchie and Sager, Progress in Physical Organic Chemistry, Vol.2, p.384.

77. Branch and Calvin, Theory of Organic Chemistry, 1941, p.203 New York, Prentice Hall. McGowan, Chemistry and Industry, 1948, p.632. Peters, Chem. Soc., 1957, p.2654. Soloway and Lipschitz, J. Org. Chem., 1958, 23, 613. Stevenson and Williamson, J. Amer. Chem. Soc., 1958, 80, 5943. Wepster, Rec. Trav. Chim., Pays-Bas, 1952, 71, 1511. Litvinenko and Grekov, J. Gen. Chem., 27, 234 (1957).

78. Sager and Richie, J. Amer. Chem. Soc., 83, 3498 (1961).

79. Wells, Linear Free Energy Relationships, Academic Press, 1968.

80. Taft, Steric Effects in Organic Compounds, ed. M.S. Newman, Wiley, New York, 1956. van Bekkum, Verkade and Wepster, Rec. Trav. Chim., 78, 815 (1959).

81. Berliner and Blommers, J. Amer. Chem. Soc., 73, 2479 (1951).