DISASSOCIATION CONSTANTS OF

SOME NAPHTHYLAMINES AND

ACENAPHTHENAMINES AND THEIR

DIMETHYL DERIVATIVES

A thesis presented for the
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G. J. Sutherland

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## CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>ABSTRACT</td>
<td>1</td>
</tr>
<tr>
<td>INTRODUCTION</td>
<td>2</td>
</tr>
<tr>
<td>FACTORS AFFECTING THE BASIC STRENGTHS OF AMINES</td>
<td>3</td>
</tr>
<tr>
<td>Electronic Effects</td>
<td>4</td>
</tr>
<tr>
<td>Substituent Effects</td>
<td>5</td>
</tr>
<tr>
<td>Steric Effects</td>
<td>10</td>
</tr>
<tr>
<td>Steric Effects in Amines</td>
<td>12</td>
</tr>
<tr>
<td>The Primary Amino Group</td>
<td>13</td>
</tr>
<tr>
<td>The Dimethylamino Group</td>
<td>16</td>
</tr>
<tr>
<td>The Protonated Amino Groups</td>
<td>20</td>
</tr>
<tr>
<td>EXPERIMENTAL</td>
<td>26</td>
</tr>
<tr>
<td>PREPARATION OF THE AMINES</td>
<td>26</td>
</tr>
<tr>
<td>Outline of Preparative Methods</td>
<td>26</td>
</tr>
<tr>
<td>(a) 4-Methyl-1-naphthylamine</td>
<td>26</td>
</tr>
<tr>
<td>(b) 4-Methyl-2-naphthylamine</td>
<td>28</td>
</tr>
<tr>
<td>(c) 4,5-Dimethyl-1-naphthylamine</td>
<td>30</td>
</tr>
<tr>
<td>(d) 4,5-Dimethyl-2-naphthylamine</td>
<td>33</td>
</tr>
<tr>
<td>(e) 5-Acenaphthenamine</td>
<td>39</td>
</tr>
<tr>
<td>(f) 4-Acenaphthenamine</td>
<td>42</td>
</tr>
<tr>
<td>The Dimethylamino Compounds</td>
<td>47</td>
</tr>
<tr>
<td>Experimental Details</td>
<td>48</td>
</tr>
<tr>
<td>(a) Preparation of 4-Methyl-1-naphthylamine</td>
<td>48</td>
</tr>
<tr>
<td>(b) Preparation of 4-Methyl-2-naphthylamine</td>
<td>50</td>
</tr>
<tr>
<td>(c) Preparation of 4,5-Dimethyl-1-naphthylamine</td>
<td>52</td>
</tr>
<tr>
<td>(d) Preparation of 4,5-Dimethyl-2-naphthylamine</td>
<td>58</td>
</tr>
</tbody>
</table>
ABSTRACT

In order to assess the relative electronic effects of the 1-methyl and "1,8-dimethyl" groups and of theacenaphthene bridge in the naphthalene series, the following amines and their N,N-dimethyl derivatives have been prepared: 4-methyl-1-naphthylamine, 4-methyl-2-naphthylamine, 4,5-dimethyl-1-naphthylamine, 4,5-dimethyl-2-naphthylamine, 5-acenaphthenamine and 4-acenaphthenamine. 1-Naphthylamine and 2-naphthylamine have been purified and their N,N-dimethyl derivatives prepared. The dissociation constants of the conjugate acids of these amines have been measured by an ultraviolet spectrophotometric method, and the results have been interpreted in terms of the electron releasing properties of the substituents.

A novel reaction between trimethyl phosphate and some 2-naphthylamines has been discovered, and this has been briefly investigated.
INTRODUCTION

Some of the recent work in this department has been concerned with the relationship of reactivity to structure in naphthalene compounds. In the most recent investigation, the dissociation constants of the unsubstituted, 4-methyl- and 4,5-dimethyl-naphthoic acids and of the acenaphthoic acids were measured and interpreted in terms of substituent effects. The present study extends that work. To obtain a better understanding of the effects of the 1-methyl, "1,8-dimethyl" and 1,8-dimethylene groups on the naphthalene nucleus, a series of amino and dimethylamino derivatives of naphthalene, 1-methylnaphthalene, 1,8-dimethylnaphthalene and acenaphthene have been synthesized, and their $pK_a$ values determined. The primary amines studied are shown in fig. 1. All have also been converted to their $N,N$-dimethyl derivatives. It should be noted that in

Throughout this thesis, acid and base strengths will be expressed as $pK_a$ values.

For acids \[ pK_a = -\log_{10} K_a \quad K_a = \frac{[H^+][A^-]}{[HA]} \]
where $A^-$ is the anion of the acid $HA$.

For bases \[ pK_a = -\log_{10} K_a \quad K_a = \frac{[H^+][B]}{[HB^+]} \]
where $HB^+$ is the conjugate acid of the base $B$.

High values of $pK_a$ therefore indicate strong bases or weak acids, and vice versa. Unless otherwise stated, $pK_a$ values quoted from the literature are in water at 25°.
acenaphthene derivatives the aliphatic carbon atoms are numbered 1 and 2, and the aromatic carbon atoms are then numbered in the same sequence as in the naphthalene series.

\[
\begin{array}{cccc}
\text{1-Naphthylamine} & \text{4-Methyl-1-naphthylamine} & \text{4,5-Dimethyl-1-naphthylamine} & \text{5-Acenaphthyamine} \\
\text{2-Naphthylamine} & \text{4-Methyl-2-naphthylamine} & \text{4,5-Dimethyl-2-naphthylamine} & \text{4-Acenaphthyamine} \\
\end{array}
\]

Some of the concepts having a bearing on the present work and to be used in discussing the results will now be considered.

**FACTORS AFFECTING THE BASIC STRENGTHS OF AMINES**

There is fairly general agreement among recent workers about the factors affecting the basic strengths of amines.
Nevertheless the data is much less extensive than that concerning carboxylic acids, and there are many areas where the relative contributions of different effects have not been fully evaluated. The present discussion will be mostly concerned with the factors affecting the basicities of aromatic amines, in particular, amines containing the NH$_2$ and NMe$_2$ groups. Any points about which different workers disagree will be noted and commented on.

**ELECTRONIC EFFECTS.**

Electronic effects on the basic strengths of aromatic amines and dimethylamines are qualitatively the same, and the discussion will be pursued mostly in terms of the former.

Figure II shows the most important canonical structures of aniline, together with the anilinium ion in which no conjugation with the functional centre can occur. In comparison with the aliphatic amines, most aromatic amines are stabilized by the resonance depicted. Added to the mesomeric effect of the aromatic nucleus is its -I (electron withdrawing) effect which results in destabilization of the anilinium ion relative to its aliphatic counterpart. Both major electronic effects therefore tend to make
aromatic amines much weaker bases than aliphatic ones, and this may be illustrated by comparing the $pK_a$ of aniline (4.58)\(^{16}\) and cyclohexylamine (10.64)\(^{16}\). Webster\(^{17}\) has shown that about half the difference between these two values results from the additional resonance stabilization of aniline, and about half results from the inductive effect of the aromatic ring destabilizing the anilinium ion.

**Substituent Effects.**

Examination of fig. II reveals that any substituent in the aromatic nucleus which enhances the conjugative transfer of electrons from the amino group to the aromatic ring will be base weakening, because it increases the importance of structure (b) and therefore stabilizes the base. Conversely a substituent inhibiting mesomerism is base strengthening. In contrast, the arylammonium ion is destabilized by the presence of electron attracting groups because they inhibit distribution of the ionic charge over the whole molecule. On the other hand, electron donors assist in the distribution of the ionic charge, thereby stabilizing the ion and weakening it as an acid. Therefore, because of their effects both on the amine and its conjugate acid, electron repelling groups make amines stronger bases, and electron attracting groups make them weaker bases.

There are several mechanisms by which substituents are considered to affect a distant reaction site, and the relative importance of each mechanism depends on the nature of the substituent.
The main methods of interaction are the inductive effect, the direct field effect and the mesomeric effect.

The "inductive effect" of a substituent is the effect of its pole or dipole relayed through the \( \sigma \) bonds of the system considered. If the group attracts electrons it has a \(-I\) effect, if it releases them it has a \(+I\) effect. Inductive effects are generally thought to fall off with increasing distance between the interacting centres, although some writers believe that they are felt less strongly at the meta position than at the ortho and para positions. Inductive effects may be inherent, and they may be enhanced by the presence of another substituent or reactant.

The "direct field effect" is the effect of the pole or dipole of a substituent transmitted through space or the solvent surrounding the molecule. In some situations it can be shown to be a very real effect, but it is usually difficult or impossible to distinguish from the inductive effect, and in practice it is almost always included in it.

The "mesomeric effect" of a substituent is exerted by means of its interaction with the \( \pi \) electrons of the aromatic nucleus. Mesomeric (or conjugative or resonance) effects are usually associated with substituents having either a lone pair of electrons (\(+M\) groups, electron donors), or an electronegative atom in an unsaturated system (\(-M\) groups, electron attracters). For example, fig. II shows the main canonical forms of aniline, in which the amino group is a typical \(+M\) substituent, and fig. III shows the
predominant canonical forms of nitrobenzene, in which the nitro group is a \(-\)M substituent. In order to exert its full mesomeric effect a group must be coplanar with the aromatic ring. As with the inductive effect, mesomerism may be inherent and it may be induced by the presence of a reactive entity in the vicinity of the molecule concerned. Resonance effects are transmitted much more strongly to the ortho and para positions of a benzene ring than to the meta position, as is shown in fig. III.

Resonance interactions may be considerably enhanced when an aromatic molecule contains two resonating groups with different M effects located ortho or para to each other. For reasons associated with steric effects (to be discussed later), resonance
interactions may in fact be destroyed when the groups are located ortho to each other. \( p \)-Nitroaniline (fig. IV) is an example of a molecule in which extended resonance does occur.

Alkyl groups, especially methyl groups, are generally thought to act by a limited type of mesomerism called hyperconjugation. Although the origins of the phenomenon are somewhat obscure, it is usually represented in the manner shown in fig. V.

"Resonance polar effect" is the term used to describe a mesomeric effect which must be relayed to the functional centre in part by induction. It occurs when a substituent is capable of conjugation with an aromatic ring, but complete "through conjugation" such as that in \( p \)-nitroaniline (fig. IV) cannot be realized. This situation arises when two potentially conjugating groups are located meta to each other, or when two groups in any relative orientations are either (i) both \(+M\) or \(-M\), or (ii) only one is capable of mesomerism with an aromatic system. Stabilizing resonance polar effects may be illustrated with reference to the canonical forms in meta- and para- amino anilinium ions (fig. VI). The presence of the effect in these systems is revealed by an examination of the \( pK_a \)
values of aniline (4.65)\textsuperscript{37}, m-phenylenediamine (4.83)\textsuperscript{40} and p-phenylene diamine (6.08)\textsuperscript{40}. If the -I effect only of the amino group was operative, the diamines would have pK\textsubscript{a} values below that of aniline, and the fact that they have higher pK\textsubscript{a} values is a result of the resonance polar electron donating properties of the amino substituents. It can be seen from fig. VI that the resonance polar effect of a meta substituent is transmitted by conjugation to the carbon atoms ortho to the reference substituent, and inductively from there. However, the resonance polar effect of an ortho or para substituent is transmitted by resonance to the carbon atom bearing the reference group, and by induction to that group. Resonance polar effects are therefore most strongly felt at the ortho and para positions.
STERIC EFFECTS.

Under this heading the four general types of steric effect will be considered. Because the spatial disposition of the nitrogen valencies is quite complicated, the applications of the general steric effects to aromatic amines will be deferred till later.

The "primary steric effect" is steric compression between two adjacent groups. As a result, molecules in which it occurs are thermodynamically less stable than those in which it does not. For example, the primary steric effect is responsible for the fact that boron trifluoride forms a stable adduct with pyridine, but does not form a compound at all with 2,6-lutidine. In many systems the primary steric effect is difficult to detect alone because it results in one of the more specialized steric effects indicated in the following paragraphs.

"Steric inhibition of mesomerism" occurs when a substituent near a potentially resonating group forces the latter to rotate out of the plane of the ring, thereby preventing it from indulging in its maximum resonance with the aromatic system. Under these circumstances the molecule assumes a rotational configuration in which the total energy is minimized. The loss in resonance energy is compensated for by the decrease in steric strain energy. Steric inhibition of resonance has been demonstrated for many systems, and an example is chosen here from the nitroaniline series.
The $pK_a$ values of some anilines are shown below. The unusually large effects of the methyl substituents on the $pK_a$ values in the

<table>
<thead>
<tr>
<th>Compound</th>
<th>$pK_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>4.25</td>
</tr>
<tr>
<td>3,5-Dimethylaniline</td>
<td>4.48</td>
</tr>
<tr>
<td>4-Nitroaniline</td>
<td>1.09</td>
</tr>
<tr>
<td>3,5-Dimethyl-4-nitroaniline</td>
<td>2.26</td>
</tr>
</tbody>
</table>

* Measured in 50% ethanol.

nitroanilines is attributed to their effect in inhibiting the mesomerism of the nitro group with the rest of the molecule.

"Steric inhibition of solvation" is a manifestation of the primary steric effect in which a nearby group interacts with the solvation shell of a substituent. It is conveniently illustrated with reference to its effect on aniline-anilinium ion equilibria. Because of its solvation shell, the $NH_2^+$ substituent is generally considered to be larger than the $NH_2$ substituent, and a nearby group should therefore be base weakening as a result of its effect in decreasing solvation of the ion. This is indeed shown by the $pK_a$ values of aniline (4.58) and o-t-butylaniline (3.78). Because of its $+I$ effect the $t$-butyl group should be base strengthening, and its "anomalous" effect in the present case is therefore attributed to steric inhibition of solvation.

Direct electrostatic interactions between two adjacent groups may occur. Usually this takes the form of hydrogen bonding or chelation. It has been used to explain the surprisingly large
H-N-H bond angle in 2-iodoanilines$^{22}$, and the high $pK_a$ of phthalic acid in its second dissociation$^{23}$. However, there appear to be no cases where such effects have been used to explain the $pK_a$ values of aromatic amines, and they will not be further considered here.

**STERIC EFFECTS IN AMINES.**

It is generally accepted that in amines, the nitrogen atom is bonded to three other atoms using bonds formed from $sp^3$ hybrid orbitals, and that the lone pair of electrons is accommodated in the fourth orbital. The bonds from the nitrogen atom are therefore directed towards three of the four corners of a tetrahedron, and the lone pair is directed towards the fourth corner. However, this ideal situation is in fact modified because the orbital containing the lone pair has more a character than the bonding orbitals. Expressed another way, repulsion between the lone pair of electrons and a pair of bonded electrons is greater than that between two pairs of bonded electrons. The result is that the nitrogen bonds are disposed at an angle rather less than the tetrahedral angle (109.5°). For example, the bond angle in ammonia is 107°. As the size of the groups attached to the nitrogen atom increases, repulsion between them becomes more important and the bond angle increases.

In considering aromatic amines, another effect on the bond angle is observed. When an amino group is attached to an aromatic ring, conjugation between the two groups is possible (see fig. II, p. 4). In the canonical form II (a), the preferred bond angle
is the tetrahedral angle of 109.5°, whereas in the canonical form II (a) it is 120°, and the benzene ring and the nitrogen bonds are coplanar. Hence the angle between the nitrogen bonds is a direct measure of the relative importance of structures II (a) and II (b) in the amine, provided that no specific interactions occur between the amino group and a neighbouring group.

The stereochemistry of amines is therefore very complicated, not only because of the pyramidal nature of the nitrogen valencies, but also because the angle between these valencies varies with the extent of conjugation between the amino group and the aromatic ring. Moreover the mesomeric interaction in these systems is dependent on the rotational orientation of the amino group, being greatest when the lone pair of electrons lies in a plane perpendicular to that of the aromatic ring. If mesomerism is inhibited therefore, whether by steric or other effects, the spatial disposition of the nitrogen valencies changes.

The Primary Amino Group.

There is very little evidence for steric inhibition of mesomerism in primary aromatic amines. For example Wepster and Burger have investigated the electronic absorption spectra of a series of ortho-substituted anilines including 2,6-di-t-butylianiline and 2,4,6-tri-t-butylianiline, and have found no systematic difference which would point to steric inhibition of mesomerism. In spite of the considerable strain of the conformation in the di-o-t-butylianilines, the amino group remains substantially in the plane of the aromatic ring. They claim that there is no doubt that
in the less heavily substituted anilines like 2,6-dimethylaniline, there is no steric compression at all.

From the results of Brown and coworkers\textsuperscript{25} on strained homomorphs, it appears likely that some strain may occur in most \textit{ortho}-substituted anilines. They calculated strains of 0.5 kcal/mole, 2 kcal/mole and 6 kcal/mole for \textit{o}-xylene, \textit{hemimellitene} and \textit{o-t}-butyltoluene respectively. An amino group cannot differ greatly from a methyl group in size, although the shapes may be slightly different. The results of Brown therefore suggest that there may be strain in \textit{o}-toluidine even if it is less than that in \textit{o}-xylene, and that 2,6-dimethylaniline and \textit{o-t}-butylaniline must be strained. However, since the spectral data shows no loss of mesomerism in the \textit{ortho}-substituted anilines, the steric strain must be less than the mesomeric interaction that would be lost on rotation to relieve it.

Data on the dipole moments of some \textit{ortho}-substituted anilines also yields no evidence for steric inhibition of mesomerism. The dipole moments of aniline, \textit{o}-toluidine, mesitylene and 1-naphthylamine are 1.53, 1.59, 1.45 and 1.50 respectively\textsuperscript{26}. Appreciable steric inhibition of mesomerism would result in dipole moments significantly lower than these.

The only evidence for steric inhibition of mesomerism in primary aromatic amines arises from some determinations of \textit{H-N-H} angles from the symmetric and asymmetric stretching frequencies of the \textit{NH}_2 group. Some representative angles\textsuperscript{22} are shown in the
accompanying table. Apart from specific interactions,

<table>
<thead>
<tr>
<th>Compound</th>
<th>Angle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aniline</td>
<td>111.7°</td>
</tr>
<tr>
<td>2-Phenylenediamine</td>
<td>109.4°</td>
</tr>
<tr>
<td>2-Nitroaniline</td>
<td>113.6°</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td>111.5°</td>
</tr>
<tr>
<td>p-Toluidine</td>
<td>110.7°</td>
</tr>
<tr>
<td>o-Iodoaniline</td>
<td>115.0°</td>
</tr>
<tr>
<td>2,4,6-Tri-t-butylaniline</td>
<td>115.8°</td>
</tr>
<tr>
<td>2-Naphthylamine</td>
<td>111.9°27</td>
</tr>
<tr>
<td>1-Naphthylamine</td>
<td>110.6°27</td>
</tr>
</tbody>
</table>

which appear to be many, the angles are said to reflect the extent of delocalization of the nitrogen lone pair of electrons. Thus the angles in o-toluidine and 1-naphthylamine are less than that in aniline because the ortho substituents inhibit coplanarity of the amino group with the benzene ring, and therefore resonance between them. The even lower angle in p-toluidine is not explained; that in p-phenylenediamine is a result of the opposed +M effects of the amino groups preventing either from conjugating. The high bond angle in 2-iodoaniline is a result of hydrogen bonding between the iodine atom and the amino hydrogen atom, while that in 2,4,6-tri-t-butylaniline is attributed to the "cage" of methyl groups forcing the amino group to be coplanar with the aromatic system. Even in the grossly hindered 5-amino-3,4-benzacridine with a bond angle of 111.0°, there is still considerable delocalization of the amino
5-Amino-3,4-benzacridine

group’s lone pair of electrons.  

In sum, the evidence therefore points to an almost complete absence of steric inhibition of mesomerism in primary aromatic amines. By analogy with other systems steric strain is almost certainly present, but its magnitude is insufficient to induce relief by twisting the amino group, with the attendant inhibition of delocalization of the nitrogen lone pair of electrons.

The Dimethylamino Group.

Because of the spatial disposition of the nitrogen valencies (described on p. 12) steric interactions with the dimethylamino group follow a complicated pattern which is not simplified by the spontaneous inversion of configuration of the nitrogen atom. Inversion of configuration results, for example in the attainability of both configurations (a) and (b) in Fig. VII even when rotation is not possible. In this case it is not difficult to deduce that

The plane of the aromatic ring is indicated by the dotted line.
(a) is more stable than (b), because in the former the lone pair of electrons is oriented almost perpendicular to the plane of the aromatic ring. However, in some cases the preferred orientation is far from obvious. When a second ortho group is present such as in (c), the configuration corresponding to (a) may become highly strained, and the configuration corresponding to (b) is probably preferred. This effect accounts for the relatively large influence of a second ortho substituent on some of the properties of dimethylanilines, compared with the small effects seen in molecules containing planar conjugating substituents such as carboxyl or nitro groups.

Steric strain resulting in inhibition of mesomerism in dimethylanilines is a well documented phenomenon. It is seen, for example, in the ultraviolet spectral data collected by Wepster and used to calculate the angle of twist $\varphi$ of the dimethylamino group:

$$\frac{\varepsilon}{\varepsilon_0} = \cos^2 \varphi,$$

where $\varepsilon_0$ and $\varepsilon$ are the extinction coefficients at the wavelengths of maximum absorption of the 250 m$\mu$ band of dimethylaniline and the ortho-substituted dimethylaniline respectively. Some values of $\varepsilon$ and $\varphi$ for various dimethylanilines are shown in the accompanying table. It can be seen therefore that considerable steric inhibition of mesomerism occurs even when the ortho substituent is quite small.

* $\varphi$ is defined as the angle between a plane perpendicular to the aromatic ring and containing the $C_{AF}-N$ bond, and a plane containing the $C_{AF}-N$ bond and the nitrogen lone pair orbital.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$\varepsilon_{\text{max}}$</th>
<th>$\varphi^\circ$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylaniline</td>
<td>15,500</td>
<td>(0)</td>
</tr>
<tr>
<td>2-Methyldimethylaniline</td>
<td>6,360</td>
<td>50</td>
</tr>
<tr>
<td>2-Ethyldimethylaniline</td>
<td>4,950</td>
<td>56</td>
</tr>
<tr>
<td>N,N,2,6-Tetramethylaniline</td>
<td>2,240</td>
<td>68</td>
</tr>
<tr>
<td>2-t-Butyldimethylaniline</td>
<td>630</td>
<td>78</td>
</tr>
</tbody>
</table>

Evidence for steric inhibition of mesomerism in ortho-substituted dimethylanilines also comes from dipole measurement on these compounds. While ortho substitution in aniline resulted in compounds with dipole moments almost the same as that of the parent amine, the dipole moments of dimethylaniline, dimethyl-o-toluidine, dimethylmesidine and 1-dimethylaminonaphthalene are 1.51, 0.96, 1.03, and 1.06 respectively. These figures are indicative of steric inhibition of mesomerism in the ortho-substituted dimethylanino compounds.

It has been found that in the alkaline saponification of a series of ethyl benzoates, the meta- and para- dimethylanino compounds react much more slowly than the parent esters, but that the retarding effect of the dimethylanino group is damped by the presence of methyl groups ortho to it. The effective $\sigma$-values for the dimethylanino group in these reactions, with and without methyl groups ortho to it, are shown below. In the meta-dimethylanino compounds, the methyl group is para to the ester group to avoid steric interaction with it. The negative $\sigma$-values show that the dimethylanino groups in these compounds
are still electron donors; i.e. although resonance is considerably inhibited it is not completely destroyed.

The $pK_a$ values of some dimethylanilines is also a source of evidence for steric inhibition of mesomerism in these compounds, but because relative $pK_a$ values are usually affected by several factors, only a simple example will be quoted here. Davies and Addis$^{32}$ found the $pK_a$ values of dimethylaniline, dimethyl-$o$-toluidine and dimethyl-$p$-toluidine to be 4.21, 5.07 and 4.77 respectively in 50% ethanol at 20°. Thus introduction of a para-methyl group into dimethylaniline results in a compound with a $pK_a$ 0.36 $pK$ units higher; introduction of an ortho-methyl group results in a compound with a $pK_a$ 0.86 $pK$ units higher. The greater effect of the ortho-methyl group is attributed to it forcing the dimethylamino group out of the plane of the aromatic ring, thereby making the base less stable (stronger) than it would be in the absence of the ortho group. Electronic effects of ortho- and para- methyl groups are assumed to be similar.

The dimethylamino group is therefore very prone to steric interference, although in no case has it been established that
its resonance with an aromatic system has been completely destroyed by groups ortho to it.

The Protonated Amino Groups.

Steric effects on protonated amino and dimethylamino groups are apparently simpler than those acting on the unprotonated groups, because of the inherent inability of the former groups to conjugate with an aromatic system. They therefore have complete freedom of rotation about the C–N bond. However, evidence from different sources does not concur in predicting the extent of steric interactions possible in all protonated amino groups, mostly because there is some disagreement concerning the amount of solvation involved. It is generally accepted that a primary ammonium ion is strongly solvated in solution, but the degree of solvation in a dimethylammonium group is not known. Some of the work which throws light on the question of solvation in protonated amines is therefore discussed below.

Sicher, Jonáš and Tichý (33) have recently assessed the effective sizes of the NH$_2$, NH$_3^+$, N(CH$_3$)$_2$ and N(CH$_3$)$_2$H$^+$ groups in aqueous solution, by measuring the difference in free energy of cyclohexane rings containing these substituents in the axial and equatorial positions. The results for the first two groups were confirmed by other workers (34) who used a different method for their determinations. The free energy differences for some cyclohexane derivatives are shown in the accompanying table. These results indicate that while an amino group is comparable in size to a
methyl group, protonation and the attendant solvation make it effectively almost as big as an i-propyl group. Similarly the dimethylamino group is effectively the same size as an i-propyl group, and is made considerably larger when it is protonated. It is difficult to see why merely embedding a proton in the lone pair of electrons of the nitrogen atom should affect the size of the dimethylamino group appreciably, so the enlargement is probably due to increased solvation. Since protonation of both the amino and the dimethylamino group appears to result in equal decreases in the stability of the cyclohexane ring with these substituents in the axial positions, solvation appears to be of equal importance in both these ammonium groups.

These results are at variance with the conclusions of several other workers. Trotman-Dickenson\textsuperscript{35} considers that in protonated amines solvation occurs through the hydrogen atoms which are hydrogen-bonded to the solvating water molecules. Since each hydrogen atom is capable of forming only one hydrogen bond, the number of solvating water molecules should decrease as the
22.

hydrogen atoms are replaced by alkyl groups, that is, as the amine considered is primary, secondary or tertiary. Therefore an anilinium ion should be associated with three water molecules and a dimethylanilinium ion with one.

This view is supported in principle by Hall\(^1\) who plotted the \(pK_a\) values of a series of alkylamines against the sum of the Taft \(\sigma^*\) values for the alkyl groups\(^2\). \(\sigma^*\) is a measure of the inductive effect of a substituent. He found that the amines fell into three distinct classes, the primary, secondary and tertiary amines for any given \(\sigma^*\) value. Ammonia occupied a place of its own. It was noticeable from the graph that the size of the alkyl substituent was important in causing deviations from the correlation lines only in the primary and secondary amines. Hall attributes the grouping phenomenon to solvation, which is strongest in the primary ammonium ions and weakest in the tertiary ammonium ions; and the deviations to steric inhibition of solvation. Since there were no deviations from linearity among the tertiary amines, he concluded that tertiary ammonium ions are either not solvated, or they are solvated with one water molecule which cannot be hindered. Further evidence for the unimportance of solvation in tertiary ammonium ions is supplied by the fact that the \(pK_a\) values of a series of dimethylanilines are more sensitive to substituents in the aromatic ring than are the \(pK_a\) values of anilines\(^3\). This is said to be indicative of a greater charge on the nitrogen atom in the former series because it is not distributed by solvating molecules.
There is considerable evidence for steric strain resulting in inhibition of solvation in primary anilinium ions. An example from the $pK_a$ values of some anilines illustrates this point. As has been pointed out by Brown and Cahn\textsuperscript{14}, the decrease in $pK_a$ with ortho substitution is a result of steric inhibition of solvation in the anilinium ion. Introduction of meta- or para- methyl groups into aniline results in compounds with higher $pK_a$ values.

In spite of the data quoted earlier concerning equilibria in cyclohexylamines, solvation effects in dimethylammonium groups are much less well documented than those in primary ammonium groups. Nevertheless the $pK_a$ values of some dimethylanilines can apparently be explained only if the dimethylammonium group is larger than its unprotonated parent, possibly because of solvation in the former.

For example, Brown and Cahn\textsuperscript{14} have systematized the $pK_a$ values of the compounds shown in the accompanying table on this basis. The effect of introducing an $o$-methyl group into dimethylaniline is

<table>
<thead>
<tr>
<th>Compound</th>
<th>$pK_a$ (50% ethanol, 25°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dimethylaniline</td>
<td>4.26\textsuperscript{19}</td>
</tr>
<tr>
<td>Dimethyl-$o$-toluidine</td>
<td>5.07\textsuperscript{19}</td>
</tr>
<tr>
<td>$N,N,2,6$-Tetramethylaniline</td>
<td>4.69\textsuperscript{19}</td>
</tr>
<tr>
<td>$o$-t-Butyldimethylaniline</td>
<td>4.32\textsuperscript{39}</td>
</tr>
</tbody>
</table>
base strengthening because the steric strain results in reduced mesomerism of the dimethylamino group with the aromatic ring.

Introduction of a second ortho- methyl group however results in a lowering of the $pK_a$ values; that is, in base weakening. Now the second methyl group is expected to further destabilize the base, and indeed ultraviolet spectral measurements on dimethy-o-toluidine and 2,6-dimethylaniline do suggest that less mesomerism occurs in the latter compound (see p. 18). That the introduction of the second methyl group is accompanied by a substantial decrease in $pK_a$ must be attributed to it causing a greater increase in steric strain in the dimethylammonium ion than in the parent amine. The effect is even more marked in 2-t-butyl-dimethylaniline which has a $pK_a$ value very close to that of dimethylaniline. Therefore the ortho-t-butyl group must destabilize the free amine (by steric inhibition of mesomerism) and the cation to a similar extent. Whether or not these destabilizing effects of large ortho groups on the dimethylammonium ion are a result of steric inhibition of solvation is a matter for conjecture. If protonation of a dimethylamino group is not accompanied by solvation, there should be little increase in size, and large ortho groups should not greatly inhibit ion formation. On the other hand, if solvation does occur in the ion, it does not appear to be affected by small ortho groups which undoubtedly do affect solvation in the primary ammonium ion. The conclusion to be drawn then is that for some
reason, the dimethylammonium ion is larger than the parent base, but that steric effects on it are observable only in highly strained systems.
EXPERIMENTAL

PREPARATION OF THE AMINES

General

Melting-points and boiling-points are uncorrected. Reference melting-points are given in brackets after the measured figures, and unless otherwise stated, are the highest quoted in Elsevier's Encyclopaedia of Organic Chemistry, Elsevier Publishing Co., Inc., New York.

Most of the solvents used were redistilled. Where benzene, ether or petroleum ether are so described, they have been distilled off phosphorus pentoxide. All solvents used in chromatography were so treated. Where a solvent is described as anhydrous, it was dried over sodium wire, distilled, and stored over sodium wire.

Analyses were carried out at the Microanalytical Laboratory, University of Otago.

OUTLINE OF PREPARATIVE METHODS

(a) 4-Methyl-1-naphthylamine.

This compound was prepared by nitration of 1-methyl-naphthalene, and reduction of the resulting nitro compound.
The nitration was accomplished by the method of Thompson\textsuperscript{42} using nitric acid and 1-methylnaphthalene without a solvent, and a yield of 13.6\% of pure 1-methyl-4-nitronaphthalene was obtained. The yield compares unfavourably with Thompson's (58\%), but he gives no criterion of the purity of his product and very little indication of how it was isolated. Fischer\textsuperscript{43} has also found this nitration unsatisfactory. In the present work a pure product was obtained only after the crude 1-methyl-4-nitronaphthalene had been subjected to several purification procedures. First a solution of the crude nitro compound in benzene was extracted with aqueous alkali to remove products of oxidation and polynitration. Following the recommendation of Vesely and Sturza\textsuperscript{44} an attempt was then made to recrystallize the product (an oil) from carbon tetrachloride, but the material was far too soluble in this solvent for any crystals to be obtained. A mixture of carbon tetrachloride and petroleum ether also proved unsatisfactory as a recrystallization solvent. After many attempts at crystallization and chromatography, neither of which were adequate alone, the following procedure was adopted. The crude nitro compound, after being washed with alkali, was dissolved in hot ethanol, and the solution was slowly cooled to room temperature. The supernatant liquid was poured off the dark oil which had separated, and cooled in a "dry-ice" alcohol bath to precipitate yellow crystals of crude 1-methyl-4-nitronaphthalene (ca. 35\%, m.p. 44-53\textdegree). Purification was completed by recrystallization from ethanol,
chromatography on alumina and recrystallization from ethanol.

The nitro compound was reduced with aluminium amalgam in aqueous ethanol as described by Morgan and Harrison for the reduction of 3-nitroacenaphthene. This reagent was found to be more convenient to use than either sodium hydrosulphite or tin and hydrochloric acid.

After the completion of this synthesis, another preparation of 4-methyl-1-naphthylamine was found in the literature. Sauer, Huisgen and Hauser acetylated 1-methylnaphthalene in the 4-position and rearranged the oxime of the resulting ketone to 4-acetyl-4-methyl-1-naphthylamine. Hydrolysis gave the required product in approximately 60% yield from 1-methylnaphthalene. This appears to be a far more satisfactory synthetic method than the procedure used.

(b) 4-Methyl-2-naphthylamine

The most convenient synthesis of this compound in the literature seems to be the seven-stage process of Sauer, Huisgen and Hauser which is outlined below.
In the present work a much shorter synthetic route was adopted. 1-Methylnaphthalene was brominated in the 4-position, and the resulting bromo compound was reacted with potassium amide in liquid ammonia.

Rearrangements involving aryne intermediates have been widely studied, but this is one of the few examples of such a rearrangement being used in preparative work. The main problem encountered was the separation of the isomeric products. The amines were separated from other products by making use of their solubility in aqueous acid. Distillation under reduced pressure was then used to isolate the 4-methylnaphthylamines from high-boiling material, but was completely unsuccessful as a method of separating the isomers.

Separation of the amines was attempted by several methods. Fractional recrystallizations from petroleum ether followed by recrystallization from ethanol was the most successful of the crystallization techniques tried. It yielded 3.5% of pure 4-methyl-2-naphthylamine. A method analogous to that used by Hodgson and Smith to separate 1- and 2-naphthylamines was also tried. The mixture of 4-methylnaphthylamines was dissolved in 1N hydrochloric acid, and the acid was neutralized with seven equal portions of 1N sodium hydroxide. After each addition of alkali, the aqueous solution was extracted with ether, and the ether was
evaporated to leave the amine as an oily residue. No separation was achieved. Chromatography of the amines on alumina was unsuccessful. An attempt at separating the amines by recrystallizing their N-acetyl derivatives met with limited success, and a very low yield of N-acetyl-4-methyl-2-naphthylamine was obtained on crystallization from acetic acid. A successful separation was achieved by chromatography of the mixture of acetylated amines on alumina using ether as an eluent. The 2-isomer was eluted first.

The proportions of the two aminated products obtained here were consistent with those obtained by other workers by amination of related compounds. Urner and Bergstrom obtained 2- and 1-naphthylamine in 43% and 2% yield respectively when they treated 1-bromonaphthalene with potassium amide in liquid ammonia. Sauer, Huisgen and Hauser obtained 65% of the 2-isomer and 28% of the 1-isomer when they treated 1-bromonaphthalene with lithium piperidide in boiling piperidine, and 66% and 26% of the 2- and 1-isomer respectively when they treated 1-bromo-4-methylnaphthalene with the same reagents. In the present work the yields from amination of 1-bromo-4-methylnaphthalene with potassium amide in liquid ammonia were 20% of the 2-amine and 12% of the 1-amine.

(c) 4,5-Dimethyl-1-naphthylamine.

4,5-Dimethyl-1-naphthylamine was prepared according to the scheme below. At the time of synthesis neither 4,5-dimethyl-1-nitronaphthalene nor its amino analogue had appeared in the
literature, but both have since been prepared by the method outlined above \(^47\).

The first step, the oxidation of acenaphthene, was carried out by the method of Graebe and Gfeller \(^48\) using acetic acid and sodium dichromate as the oxidizing agent. Steps 2, 3 and 4 are the same as those used by Mitchell, Topsom and Vaughan \(^9\), the reagents used being lithium aluminium hydride, phosphorus tribromide and lithium aluminium hydride respectively. Yields for all of the first four steps were good.

Nitration of 1,8-dimethylnaphthalene was initially carried out in acetic acid at 25\(^\circ\) in a manner analogous to that used by Okazaki, Tanaka and Taniguchi \(^49\) for nitrating acenaphthene. However it was found that 1,8-dimethylnaphthalene did not nitrate appreciably at this temperature, and later reactions were therefore carried out at 100\(^\circ\). It was also found advantageous to use less acetic acid solvent than that used by Okazaki and colleagues,
thus ensuring that most of the nitration product precipitated when the reaction mixture was cooled. Repeated crystallizations from ethanol and petroleum ether gave a pure sample of 4,5-dimethyl-1-nitronaphthalene, but the best method of purification was chromatography on alumina followed by recrystallization from petroleum ether.

Reduction to 4,5-dimethyl-1-naphthylamine was carried out with aluminium amalgam, and the product was purified by vacuum distillation and recrystallization from petroleum ether. The ultraviolet spectrum of the amine in the region 360-300 nm was consistent with it being an α-aminonaphthalene.

In an effort to establish conclusively the orientation of the nitro group in the nitrated 4,5-dimethylnaphthalene, an attempt was made to oxidize it, with sodium dichromate and acetic acid, to the corresponding naphthalic anhydride. Only starting material was isolated from the reaction mixture, while longer periods of refluxing gave rise to a sweet-smelling liquid but not to a naphthalic anhydride. It was found however, that 1,8-dimethylnaphthalene and 5-nitroacenaphthene could be oxidized to the corresponding naphthalic anhydrides by the method used above. Other workers have recently reported that they were also unsuccessful in attempts to oxidize 4,5-dimethyl-1-nitronaphthalene to a naphthalic anhydride.

The orientation of the amino group in the product of reduction of the nitro compound was established. The amine was diazotized in aqueous acetic acid, and the diazonium group was replaced by bromine using hydrobromic acid and cuprous bromide. The product was
extracted and purified, and melted at 31-31.5° (30.5°)°.

(d) 4,5-Dimethyl-2-naphthylamine.

Several preparative routes to this compound, which has not appeared in the literature, were considered. They are outlined below.

Although method I seems feasible, and has recently been used in the synthesis of 4,5-dimethyl-2-nitronaphthalene, it was discarded as unwieldy because it requires a total of twelve steps from acenaphthene. When the synthesis was considered, the last seven steps would have involved unknown compounds.
This route appeared much more acceptable because it involves only six steps fromacenaphthene. However, the last step results in the production of two isomers which could prove difficult to separate. In view of the low yields obtained in the amination of 1-bromo-4-methylnaphthalene, and the difficulty experienced in isolating the products, it was decided to avoid the method if possible.

In the third route to be considered, the first two steps have previously been carried out in good yield using sodium nitrate and concentrated sulphuric acid, and stannous chloride and hydrochloric acid respectively. However, the remaining steps are uncertain. The only reagent found suitable for the reduction of naphthalic anhydrides under mild conditions is lithium aluminium hydride, which would therefore be essential for step 3. However, lithium aluminium hydride acts on an amino group, in the same way as a Grignard reagent, to form a complex and liberate hydrogen.
Complexes of this type often cause considerable difficulty in the attempted reduction of amino acids because they are so insoluble that they are thrown out of solution before reduction can take place\textsuperscript{78}. Since naphthalic anhydride is almost insoluble in ether, it is probable that the complex formed from lithium aluminium hydride and 3-aminonaphththalic anhydride would be so insoluble as to be not reducible. The direct reduction of 3-nitronaphthalic anhydride with lithium aluminium hydride is not feasible because the latter reagent reduces aromatic nitro compounds to azo compounds.

This is unfortunate, as if 4,5-di(hydroxymethyl)-2-naphthylamine could be synthesized it could then be reduced catalytically in the presence of palladium on charcoal to 4,5-dimethyl-2-naphthylamine. Boekelheide and Goldman\textsuperscript{55} have successfully used this method of reduction to convert 1,8-di(hydroxymethyl)naphthalene to 1,8-dimethylnaphthalene.

IV

\[
\begin{align*}
\text{O} & \text{O} \\
\text{C} & \text{C} = \text{O} \\
\text{O} & \text{O} \\
\text{C} = \text{O} \\
\end{align*}
\]

\[\text{2} \rightarrow \]

\[
\begin{align*}
\text{O} & \text{O} \\
\text{C} & \text{C} = \text{O} \\
\text{CH}_3 & \text{CH}_3 \\
\end{align*}
\]

\[\text{3, 4, 5} \rightarrow \]

\[
\begin{align*}
\text{Br} \\
\text{Br} \\
\end{align*}
\]

\[\text{6} \rightarrow \]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{COCH}_3 \\
\end{align*}
\]

\[\text{7} \rightarrow \]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{NHC(O)CH}_3 \\
\end{align*}
\]

\[\text{8} \rightarrow \]

\[
\begin{align*}
\text{CH}_3 & \text{CH}_3 \\
\text{NH}_2 \\
\end{align*}
\]
The fourth route considered appeared the most feasible. It involves eight steps from aceanaphthene, but all are reasonably well known reactions. The first five steps have been carried out in good yield by other workers. Some choice of method is available for the replacement of the bromine atom by an amino group. The method most commonly used for this conversion in other compounds is carbonation of the aryl metallic derivative followed by a Schmidt rearrangement of the azide of the resulting acid as shown below for 2-bromo-4,5-dimethylnaphthalene.

However, neither carbonation nor the rearrangement gives a high yield, and a total yield of 25% could be expected. In contrast, acetylation of the bromo compound (as its cadmium derivative) followed by a Schmidt rearrangement of the resulting 2-acetyl-4,5-dimethylnaphthalene should yield at least 35% of the N-acetylated naphthylamine.

Method IV was chosen. Although it is longer than method III, it was more certain to be successful. Further, all steps except the fifth are the same or paralleled in the synthesis of 5-acenaphthenamine.
Naphthalic anhydride was brominated with bromine and silver sulphate in concentrated sulphuric acid as described by Mitchell, Topsom and Vaughan, but their method was modified to enable larger amounts of anhydride to be brominated conveniently. Using a 3% excess of silver sulphate instead of the above workers' 25%, a slightly lower yield of 3-bromonaphthalic anhydride was obtained, but it was of higher purity.

In the reduction of 3-bromonaphthalic anhydride, the product was not satisfactorily isolated by the method used by Mitchell and coworkers. When the organic solution of the dialcohol was boiled down, only a gummy precipitate was obtained on cooling the solvent. Repeated crystallizations of this material gave well formed crystals of 2-bromo-4,5-di(hydroxymethyl)naphthalene in low yield. However a 64% yield of this compound was obtained when it was precipitated from ethanolic solution with 10% sulphuric acid in water. The melting-point was however 5° below that recorded by the previous workers, and was not raised by repeated crystallizations from ethanol.

Conversion to 2-bromo-4,5-dimethylnaphthalene via 2-bromo-4,5-di(bromomethyl)naphthalene was as described in reference 9 and gave a slightly higher yield of product melting at 84.5-85.5°. (Mitchell, Topsom and Vaughan quote 83°). The melting-point was not raised when the compound was repeatedly recrystallized from ethanol, and the analysis figures were good. The residues from recrystallization were recovered and recrystallized,
and were found to melt at 90-91°. This melting point is fairly consistent with that found by Jameson\(^57\) (88-89°) who determined the crystal structure of the compound.

Acetylation of 2-bromo-4,5-dimethylnaphthalene was carried out by a method taken from several sources, notably papers by Cason\(^56\), de Benneville\(^58\), Gilman and Nelson\(^59\), and Cason and Prout\(^60\). The bromo compound was treated with n-butyllithium in ether to give the lithium derivative\(^61\), and this was treated with anhydrous cadmium chloride to yield the cadmium diaryl. The ether was distilled off and replaced with benzene to prevent side reactions with the ether\(^56\), and to allow faster reaction in the higher boiling solvent. Addition of acetyl chloride completed the acetylation to give the hitherto unknown 2-acetyl-4,5-dimethylnaphthalene. The yield was 44% after purification, which is somewhat lower than is generally obtained from these reactions.

Some attempts were made to purify the recrystallization residues of the acetyl compound via the water-soluble compound it should form with Girard "P" reagent. However, no compound was formed when these residues and Girard's reagent were heated together under the conditions described by Wild\(^62\). Recrystallization of the residues was also unsuccessful, and they were subsequently used in the following step without purification.

N-Acetyl-4,5-dimethyl-2-naphthylamine, which was also unknown, was prepared from 2-acetyl-4,5-dimethylnaphthalene by heating it with sodium azide in trichloracetic acid as described by Edwards and Petrow\(^63\) for the conversion of 3-acetylcenaphthene to
N-acetyl-3-acenaphthenamine. The reaction gave a high yield of product of good purity unless the reactant ketone was impure. In this case the product acetylamine compound was purified only by repeated recrystallization.

(e) 5-Acenaphthenamine.

The obvious method of synthesizing this compound is by nitrating acenaphthene in the 5-position, and reducing the nitration product to 5-acenaphthenamine\(^64\). However, the amine produced by this method was found, by vapour phase chromatography, to be impure. Since acenaphthene can be nitrated in the 3-position using a suitable nitrating agent\(^76\), it was considered probable that the contaminant was 3-acenaphthenamine. Subsequently the 5-nitroacenaphthene obtained was also shown, by vapour phase chromatography, to be impure. Its melting point was 102-103\(^\circ\) compared with a literature value of 108\(^\circ\). Zone melting, and repeated recrystallizations from ethanol and from petroleum ether, failed to give a pure product. Wright\(^66\) has also found it extremely difficult to obtain even a small sample of pure 5-nitroacenaphthene after many varied attempts at purification. Samples prepared according to two sets of directions had the same melting-point (102-103\(^\circ\)).

The impure nitro compound was reduced to 5-acenaphthenamine, and attempts were made to purify this. However, no purification was effected by zone melting, vacuum distillation, and recrystallizations from petroleum ether and aqueous ethanol. Recrystallization of
the acetyl derivative from acetic acid or ethanol followed by hydrolysis to the amine was unsuccessful as a purification method, as was recrystallization of the hydrochloride from aqueous ethanol. The picrate was found to be unsuitable for recrystallization from ethanol, benzene, acetone, chloroform and dioxan.

Another synthetic route was therefore sought. Two were apparently available. The first method was not used because acenaphthene is known to acetylate in both the 3- and 5-positions, and the isomers may be difficult to separate. In contrast, II

bromination is thought to give only 5-bromoacenaphthene. Acenaphthene was therefore brominated in carbon tetrachloride solution. The product obtained, after two distillations under reduced pressure and a recrystallization from ethanol, melted at 52-53°, the accepted melting-point. However, it was shown by vapour phase chromatography to be impure. Repeated crystallizations
from ethanol gave a product melting at 53-53.5°, but with almost the same vapour phase chromatographic characteristics as the original sample.

The impure 5-bromoacenaphthene was treated with n-butyllithium followed by carbon dioxide to give 5-acenaphthoic acid which was readily purified by recrystallization from glacial acetic acid.

5-Acenaphthoic acid was converted to 5-acenaphthenamine by reacting it with sodium azide in polyphosphoric acid, but with much less success than previous workers (Stockel and Hall67) who claim yields of 48-91%. They state only that their rearrangements were carried out in polyphosphoric acid at room temperature in the presence of excess sodium azide. Their yields are given but not the composition or amount of polyphosphoric acid used, or the duration of the reaction. An attempt was therefore made to rearrange 5-acenaphthoic acid in polyphosphoric acid prepared according to Vogel68, containing 92% of phosphorus pentoxide. Excess sodium azide was added and the mixture was allowed to stand with occasional stirring for a period of five days. At the end of that time it was heated to 40-50° for four hours. After working up the reaction mixture, most of the acenaphthoic acid was recovered but no amine was obtained. The process was repeated with variations many times. The temperature was varied from room temperature, when no reaction occurred, to 200°, when no acenaphthoic acid or acenaphthoic acid or acenaphthenamine could be isolated from the reaction mixture. A series of rearrangements were carried out in polyphosphoric acid having a phosphorus pentoxide content of 83%,
which is the composition generally used. Different batches of sodium azide were used, including a batch activated by the method of Smith, but this variation had no effect. The best yield of 5-acenaphthenamine was only 22%. However, sufficient product was obtained for use in this work, and no other method of preparation was investigated.

As a check on the method, an attempt was made to rearrange 1-naphthoic acid in polyphosphoric acid. Under conditions similar to those found most successful in the synthesis of 5-acenaphthenamine, crude 1-naphthylamine was obtained in 30% yield, which is still below the yields quoted by Stockel and Hall. The acids rearranged by these authors were all benzoic acids which are almost certainly more soluble than naphthoic acids in polyphosphoric acid. It is suggested that the low yield obtained in the present work is a result of the low solubility of 5-acenaphthoic acid in polyphosphoric acid.

(f) 4-Acenaphthenamine.

Three synthetic routes to 4-acenaphthenamine were considered. Firstly there is the method of Vorozhtsov and Tochilkin which involves the bromination of acenaphthene and the subsequent amination of the resulting 5-bromacenaphthene with potassium azide in liquid ammonia. The yield of 4-acenaphthenamine obtained by these authors was 4-6%, the main product being polyacenaphthylene. The amino
compound was apparently isolated only as its acetyl or benzoyl derivative. An average yield of 4% of acid soluble material was found on repeating the experiment, but it was found difficult to purify. Recrystallizations from petroleum ether and aqueous ethanol, chromatography on alumina, and vacuum distillation were all ineffective. No purification was observed when the amine hydrochloride was recrystallized from benzene or precipitated from ethanol with ether. The acetyl derivative was also the subject of many attempts at purification, and a small sample of pure N-acetyl-4-acenaphthenamine was obtained after the crude acetylated amine was chromatographed on alumina and recrystallized from benzene and ethanol. A compound thought to be N-acetyl-5-acenaphthenamine also emerged from the chromatography column, but because of the small quantity obtained and its low state of purity, its identity was not established. The amount of pure N-acetyl-4-acenaphthenamine obtained after a series of aminations was so small that the method was abandoned.

The second route investigated is a variation of a method used in the synthesis of 4-acenaphthoic acid. It was initially/in preference to the more usual route to 4-acenaphthenamine (see p. 45) because the first three steps were also useful in the synthesis of
4,5-dimethyl-2-naphthylamine. These steps were discussed on page 37.

2-Bromo-1,8-di(bromomethyl)naphthalene was allowed to react with phenyllithium to give 4-bromoacenaphthene. The subsequent steps were the same in technique if not in yields as those used in the synthesis of 4,5-dimethyl-2-naphthylamine.

In the first attempt at acetylation of 4-bromoacenaphthene, it was decided to prepare the cadmium derivative of the bromo compound via the Grignard reagent. However, in spite of the fact that various methods of inducing Grignard reagent formation were used, it could not be obtained. The use of a lithium derivative formed from n-butyllithium and 5-bromoacenaphthene proved satisfactory. In fact, whenever the present work has required the conversion of a bromine atom to another group via an organometallic intermediate, the lithium derivative has been used. Formation and purification of 4-acetylacenaphthene was always much less satisfactory than that
of 2-acetyl-4,5-dimethylnaphthalene, the maximum yields being 20% and 40% respectively. Chromatography on alumina was found to be unsatisfactory for the purification of 4-acetylenaphthene which was therefore purified by recrystallization. Vapour phase chromatography of the recrystallization residues (an oil) failed to reveal any compound other than the required ketone. However, infrared spectra of these residues suggested that the contaminant was a styrene oracenaphthylene, so an attempt was made, without success, to separate the ketonic material as its derivative with Girard "P" reagent. A semicarbazone formed from the residues melted over a wide range of temperature about 20° below the melting-point of a sample of pure 4-acetylenaphthene semicarbazone, which suggests that the impurity may be another ketone.

The Schmidt rearrangement of pure 4-acetylenaphthene to N-acetyl-4-acenaphthenamine was completely satisfactory, but it was not successful when it was applied to impure ketone. An impure acetylamino compound was obtained in low yield, this again indicating that the impurity in the ketone was at least partly another ketone. Hydrolysis of the acetyl amine was carried out in ethanolic hydrochloric acid as usual.

Because the preparation discussed above was not as satisfactory as expected, the traditional synthesis of 4-acenaphthenamine was also used.

Acenaphthene was nitrated in acetic acid and the nitration product was catalytically reduced to give 5-acenaphthenamine in
higher yield than that obtained by other workers\textsuperscript{71}. Nitration of the formylated amino compound in acetic acid gave a lower yield of 5-formylamino-4-nitroacenaphthene than that obtained by Morgan and Stanley\textsuperscript{72}. Hydrolysis to the nitro-amino was accomplished by refluxing the formylamino compound with alcoholic hydrochloric acid\textsuperscript{64}, while the deamination was carried out in the presence of cuprous oxide and boiling ethanol\textsuperscript{63}. Vorozhtsov and Tchilkin\textsuperscript{73} used a higher yielding method in their deamination of 4-nitro-5-acenaphth- enamine, but the volume of solvent used by them made the experiment cumbersome on a larger scale. Therefore the method of Edwards and Petrow\textsuperscript{63}, although lower yielding, was used. The yield obtained here was not as high as that obtained by Edwards and Petrow, and when the deamination was carried out in methanol, the solvent used by them, an even lower yield of 4-nitroacenaphthene was obtained. Ethanol appeared to be a better solvent. After the reaction
product had been diluted with water and filtered, Edwards and Petrow extracted the solid with ethanol. In the present work this procedure yielded crystals of low purity, and extraction with petroleum ether yielded a much purer sample of 4-nitroacenaphthene in equal quantity.

Reduction was carried out as usual with aluminium amalgam in aqueous ethanol.

Preparation of the Dimethylamino Compounds

All the amines were dimethylated with trimethyl phosphate at about 200°, but because some surprising results were obtained from some of these reactions, they are fully discussed in the appendix.
EXPERIMENTAL DETAILS

(a) **Preparation of 4-Methyl-1-naphthylamine.**

1-Methyl-4-nitronaphtalene.  

1-Methylnaphthalene (L. Light and Co., pure) was distilled, and the fraction boiling at 114-115°/15 mm was collected.

1-Methylnaphthalene (20 g) was placed in a three-necked flask fitted with a thermometer and a dropping funnel. Nitric acid (d 1.42, 65 ml) was added dropwise while the flask was vigorously shaken and periodically immersed in an ice-salt bath to maintain the temperature at 13-18°. Water (100 ml) was then added and the organic products were extracted with benzene (3 x 50 ml). The benzene solution was washed with aqueous sodium hydroxide (5%, 5 x 50 ml) and water (50 ml), and added to hot ligroin (200 ml). The supernatant liquid was poured off the dark oil which separated on cooling, and cooled in a "dry-ice" alcohol bath to precipitate 8.83 g of yellow crystals, m.p. 44-53°. The crystals were combined with 8.93 g of similar product from another preparation, and recrystallized from ethanol. The crystalline product was chromatographed on alumina (860 g) using ether as eluent. Evaporation of the solvent gave 7.6 g (14%) of 1-methyl-4-nitronaphthalene, m.p. 69.5 - 70.5°. One recrystallization from redistilled ethanol raised the melting point to 70-71° (71-72°).
4-Methyl-1-naphthylamine

The aluminium amalgam used in this reduction was prepared as described below. Aluminium foil (26 g) in strips (ca. 20 cm x 2 cm x 0.05 mm) in a 1.5 l beaker was covered with warm aqueous 10% sodium hydroxide. Vigorous evolution of hydrogen was allowed to continue for several minutes before the alkali was poured off. The foil was thoroughly washed by decantation, first with water and then with redistilled ethanol. Mercuric chloride solution (2%, 600 ml) was added and allowed to cover the aluminium for two minutes, before it was poured off. The amalgam was washed with water and with redistilled ethanol, and was kept under redistilled ethanol until it was used later the same day.

1-Methyl-4-nitronaphthalene (20 g) was dissolved in redistilled boiling ethanol (400 ml), and hot water (50 ml) and then aluminium amalgam (prepared from 26 g of aluminium) were added. The reaction was sufficiently exothermic to keep the mixture boiling for several minutes. Further additions of water were made till a total of 200 ml had been added, and the reaction mixture was then gently boiled for 30 min to remove most of the ethanol. When the reaction mixture had cooled, water (400 ml) was added, and the suspension was extracted with benzene (8 x 150 ml). The benzene extract was washed with water (200 ml), dried over anhydrous magnesium sulphate, and filtered. Evaporation of the benzene left a pale grey solid which was twice distilled through a short Vigreux column to give 11.3 g (68%) of 4-methyl-1-naphthylamine, b.p. 114-116°/1 mm. Two recrystallizations from redistilled
petroleum ether (b.p. 55-65°) gave fine white needles melting at 51.5-52° (51-52°). Vapour phase chromatography showed the compound to be pure.

(b) Preparation of 4-Methyl-2-naphthylamine.

1-Bromo-4-methylnaphthalene.

1-Methylnaphthalene (75 g) was dissolved in carbon tetrachloride (190 ml) in a 1 l. three-necked flask fitted with a stirrer, a thermometer and a dropping funnel. A small amount of iron powder and a few crystals of iodine were added as catalysts. The solution was cooled to -10° C by immersing the flask in an ice-salt bath, and light was excluded by wrapping the apparatus in a grey cloth. Bromine (87 g) in carbon tetrachloride (150 ml) was added at such a rate that the temperature remained at -8° to -5°, the total time of addition being 1.5 hr. Stirring was continued for a further 1.5 hr while the temperature gradually rose to 15°. The solution was washed free of excess bromine by shaking it with aqueous sodium hydroxide (2N, 3 x 100 ml) and with water (100 ml). The carbon tetrachloride was distilled off under gradually diminishing pressure, and the residue was distilled twice under reduced pressure. The yield of 1-bromo-4-methylnaphthalene, b.p. 90-100°/1 mm was 77.8 g (67%).

N-Acetyl-4-methyl-2-naphthylamine.

The apparatus for this reaction is shown in diagram 1. Liquid ammonia was condensed in each flask by removing the connecting tube.
APPARATUS FOR REACTIONS
IN LIQUID AMMONIA
Diagram 1
and introducing gaseous ammonia from a cylinder.

A potassium amide solution was made in flask A by dissolving potassium (8 g) in liquid ammonia (ca. 300 ml) in the presence of trace quantities of ferric nitrate hydrate and ferric oxide. The mixture was stirred for 8 hr before use.

In flask B, 1-bromo-4-methylnaphthalene (30 g) was stirred with anhydrous ether (200 ml) and liquid ammonia (150 ml) till solution was complete. Potassium amide solution in flask A was forced into flask B under dry nitrogen pressure as rapidly as possible. The rate of addition was limited by the boiling of the reaction mixture, and mixing was completed after 2 min. The reaction was allowed to proceed for 10 min before it was stopped by adding ammonium nitrate (50 g). The ammonia was allowed to evaporate overnight. Water (400 ml) was added and the mixture was extracted with ether (200 ml, 3 x 100 ml). The ethereal extracts were filtered and extracted with hydrochloric acid (16%, 100 ml, 4 x 50 ml), and the aqueous extract was made alkaline with sodium hydroxide. The liberated amine was extracted with ether (200 ml, 4 x 50 ml), and the ether solution was washed with water (100 ml) and dried over anhydrous magnesium sulphate. The drying agent was filtered off and the ether was evaporated. Distillation of the residue gave 7.6 g of low melting solid, b.p. 123-130°/1 mm.

The amine mixture was acetylated by adding it to acetic anhydride (7.5 ml) in glacial acetic acid (50 ml) and heating the mixture to 100-110° for 10 min. The cooled solution was added to water (100 ml), and then sodium hydroxide (50 g) in water (100 ml)
was added. When the mixture had cooled to room temperature, the acetyl amines were filtered off, washed with water, and dried. They were dissolved in benzene (100 ml) and acetone (15 ml) and chromatographed on activated alumina (600 g). The first fraction, which was eluted with ether, was 5.3 g (19.5%) of N-acetyl-4-methyl-2-naphthylamine, m.p. 171-5-172.5°. Recrystallization from ethanol raised the melting-point to 172-173° (172-173°). After a distinct gap, 2.7 g (10.0%) of N-acetyl-4-methyl-1-naphthylamine, m.p. 165.5-166.5° was eluted, also with ether. After recrystallization from redistilled ethanol, this product melted at 166-167° (171°) and the melting-point was not depressed by addition of an authentic sample (m.p. 166-167°) prepared by acetylation of 4-methyl-1-naphthylamine. In addition, 0.70 g of slightly impure N-acetyl-4-methyl-2-naphthylamine and 0.52 g of slightly impure N-acetyl-4-methyl-1-naphthylamine were recovered from the column.

(c) Preparation of 4,5-Dimethyl-1-naphthylamine.

Naphthalic Anhydride.

Commercial grade acenaphthene (100 g) was dissolved in glacial acetic acid (1.2 l.) in a three-necked 2 l. flask fitted with a thermometer, a reflux condenser, and a link stirrer. The solution was warmed to 80°, and crystalline sodium dichromate was added with stirring over a period of 2 hr. The temperature was kept at 75-85°. Cooling in ice was necessary during addition of the first 500 g of sodium dichromate, warming was required during the addition
of the last 180 g. The mixture was stirred at 90° for 1.5 hr, and refluxed for 3 hr, after which it was poured into warm water and allowed to stand overnight.

The crude naphthalic acid was filtered off, washed with water, and warmed with sodium hydroxide solution (5%, 2.5 l). The solution was filtered and the remaining solid was warmed with more sodium hydroxide solution (5%, 400 ml). The two filtrates were combined, and naphthalic acid was precipitated from them by adding concentrated hydrochloric acid till the solution was acid to litmus. The creamy white solid was filtered off, washed with water, and dried in a vacuum oven to give 113 g (96%) of naphthalic anhydride, m.p. 274°. It was recrystallized from acetic anhydride to give 95 g of white crystals, m.p. 274° (274°).

1,8-Di(hydroxymethyl)naphthalene

Lithium aluminium hydride (50 g) was stirred for 2 hr with anhydrous ether in a 2 l. flanged reaction vessel fitted with a stirrer and a reflux condenser. Anhydrous benzene (200 ml) was added. Naphthalic anhydride (100 g) was made into a slurry with anhydrous benzene (250 ml) and added to the lithium aluminium hydride solution over a period of 2 hr. The mixture was stirred and refluxed for 3 hr before removing most of the ether by distillation. Excess lithium aluminium hydride was destroyed by dropwise addition of ethyl acetate (ca. 140 ml). After the reaction mixture had cooled, saturated potassium hydroxide solution (60 ml) was added carefully with stirring. This caused some
coagulation of the inorganic products, and the solid mass was extracted by refluxing it with a 10% solution of ethanol in benzene (6 x 500 ml) and decanting the liquid. The resulting extract was distilled till 1 l. of solution remained, and this was filtered. The filtrate was further distilled with addition of ethanol till 300 ml of ethanolic solution remained. Sulphuric acid solution (10%, 400 ml) was added, and the resulting suspension was cooled in ice and filtered. The filtered crystals were washed with ethanol (150 ml) in water (900 ml) and dried in a vacuum desiccator to give 76 g (81%) of 1,8-di(hydroxymethyl)naphthalene. Recrystallization from redistilled ethanol gave 66 g (70%) of this compound, m.p. 154.5-156° (158°).  

1,8-Di(bromomethyl)naphthalene.  

1,8-Di(hydroxymethyl)naphthalene (62 g), anhydrous benzene (1 l.) and anhydrous ether (400 ml) were stirred in a 2 l. flanged reaction vessel fitted with a sealed stirrer, a dropping funnel, and a reflux condenser. Freshly distilled phosphorus tribromide (56 g) in anhydrous ether (200 ml) was added to the stirred suspension over a period of 2 hr. Gentle heating was commenced during the last 15 min of addition, and the suspension cleared to a pale straw-coloured solution. After being refluxed for 1 hr, the reaction mixture was poured onto ice (2 l.) and the yellow organic layer was separated. It was washed with saturated sodium bicarbonate solution (2 x 300 ml) and water (5 x 300 ml) and dried over anhydrous magnesium sulphate. After removing the drying agent,
the solution was distilled with addition of anhydrous benzene till 750 ml of benzene solution remained.

1,8-Dimethylnaphthalene.

Lithium aluminium hydride (30 g) was stirred with anhydrous ether (1.2 l.) for 2 hr in a flanged reaction vessel fitted with a stirrer, a dropping funnel, and a reflux condenser. Most (94.5%) of the solution produced in the previous reaction was added through the dropping funnel over a 2 hr period with stirring. Ether (300 ml) was distilled off, and the excess lithium aluminium hydride was destroyed by cautiously adding ethyl acetate (100 ml). Saturated aqueous potassium hydroxide (60 ml) was added fairly rapidly to the stirred solution, and after a few minutes a white precipitate partly separated from a yellow liquid. The hot liquid was decanted and the residual sludge was extracted by decantation with a hot solution of 25% ether in benzene (5 x 400 ml). The organic extract was filtered and the solvent was evaporated. Distillation of the residue gave 34.7 g (71%) of 1,8-dimethyl-naphthalene, m.p. 57-60°. Recrystallization from ethanol reduced this to 28.8 g (59%), m.p. 62-65° (62.5°)⁹. A small sample again recrystallized from redistilled ethanol melted at 63-64°.

4,5-Dimethyl-1-nitronaphthalene.

1,8-Dimethylnaphthalene (5.0 g) was dissolved in hot redistilled glacial acetic acid (10 ml) in a small reaction vessel fitted with a stirrer and a dropping funnel. The apparatus was heated on a boiling water-bath while concentrated nitric acid (d 1.42, 2.9 ml)
in redistilled glacial acetic acid (3.5 ml) was added over a period of 30 min. Heating and stirring were continued for another 30 min before the mixture was cooled to 5° and filtered. The solid product was washed with 50% aqueous acetic acid, and water, and dried to give 5.33 g (55%) of crude 4,5-dimethyl-1-nitronaphthalene, m.p. 56-59°. It was chromatographed on activated alumina (200 g) and eluted with a mixture of benzene (2 parts) and petroleum ether (b.p. 55-65°, 1 part). After evaporation of the solvent, the residual nitro compound was recrystallized from ethanol to give 2.80 g (43%) of pure 4,5-dimethyl-1-nitronaphthalene, m.p. 64-65° (66-67°) 47. (Found: C, 71.75; H, 5.75; N, 7.2; 0, 15.75. Calcd. for C_{12}H_{11}NO_{2}: C, 71.6; H, 5.5, N, 6.95; O, 15.9%).

4,5-Dimethyl-1-naphthylamine.

4,5-Dimethyl-1-nitronaphthalene (6.0 g) in redistilled ethanol (200 ml) was reduced with aluminium amalgam prepared from 6.5 g of aluminium foil (see p. 49). Distillation gave 4.03 g (82%) of 4,5-dimethyl-1-naphthylamine, b.p. 134-136°/1 mm. Two recrystallizations from redistilled petroleum ether (b.p. 50-70°) gave 2.95 g of product melting at 85.5-86° (86-86.5°) 47. (Found: C, 84.2; H, 7.55; N, 8.15. Calcd. for C_{12}H_{12}N: C, 84.15; H, 7.65; N, 8.2%).

The acetyl derivative melted at 185-185.5° after three recrystallizations from redistilled ethanol. (Found: C, 78.6; H, 6.9; N, 6.5, O, 7.2. C_{14}H_{15}NO requires C, 78.85; H, 7.1; N, 6.55; O, 7.5%).
Conversion of 4,5-Dimethyl-1-naphthylamine to 1-Bromo-4,5-dimethylnaphthalene.

4,5-Dimethyl-1-naphthylamine (1.50 g) was dissolved in aqueous acetic acid (50%, 18 ml), the solution was cooled to 0°C, and ice (ca. 5 g) was added. Aqueous sodium nitrite (35%, 4 ml) was quickly added to the stirred solution, and stirring was continued for a further 20 min, during which time a red precipitate formed.

Cuprous bromide (3 g) was dissolved in concentrated hydrobromic acid (d 1.46 - 1.49, 18 ml) and the solution was cooled to 0°C before ice (ca. 10 g) was added. The diazonium acetate was slowly added down a wide tube reaching to the bottom of the stirred cuprous bromide solution. Nitrogen was evolved, and the temperature did not exceed 3°C during the addition. Stirring was continued at 0°C for 1 hr, and at 20°C for 2 hr, during which time the solution effervesced steadily. The solution was allowed to stand overnight, boiled for a few minutes, and cooled. It was extracted with ether (100 ml, 3 x 30 ml) and the combined ether extracts were filtered and washed with aqueous sodium hydroxide (10%, 50 ml), and then with water (50 ml). Because separation was poor, the ethereal solution was filtered and again washed with aqueous sodium hydroxide (5%, 50 ml), and water (3 x 20 ml). It was dried over anhydrous magnesium sulphate, filtered, and the ether was evaporated. The residue was chromatographed on alumina using petroleum ether (b.p. 55-65°C) as eluent, and recrystallized from redistilled ethanol. The product was 1-bromo-4,5-dimethyl-naphthalene, m.p. 31-31.5°C (30.5°C).
(a) Preparation of 4,5-Dimethyl-2-naphthylamine.

**3-Bromonaphthalic Anhydride**

Naphthalic anhydride (100 g) and concentrated sulphuric acid (1.2 l.) were stirred together in a three-necked 2 l. flask fitted with a stirrer, a thermometer, and a dropping funnel. Silver sulphate (81 g) and bromine (95 g) were added in turn. Reaction was rapid and was accompanied by the formation of a precipitate of silver bromide. The mixture was stirred at 60° for 3 hr, cooled, and the silver bromide was filtered off on a sintered glass funnel. It was washed with a small amount of concentrated sulphuric acid, and the filtrate and washings were carefully added to water (3 l.). The precipitate was filtered, washed thoroughly with water, and dried. Recrystallization from acetic anhydride gave 109 g (78%) of 3-bromonaphthalic anhydride, m.p. 239-242°. Another recrystallization from acetic anhydride raised the melting-point of the product to 242.5-244° (244°)33.

**2-Bromo-4,5-di(hydroxymethyl)naphthalene**

Lithium aluminium hydride (50 g) and anhydrous ether (1.2 l.) were stirred together for 1.5 hr in a 2 l. flanged reaction vessel fitted with a reflux condenser and a link stirrer. Anhydrous benzene (200 ml) was added, followed by a suspension of 3-bromonaphthalic anhydride (98 g) in anhydrous benzene (170 ml). The addition took 45 min, and was accompanied by vigorous reaction. The mixture was refluxed for 6 hr, and ethyl acetate (170 ml) was carefully added over the next 2 hr, this rate of addition being
sufficient to maintain vigorous boiling. A solution of potassium hydroxide (55 g) in water (50 ml) was then added, also over a period of 2 hr. The colloidal inorganic salts were extracted with a mixture of benzene, ether and ethanol in the ratio 7:3:2 (8 x 700 ml). The solvent was removed by distillation, ethanol being added at intervals so that the product was finally contained in 200 ml of this solvent. The ethanolic solution was poured into dilute sulphuric acid (10%, 400 ml) and the resulting solid was filtered off. It was washed with water and then recrystallized from ethanol (500 ml) to give 61 g (64%) of 2-bromo-4,5-di(hydroxymethyl)naphthalene, m.p. 156.5-158°. A sample recrystallized again from redistilled ethanol melted at 157.5-158° (162-163°)⁹. Further recrystallizations did not yield a product of higher melting-point.

2-Bromo-4,5-di(bromomethyl)naphthalene.

2-Bromo-4,5-di(hydroxymethyl)naphthalene (53 g) was suspended in anhydrous benzene (1 l.) and anhydrous ether (200 ml) in a three-necked 2 l. flask fitted with a stirrer, a reflux condenser, and a dropping funnel. Redistilled phosphorus tribromide (40 g) in anhydrous ether (200 ml) was added to the stirred mixture over a period of 1 hr. The suspension cleared to a straw-coloured solution. The mixture was stirred and refluxed for 2 hr, and poured into cold water (600 ml). The aqueous layer was separated, and the organic layer was washed with water (300 ml), saturated sodium bicarbonate solution (400 ml) and water (2 x 300 ml), in that order, before it was dried over anhydrous magnesium sulphate.
The drying agent was filtered off, and the solvent was distilled till 400 ml of solution remained. It was used in the following reaction.

2-Bromo-4,5-dimethylnaphthalene

Lithium aluminium hydride (25 g) and anhydrous ether (1 l.) were stirred and refluxed together in a 2 l. flanged reaction vessel fitted with a stirrer, a reflux condenser, and a dropping funnel. The benzene solution of 2-bromo-4,5-di(bromomethyl)naphthalene from the previous reaction was added over a period of 45 min to the unheated, stirred solution. The reaction mixture was stirred for 1 hr, and then refluxed with stirring for a further 2 hr before the excess lithium aluminium hydride was decomposed with ethyl acetate added cautiously over a period of 1.5 hr. Concentrated potassium hydroxide solution (30 ml) was added during the next hour, and this was followed by water (20 ml) and ethanol (20 ml). The reaction product was boiled for 1 hr, and extracted by decantation with a mixture of benzene, ether and ethanol in the ratio 10:4:1 (7 x 400 ml). The extracts were combined and filtered, and the solvent was evaporated. An attempt at distillation of the residue was thwarted by the presence of inorganic material. The product was dissolved in ether (800 ml) and the ethereal solution was washed with dilute sulphuric acid (200 ml), and then with water (2 x 200 ml) before it was dried over anhydrous magnesium sulphate. The drying agent was removed by filtration, and the ether was distilled off. Distillation
of the residue afforded 38.5 g (83%) of 2-bromo-4,5-dimethyl-naphthalene, b.p. 123-128°/1 mm, m.p. 79-81°. After being recrystallized twice from redistilled ethanol, the product was obtained as white needles (33 g, 71%), m.p. 84.5-85.5° (88-89°)57. Further recrystallizations failed to produce a product of higher melting-point. (Found: C, 61.6; H, 4.7; Br, 31.95. Calcd. for C₁₂H₁₁Br: C, 61.3; H, 4.7; Br, 34.0%).

More 2-bromo-4,5-dimethyl-naphthalene was recovered from the recrystallization residues, and after recrystallization from redistilled ethanol, it melted at 90-91°.

2-Acetyl-4,5-dimethyl-naphthalene60.

n-Butyllithium for use in this preparation was formed as follows84. Anhydrous ether (200 ml) was placed in a three-necked flask fitted with a stirrer, a low temperature thermometer, and a pressure-equalizing dropping funnel. After the apparatus had been swept dry with nitrogen, lithium strips (10 g) were cut to allow the pieces fall into the flask against the stream of dry nitrogen. With the stirrer started, about 40 drops of a solution of distilled n-butyl bromide (90 g) in anhydrous ether (100 ml) was added from the dropping funnel. When bright spots appeared on the lithium indicating that the reaction had started, the mixture was cooled to -10° by immersing the flask in a "dry-ice" acetone bath at -30° to -40°. The remainder of the butyl bromide solution was added at an even rate over 0.5 hr while the internal temperature was maintained at -10°. After addition was complete, the reaction mixture was
allowed to warm to $5^\circ$ over 1 hr, and was then stirred at $5^\circ$ for another 2 hr. It was filtered, under dry nitrogen, through glass wool into a measuring cylinder previously flushed dry with nitrogen, and stored overnight in a stoppered flask in a refrigerator.

A 1 ml aliquot was hydrolysed with distilled water (2 ml) and the hydrolysate was titrated with standard acid using phenolphthalein indicator. A second 1 ml aliquot was added to freshly distilled benzyl chloride (1 ml) in ether (2 ml), and water (5 ml) was added to the mixture after 5 min. This mixture was also titrated with acid with vigorous shaking near the end-point (because the aqueous layer decolourizes before the organic layer). Titrations were repeated till three successive readings were consistent. The difference in titration figures represents the $\eta$-butyllithium present. The yield was 86%.

A three-necked 250 ml flask was fitted with a sealed Hershberg stirrer, a pressure equalizing dropping funnel, and a reflux condenser with a calcium chloride drying tube. The system was flushed with dry nitrogen, and $\eta$-butyllithium (65 ml, 48% excess) was placed in the flask. 2-Bromo-4,5-dimethylnaphthalene (10.0 g) in anhydrous ether (150 ml) was added over a period of 5 min, this causing some evolution of heat. A solid appeared, and the solution turned green. After a further 5 min of stirring, powdered anhydrous cadmium chloride (6.2 g) was added all at once, and the reaction mixture was refluxed on a water-bath for 5.5 hr. A considerable amount of solid appeared during this period and made
stirring difficult. The ether was distilled off and was gradually replaced by anhydrous benzene (150 ml) added from the dropping funnel. Redistilled acetyl chloride (6.0 g, 10% excess) in anhydrous benzene (25 ml) was quickly added to the cool, stirred reaction mixture, this causing an appreciable rise in temperature and the formation of more precipitate. The reaction mixture was heated to 80° with stirring over a period of 1 hr, and refluxed on a water-bath for 30 min. It was cooled and poured into aqueous sulphuric acid (200 ml, 3%) and allowed to stand overnight. Benzene (250 ml) was added, and the organic layer was separated and washed with water (2 x 80 ml). The combined aqueous layers were extracted with benzene (100 ml) which was in turn washed with water (2 x 50 ml). The combined benzene solutions were dried over anhydrous magnesium sulphate, filtered, and the benzene was distilled off.

Distillation of the residue afforded 5.76 g of an oil, b.p. 144-164°/1 mm, which was chromatographed on activated alumina (250 g). The first fraction, eluted with petroleum ether (b.p. 55-65°) was 1,8-dimethylnaphthalene (0.92 g, 15%), and after recrystallization it melted at 63-64°. The melting-point was not depressed by addition of an authentic sample. A 1:1 mixture of petroleum ether (b.p. 55-65°) and benzene eluted 4.77 g of an oil which yielded 3.72 g (44%) of 2-acetyl-4,5-dimethylnaphthalene, m.p. 43-44°, after crystallization from redistilled ethanol. Successive recrystallizations from redistilled ethanol and redistilled petroleum ether (b.p. 55-65°) raised the melting point to 45-46°. (Found: C, 85.05; H, 7.15; O, 8.25. C_{14}H_{14}O requires C, 84.8, H, 7.1, O, 8.05%.)
The 2,4-dinitrophenylhydrazone melted at 280-281.5° after recrystallization from dioxan.

N-Acetyl-4,5-dimethyl-2-naphthylamine

2-Acetyl-4,5-dimethylnaphthalene (1.13 g) was mixed with redistilled trichloracetic acid (20 g) in a 50 ml flask fitted with a vertical air condenser connected to a calcium chloride drying tube. The flask was heated to 60° on a water-bath, and crystalline sodium azide (1.0 g) was introduced. The reaction mixture was swirled occasionally, and maintained at 60-65° for 1 hr before it was poured into water (60 ml). The resulting suspension was cooled in ice, and ammonia (d 0.880, 20 ml) was added at such a rate that the temperature did not exceed 20°. The solid product was filtered off, washed with water, and dried to give 1.17 g (96%) of

N-acetyl-4,5-dimethyl-2-naphthylamine, m.p. 187-190°. Recrystallization from redistilled benzene reduced the yield to 0.95 g (78%), m.p. 192-193°. A recrystallization from redistilled ethanol removed a pale brown colour from the crystals, but failed to raise their melting-point. (Found: C, 79.35; H, 7.0; N, 6.9. C_{14}H_{15}NO requires C, 78.85; H, 7.1; N, 6.55%).

4,5-Dimethyl-2-Naphthylamine Hydrochloride.

Redistilled ethanol (100 ml) containing "AnalaR" concentrated hydrochloric acid (12 ml) and N-acetyl-4,5-dimethyl-2-naphthylamine (10.0 g) was refluxed for 3 hr. Redistilled ether (600 ml) was added to the cooled mixture, and the resulting white precipitate
was filtered off, washed with redistilled ether, and dried to
give 9.2 g (94%) of 4,5-dimethyl-2-naphthylamine hydrochloride.
(Found: C, 70.2; H, 7.1; N, 6.25. \( \text{C}_{12}\text{H}_{14}\text{NCl} \) requires C, 69.4; H, 6.8; N, 6.75%).

4,5-Dimethyl-2-naphthylamine.

4,5-Dimethyl-2-naphthylamine hydrochloride (7.18 g) was shaken
for 30 min with sodium hydroxide (3 g), water (100 ml) and ether
(100 ml). The layers were separated, and the aqueous layer was
extracted with ether (2 x 20 ml). The combined organic layers
were washed with water (20 ml), dried over anhydrous magnesium
sulphate, filtered, and the ether was distilled off. Distillation
of the residue afforded 5.4 g (92%) of 4,5-dimethyl-2-naphthylamine,
b.p. 157-161\(^{\circ}\)/1 mm, m.p. 91-93\(^{\circ}\). Recrystallization from aqueous
methanol reduced the yield to 4.7 g (79%), of product m.p. 95-95.5\(^{\circ}\),
shown by vapour phase chromatography to be pure. (Found: C, 83.8,
H, 7.7, \( \text{C}_{12}\text{H}_{13}\text{N} \) requires C, 84.15; H, 7.65%).

(a) Preparation of 5-Acenaphthenamine.

5-Bromoacenaphthene.\(^{10}\)

Commercial grade acenaphthene (154 g) was suspended in carbon
tetrachloride (350 ml) in a 1 l three-necked flask fitted with a
stirrer, a dropping funnel, and a thermometer. An ice-salt bath
was used to cool the mixture to -14\(^{\circ}\), and the apparatus was wrapped
in a grey cloth to exclude light. Small quantities of iodine and
(180 g) iron powder were added to the mixture, and then bromine was added
over a period of 1.5 hr. This rate of addition kept the reaction temperature at \(-7^\circ\) to \(-12^\circ\). The reaction mixture was stirred for a further 45 min at \(-10^\circ\), and then allowed to warm up to room temperature during the next 2.5 hr with continued stirring. The product was poured into water (400 ml), and the organic layer was separated before being shaken with aqueous sodium hydroxide (2N, 500 ml) and carbon tetrachloride. A fine white precipitate hampering separation of the layers was filtered off, and the organic layer was separated, and washed with aqueous sodium hydroxide (2N, 300 ml), and water (2 x 200 ml). It was dried over anhydrous magnesium sulphate, filtered, and the carbon tetrachloride was distilled off. Two distillations gave 98.1 g (42%) of 5-bromoacenaphthene, b.p. 138-146\(^\circ\)/1 mm, reduced to 77.6 g (33%), m.p. 52-53\(^\circ\) (54\(^\circ\))\(^1\) after recrystallization from redistilled ethanol.

Vapour phase chromatography showed this compound to be 90-95% pure. It contained a very small percentage of acenaphthene, and a larger percentage of a compound thought to be another bromo-acenaphthene. A sample recrystallized again from redistilled ethanol melted at 53-53.5\(^\circ\), but had virtually the same vapour phase chromatographic characteristics as the previous sample.

5-Acenaphthoic Acid\(^1\).

\(\alpha\)-Butyllithium used in this preparation was prepared as described on p. 61.

5-Bromoacenaphthene (66 g) in anhydrous ether (100 ml) was added to a solution of \(\alpha\)-butyllithium (280 ml, 50% excess) in a
round-bottomed flask. The flask was cooled in ice and the contents were swirled for 7 min before they were poured on to dry lumps of solid carbon dioxide (300 g) in anhydrous ether (300 ml). When all the "dry-ice" had evaporated, the ethereal suspension was extracted with hydrochloric acid (2.5 N, 400 ml), and then with aqueous sodium hydroxide (2N, 400 ml, 200 ml). The alkaline extracts were boiled with animal charcoal and filtered while hot. Concentrated hydrochloric acid (150 ml) was added, with stirring, to precipitate a creamy white solid which was filtered from the cooled solution and washed with water. After it was recrystallized from redistilled ethanol, 23.6 g (42%) of 5-acenaphthoic acid, m.p. 212-214°, was obtained. A subsequent recrystallization from glacial acetic acid gave 19.3 g (34%) of product, m.p. 218-219° (221-223°).¹

5-Acenaphthenamine.

Polyphosphoric acid was prepared by heating phosphorus pentoxide (21 g) and orthophosphoric acid (90%, 20 g) at 200° for several hours until the mixture was homogeneous.

5-Acenaphthoic acid (3.0 g) was stirred with the polyphosphoric acid, and crystalline sodium azide (4.0 g) was added. The mixture was allowed to stand overnight, and then it was heated on an oil-bath at 120° till effervescence had ceased (ca. 45 min). Frequent stirring was necessary to prevent the mixture from bubbling over. The cooled reaction mixture was poured into water (500 ml) containing potassium hydroxide (60 g), and the product was extracted with ether (3 x 200 ml). The ethereal extract was washed with water (400 ml) which was then extracted with ether.
(300 ml). The combined ethereal extracts were filtered, dried over anhydrous magnesium sulphate, filtered, and the ether was distilled off. Distillation of the residue gave 0.55 g (22%) of 5-acenaphthenamine, b.p. 158-166°/1 mm. It was combined with other samples prepared similarly, redistilled, and recrystallized from aqueous redistilled methanol to give fine white crystals melting at 107.5-108° (108°). Vapour phase chromatography showed the product to be pure.

(f) Preparation of 4-Acenaphthenamine.

Method I

2-Bromo-4,5-di(bromomethyl)naphthalene.

The preparation of this compound is described on p. 59 but in that instance the product was not isolated.

The organic solution of product from the bromination of 73 g of 2-bromo-4,5-di(hydroxymethyl)naphthalene was boiled down, and redistilled petroleum ether (b.p. 85-95°) was added to the hot solution. Subsequent cooling and filtration gave 91 g (85%) of 2-bromo-4,5-di(bromomethyl)naphthalene, m.p. 130-131° (130-131.5°) as very dense pale yellow prisms.

4-Bromoacenaphthene.

Phenyllithium for use in this preparation was synthesized as follows. Anhydrous ether (100 ml) was placed in a 250 ml three-necked flask fitted with a sealed stirrer, a dropping funnel, and a reflux condenser. After the apparatus had been flushed with
dry nitrogen, lithium (4.0 g, in small pieces) was allowed to fall into the flask against a stream of nitrogen. With the stirrer started, about 40 drops of a solution of redistilled bromobenzene (42 g) in anhydrous ether (250 ml) was added. After a few minutes the solution became cloudy, and the bromobenzene was added to such a rate that the reaction mixture refluxed gently. The resulting solution was cooled, and filtered, under nitrogen, through glass wool to remove the lithium bromide. The concentration of phenyllithium was found by titrating the alkali from a hydrolysed aliquot with standard sulphuric acid.

2-Bromo-4,5-di(bromomethyl)naphthalene (50 g) was dissolved in anhydrous benzene (600 ml) in a 1 l. three-necked flask fitted with a sealed stirrer, a reflux condenser with a drying tube, and a pressure equalizing dropping funnel. When the system had been flushed dry with nitrogen, phenyllithium solution (210 ml, 5% excess) was added to the stirred mixture over a period of 30 min. The reaction mixture was stirred and refluxed for 1 hr, and poured into water (400 ml). The solution was acidified with concentrated hydrochloric acid, and the layers were separated. The organic layer was washed with water (2 x 400 ml) and dried over anhydrous magnesium sulphate before it was filtered and the solvent was distilled off. After two distillations under reduced pressure, the residue yielded 20.5 g (69%) of 4-bromoacenaphthene, b.p. 134-138°/1 mm, m.p. 63-64°. One recrystallization from redistilled ethanol
reduced the yield to 17.8 g (60%), m.p. 64-65° (65-65.5°)\textsuperscript{1}.

4-Acetylanaphthene.

\textit{n}-Butyllithium for use in this preparation was formed as described on p. 61.

A three-necked 250 ml flask was fitted with a Hershberg stirrer, a pressure equalizing dropping funnel, and a reflux condenser with a drying tube. When the apparatus had been flushed dry with nitrogen, \textit{n}-butyllithium (55 ml, 50% excess) was placed in the flask. 4-Bromoacenaphthene (10.0 g) in anhydrous ether (30 ml) was added to the stirred \textit{n}-butyllithium, and the two were allowed to react over a period of 10 min. A white precipitate formed. Cadmium chloride (9 g, 50% excess) was added, and the mixture was stirred and refluxed on a water-bath for 8 hr. The ether was distilled off and replaced with anhydrous benzene (150 ml). Redistilled acetyl chloride (5.4 g, 5% excess) in anhydrous benzene (25 ml) was added rapidly to the cooled solution. The quickly darkening reaction mixture was heated to 70° over a period of 20 min, and poured into water (200 ml). The resulting mixture was extracted with benzene (250 ml, 100 ml), and the benzene solution was washed with water (2 x 100 ml), dried over anhydrous magnesium sulphate, and filtered. Evaporation of the benzene left an oily residue which yielded 4.34 g of sticky solid after two distillations at low pressure. It was recrystallized from redistilled ethanol to give 1.65 g (20%) of 4-acetylanaphthene, mp. 81-83°. After recrystallization from redistilled petroleum ether (b.p. 55-65°) it melted at 86.5-87.5°
and was shown to be pure by vapour phase chromatography. (Found: C, 85.7; H, 5.8; O, 8.3. \( \text{C}_{14}\text{H}_{12}\text{O} \) requires C, 85.7; H, 6.15; O, 8.15%).

The 2,4-dinitrophenylhydrazene decomposed at about 300°. (Found: C, 63.65; H, 4.7; N, 15.5. \( \text{C}_{20}\text{H}_{16}\text{N}_{4}\text{O}_{4} \) requires C, 63.8; H, 4.3; N, 14.9%).

The residue from recrystallizations of the product was an oil, and on passing a sample through the vapour phase chromatograph, the only peak found had a retention time identical with that of 4-acetylanacenaphthene.

**N-Acetyl-4-acenaphthenamine.**

The apparatus and process used was identical with that used in the preparation of N-acetyl-4,5-dimethyl-2-naphthylamine (p. 64). From 3.03 g of 4-acetylanacenaphthene, 3.23 g (99%) of crude N-acetyl-4-acenaphthenamine, m.p. 171-173°, was obtained. It was recrystallized from aqueous ethanol with a little animal charcoal to give 2.39 g (71%) of product m.p. 175-176° (175-176°).

**4-Aacenaphthenamine Hydrochloride.**

N-Acetyl-4-acenaphthenamine (2.1 g) was refluxed for 3 hr with concentrated hydrochloric acid (3 ml) in redistilled ethanol (25 ml). Cooling the solution resulted in precipitation of pale yellow crystals which were filtered off, washed with aqueous ethanol, and dried to give 1.30 g (64%) of 4-acenaphthenamine hydrochloride. It was recrystallized twice from ethanol before using it in a pK\(_a\) determination.
A small sample was dissolved in a mixture of aqueous sodium hydroxide and benzene. Vapour phase chromatography of the organic layer showed that it contained pure 4-acenaphth enam ine with a retention time identical with that of the product of reduction of 4-nitroacenaphthene (below).

**Method II**

5-Nitroacenaphthene

A solution of commercial acenaphthene (154 g) in hot glacial acetic acid (600 ml), in a three-necked 1 l. flask fitted with a thermometer, a link stirrer, and a dropping funnel, was cooled with vigorous stirring to separate fine crystals of acenaphthene. Nitric acid (d 1.40, 98.4 g) was added over a period of 1 hr, while the reaction temperature was kept at 22–27° by periodically immersing the flask in ice-water. After about half the nitric acid had been added, a yellow magma of 5-nitroacenaphthene formed and made stirring difficult. The mixture was stirred for 1 hr at 25°, warmed to 70° over a period of 30 min, and cooled in ice. The precipitated product was filtered on a Buchner funnel and washed successively with glacial acetic acid, 50% aqueous acetic acid, and water. After it was dried, 168 g (84%) of 5-nitroacenaphthene, m.p. 102–103° (108°) was obtained.

5-Acenaphthenamine.

Raney nickel used in this preparation was prepared as follows. A solution of sodium hydroxide (60 g) in water (250 ml) was stirred
mechanically in a 1 l. beaker. Raney's alloy (50 g) was added over a period of 1 hr, this rate of addition being sufficient to keep the solution boiling. The suspension was stirred for 1 hr, and then gently boiled with stirring for 8 hr, during which time water was added to keep the volume constant. The aqueous solution was poured off, and the residual nickel was washed by decantation with distilled water (3 x 300 ml). Sodium hydroxide (10 g) in distilled water (100 ml) was added and decanted. The Raney nickel was washed by decantation with distilled water (30 x 300 ml) and with redistilled ethanol (3 x 300 ml). It was kept under redistilled ethanol until it was used.

5-Hydroacenaphthene (50 g) was suspended in redistilled ethanol (150 ml) in a 200 ml autoclave flask, and Raney nickel (15 ml) was added. Hydrogenation was carried out at room temperature in a vigorously shaken autoclave over a period of 4.5 hr. To avoid excessive heating as a result of the exothermic reaction, hydrogen was introduced at 30 min intervals, and the internal pressure was never allowed to exceed 80 p.s.i. The product solution was boiled and diluted with hot water till it was saturated with amine. Animal charcoal was added, and the hot solution was filtered, and cooled to precipitate pale brown needles of product. After it was filtered, washed with dilute ethanol, and dried, the yield of 5-acenaphtheneamine, m.p. 105-106° (108°) was 33.8 g (80%).
5-Formylaminoacenaphthene

5-Aacenapthenamine (20 g) and "AnalaR" formic acid (66 ml) were refluxed together for 45 min. When the solution had cooled to 70°, water (10 ml) was added, and the product was precipitated by cooling in ice. It was filtered, washed successively with formic acid, water, and methanol; and dried to give 19.5 g (84%) of 5-formylaminoacenaphthene, m.p. 168.5-169.5°. Recrystallization from ethanol yielded 17.5 g (75%) of slightly discoloured prisms, m.p. 169-170° (172°).

5-Formylamino-4-nitroacenaphthene

5-Formylaminoacenaphthene (17.0 g) in glacial acetic acid (70 ml) was nitrated with "AnalaR" nitric acid (d 1.42, 20 ml) added in two batches. While the temperature was maintained at 15-30°, the first 10 ml of nitric acid was added with stirring; the second 10 ml was then added quickly. After it was allowed to stand at room temperature for 2 hr, the mixture was gently warmed to 50°, and cooled in ice to precipitate a yellow solid that was filtered off. It was washed with a little glacial acetic acid, and recrystallized from the same solvent to yield 8.4 g (42%) of 5-formylamino-4-nitroacenaphthene, m.p. 226-227° (229°).

4-Nitro-5-acenaphthenamine

5-Formylamino-4-nitroacenaphthene (40 g), in ethanol (600 ml) and hydrochloric acid (33%, 80 ml) were refluxed for 30 min. Red needles slowly separated and were filtered from the cooled solution.
After it was washed with ethanol and dried, 35.8 g (99%) of 4-nitro-5-acenaphthenamine, m.p. 212-213°, was obtained. Recrystallization from glacial acetic acid gave a sample melting at 213-213.5° (222-224°).

4-Nitroacenaphthene 63.

4-Nitro-5-acenaphthenamine (5.0 g) was suspended in a mixture of glacial acetic acid (50 ml) and concentrated sulphuric acid (25 ml) in a 100 ml beaker. Crystalline sodium nitrite (5.0 g) was quickly added to the stirred mixture, and the whole was set aside for 1 hr. During this period the reaction mixture darkened, bubbled a little and warmed to about 30°. It was then added over a period of 5 min to a vigorously stirred mixture of redistilled ethanol (200 g) and cuprous oxide (10 g, freshly prepared from cupric acetate and glucose 86) initially at 70°. Reaction was marked by boiling of the solution and vigorous evolution of nitrogen. The reaction solution was boiled for another 5 min and poured into water (600 ml), and the mixture was cooled to 0° and filtered. The resulting black solid was washed with water, dried, and extracted with petroleum ether (b.p. 50-70°, 100 ml, 50 ml). The organic solution was evaporated to 100 ml, and cooled to precipitate 2.36 g of yellow-brown needles, m.p. 124-126°. They were recrystallized from redistilled ethanol to yield 1.86 g (40%) of 4-nitroacenaphthene, m.p. 129-130° (129°) as yellow needles. No more product of reasonable purity was obtained by further extractions of the black solid.
4-Acenaphthenamine

4-Nitroacenaphthene (11.0 g) was dissolved in redistilled ethanol (300 ml) at 70° in 1 l beaker. Hot water (40 ml) was added, and then aluminium amalgam prepared from 14 g of aluminium (see p. 49). Gentle boiling was maintained by heating the mixture on a hot-plate. Water (210 ml) was added over a period of 1 hr, followed by sufficient ethanol to keep the volume constant over the subsequent 1.5 hr of heating. The aluminium hydroxide was filtered off and washed liberally with ethanol. The filtrate and washings were mixed, and distilled with additions of water till about 300 ml of aqueous solution remained. This was cooled and extracted with ether (200 ml, 2 x 100 ml). The ether solution was washed with water (100 ml), dried over anhydrous magnesium sulphate and filtered, and the ether was distilled off. Two distillations of the residue through a short Vigreux column gave 7.04 g of white solid, b.p. 154-158°/1 mm, reduced to 6.52 g (85%) of 4-acenaphthenamine, m.p. 89-89.5° (87°) after recrystallization from redistilled methanol. It was shown to be pure by vapour phase chromatography.

Preparation of the Dimethylamino Compounds

1-Dimethylaminonaphthalene.

Crude 1-naphthylamine (5 g) and redistilled trimethyl phosphate (5 g), in a small pear-shaped flask fitted with an air condenser, were cautiously heated with a microburner. A vigorous reaction was moderated by partly immersing the flask in a beaker of cold water, and the reaction mixture was then refluxed for 1 hr.
phosphate had been used. The dimethylamino compounds prepared are listed below. All have been subjected to vapour phase chromatography, and their purity as estimated by this technique is shown.

4-Methyl-1-dimethylaminonaphthalene.

Yield 64%. Purity 98%. b.p. 137-139°/1 mm.
(Found: C, 84.3; H, 8.25; N, 7.55. C_{13}H_{15}N requires C, 84.3; H, 8.15; N, 7.55%).

4,5-Dimethyl-1-dimethylaminonaphthalene.

Yield 59%. Purity 97%. b.p. 142-144°/1 mm.
(Found: C, 83.95; H, 8.6; N, 6.2. C_{14}H_{17}N requires C, 84.35; H, 8.6; N, 7.05%).

5-Dimethlaminoacenaphthene.

Yield 59%. Purity 100%. b.p. 151-152°/1 mm.

m.p. 45.5-46.5° (45-46°). (Found : C, 85.15; H, 7.9; N, 7.35.
Calcd. for C_{14}H_{15}N: C, 85.25; H, 7.65; N, 7.1%).

2-Dimethylaminonaphthalene.

Yield 65%. Purity 100%. b.p. 130-132°/1 mm. m.p. 46-47° (46°)

4-Methyl-2-dimethylaminonaphthalene.

Yield 11% after chromatography on alumina and two distillations. Purity 98%. b.p. 136-138°/1 mm. (Found: C, 84.3; H, 8.4; N, 7.6.
C_{13}H_{15}N requires C, 84.3; H, 8.15; N, 7.55%).
4,5-Dimethyl-2-dimethylaminonaphthalene.

Yield 17.5% after distillation and several recrystallizations from redistilled methanol. Purity 100%. b.p. 157-161/1 mm. m.p. 56-57°. (Found: C, 84.0; H, 3.9; N, 6.95. C_{14}H_{17}N requires C, 84.35; H, 8.6; N, 7.05%).

4-Dimethylaminoacenaphthene.

Yield 18.5% after chromatography on alumina, distillation and recrystallization. Purity 100%. b.p. 154-158°/1 mm (for an impure sample). m.p. 53-54°. Found: C, 85.35; H, 7.6; N, 7.5. C_{14}H_{15}N requires C, 85.25; H, 7.65; N, 7.1%).

Preparation of 1-Naphthylamine Hydrochloride

Crude 1-naphthylamine was heated to 100° with 25% acetic anhydride in acetic acid, and the mixture was cooled to precipitate N-acetyl-1-naphthylamine. It was recrystallized twice from aqueous ethanol, and melted at 159-160° (160°). The acetyl amine was hydrolysed by refluxing it for 3 hr in ethanol containing 10% concentrated hydrochloric acid. The precipitated hydrochloride was recrystallized three times from distilled water.

Preparation of 2-Naphthylamine Hydrochloride

Pure 2-naphthylamine hydrochloride was prepared from N-acetyl-2-naphthylamine m.p. 131-131.5° (134°) as described above.
The Determination of Amine

Base Strengths

The base strengths of the amines were determined by an ultraviolet spectrophotometric method; the compounds studied were insufficiently soluble in aqueous solvents for a titration method to be feasible. The absorptions of each compound in acid, alkaline and buffered solutions were compared at a particular wavelength. The ratio of amine to conjugate acid was thus obtained, and was used in conjunction with the calculated pH of the buffer solution to determine the base strengths. Rough spectra used to select a suitable wavelength for the final absorption measurements were made, in the region 36-230 m\(\mu\), on a Beckmann DK2A recording spectrometer. Accurate absorption measurements were then made on a Hilger "Uvispek", a single beam instrument with interchangeable hydrogen and filament lamps and a quartz prism. The silica cells were cleaned by heating them in concentrated nitric acid for 24 hr, and then rinsing them thoroughly with distilled water. They were housed in a cell block kept at 25.0\(\pm\)0.1\(^\circ\)C by circulation of water from a thermostatted bath, and they were not moved during a \(pK_a\) determination.

While water was a suitable solvent in which to determine the \(pK_a\) values of the primary amines, the dimethylamines were not sufficiently soluble in this solvent. 20% Dioxan/water was therefore used. It was a convenient solvent because in addition (a)
the acid dissociation constants of formic and acetic acids, required for preparing buffer solutions, have been determined in this medium\textsuperscript{89,90}, and (b) it does not absorb greatly in the wavelength range used.

**Preparation of Reagents.**

Dioxan. Fluka "pure" dioxan (101.) was refluxed for 12 hr with hydrochloric acid (1N, 11.). Tin (50 g) was added and the mixture was refluxed for a further 12 hr. The solution was saturated with potassium hydroxide and the aqueous layer was separated. The dioxan was dried over potassium hydroxide pellets and then over sodium wire, and then refluxed over sodium for a week. It was fractionated at a reflux ratio of 1:10, off sodium through a 5' vapour jacketed column of glass helices fitted with silica gel drying tubes. The 5 l. middle fraction, b.p. 101.0°/755 mm (101.3°/ 760 mm)\textsuperscript{91} was collected and stored in an aspirator fitted with a soda-lime and a silica gel guard tube in series.

Dioxan/water (20% w/w) was prepared from this anhydrous dioxan and boiled out deionized water.

Borax. "AnalaR" borax was recrystallized from distilled water below 55°, and stored in a desiccator over a saturated aqueous solution of sucrose and sodium chloride.

**Aqueous Hydrochloric Acid.** Concentrated "AnalaR" hydrochloric acid was diluted with boiled out deionized water till it was approximately 0.2N. It was titrated with weighted samples of borax, using methyl red/bromocresol green as an indicator, till
four successive titration agreed to within 0.2%.

**Aqueous Sodium Hydroxide.** A saturated solution of "Analar" sodium hydroxide was centrifuged to free it from sodium carbonate. It was diluted with boiled out deionized water to give an approximately 0.2N solution and standardized volumetrically against hydrochloric acid using phenolphthalein as indicator. The pipette used in this and all other titrations was calibrated with boiled out deionized water at 20°C ± 0.2°C.

**Aqueous Acetic Acid.** "Analar" glacial acetic acid was fractionated, through a 12" vacuum jacketed column of glass helices, at a reflux ratio of 1:10. The fraction boiling at 117.4-117.5°C/756 mm (117-72°C/760 mm) was collected. An approximately 0.2N solution was made up in boiled out deionized water, and this was standardized against sodium hydroxide, using phenolphthalein indicator, till four successive titrations agreed to within 0.2%.

**Aqueous Formic Acid** "Analar" 90% formic acid was fractionated through the same column as that used for acetic acid. The fraction boiling at 100.4-100.7°C/760 mm (100.70°C/760 mm) was collected, and a 0.2N solution was made up and standardized as described for acetic acid above.

**20% Dioxan Solutions.** All the solutions above were also made up in 20% dioxan/water. They were initially made up to about 0.27N in water, and standardized. From the normality, density and total weight of the solution, the total weight of water was calculated, and anhydrous dioxan (weighing 25% of the weight of water) was carefully added. The solution was then standardized as described
for the aqueous solutions above.

**Preparation of Buffer Solutions.**

Essentially the same technique was used in preparing buffer solutions in water and in 20% dioxan. Large quantities of buffer were more conveniently made up by weight than by volume. However, the solutions used to make up the buffers were standardized by volume, so that it was necessary to know the densities of the constituent solutions in order to calculate the buffer pH. For aqueous solutions the densities were obtained from the "Handbook of Chemistry and Physics", Chemical Rubber Publishing Co., Cleveland, Ohio, U.S.A. (1963). For solutions in 20% dioxan, the solution discharged from a 5 ml pipette (previously calibrated with boiled out distilled water) was weighed, and from this weight the density of the solution was calculated. Ten separate weighings were made, and averaged, for each solution. The densities so obtained are shown below.

<table>
<thead>
<tr>
<th>20% w/w Dioxan/water</th>
<th>1.014</th>
<th>1.013672</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.21 N Acetic acid</td>
<td>1.0165</td>
<td></td>
</tr>
<tr>
<td>0.22 N Sodium hydroxide</td>
<td>1.0252</td>
<td></td>
</tr>
<tr>
<td>0.20 N Formic Acid</td>
<td>1.0167</td>
<td></td>
</tr>
</tbody>
</table>

The error of 0.0005 density units or 0.05% in the density of 20% dioxan/water is very small compared with other experimental errors.

Buffer solutions were made up by accurately weighing sodium hydroxide solution, acetic or formic acid solution, and water or 20% dioxan into a bottle. The density of each solution was
Fig. VIII
ULTRAVIOLET SPECTRUM
1-NAPHTHYLAMINE
SOLVENT: WATER
Fig. IX
ULTRAVIOLET SPECTRUM
2-NAPHTHYLAMINE
SOLVENT: WATER
Fig X

ULTRAVIOLET SPECTRUM
1-DIMETHYLAMINONAPHTHALENE
SOLVENT: 20% DIOXAN/WATER
ULTRAVIOLET SPECTRUM
2-DIMETHYLAMINONAPHTHALENE
SOLVENT: 20% DIOXAN/WATER
then used to calculate the volume used, and from the volume of each solution and its normality, the ratio of acid to alkali was determined. This ratio was used in the calculations which are described later. All buffer solutions were made up to have an ionic strength of about 0.5, and they were later diluted volumetrically to the concentrations required for the \( pK \) determinations.

**Experimental Technique.**

Rough spectra of all amines in acid, alkaline and buffered solutions were first determined over the range 360-230 \( \mu \) m. From these spectra, a suitable wavelength, at which accurate spectral measurements could be made, was selected. Ideally, accurate spectral measurements should be made at a wavelength where (a) one species, either the amine or its conjugate acid, absorbs much more strongly than the other, and (b) the absorption of neither species is changing rapidly with wavelength. Both conditions were found to apply to the \( \beta \)-amino naphthalenes, but in the \( \alpha \)-amino compounds it was found necessary to make the measurements on the side of an absorption peak to ensure that absorption of the two species differed widely. Typical spectra are shown in figs. VIII, IX, X, XI.

Approximate \( pK_a \) values were also calculated for each amine, so that they could later be determined more accurately in buffer solutions with \( pH \) values close to the \( pK_a \) of the amine. This allows more accurate \( pK_a \) determinations than when the buffer solution has a \( pH \)
differing widely from the $pK_a$ of the amine. The rough spectra also yielded the extinction coefficients of the amines at the wavelengths used, and accurate solutions could therefore be made up so that optical densities would be in the range 0.2 to 0.8, the range in which Beer's Law was found to hold for the instrument used.

Because the primary amines used were difficult to dissolve, stock solutions were made from the amine hydrochlorides. Each amine was converted to its hydrochloride by passing dry hydrogen chloride through its ethereal solution, and the precipitated salts were filtered off, washed with ether, and dried. An attempt was also made to prepare the hydrochloride of 2-dimethylamino-naphthalene by the same method, but the compound was found to be unstable. Therefore no attempt was made to convert the other dimethyl amines to their solid hydrochlorides. To dissolve the dimethyl amines in 20% dioxan/water, it was necessary to add 1 ml of redistilled methanol and the stoichiometric amount of hydrochloric acid (in 20% dioxan) to neutralize them. The remainder of the 250 ml volumetric flask was then filled with 20% dioxan, so that the final solution of amine hydrochloride contained about 0.4% of methanol. Before a $pK_a$ was determined, these solutions were diluted to 1/5 of their original concentration, so it may confidently be assumed that the methanol added affected the $pK_a$ values negligibly.

All solutions used in the final $pK_a$ determinations were made
up of a suitable number of 20 ml aliquots (delivered from the same pipette throughout) of solutions of amine hydrochloride, water or 20% dioxan, buffer solution, sodium hydroxide, and hydrochloric acid. The number of aliquots

<table>
<thead>
<tr>
<th>Flask No.</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amine</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>Buffer</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>2</td>
<td>3</td>
<td>4</td>
</tr>
<tr>
<td>Water (or 20% dioxan)</td>
<td>2</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>Sodium Hydroxide</td>
<td>2</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Hydrochloric Acid</td>
<td>-</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

of each solution is shown in the accompanying table. Although the technique is rather laborious, it ensures that the amine concentration is the same in every solution. Two solutions were made up in alkali because a small error in concentration in this solution (for which the optical density was highest) has more effect on the final $pK_a$ than comparable errors in other solutions.

Surprisingly, differences of up to 0.004 density units (0.5% of the total optical density) were found in pairs of apparently identical amine solutions, but usually the difference did not exceed 0.002 units. The buffer solutions made up by the method described have ionic strengths of about 0.04, 0.03, 0.02 and 0.01 respectively. $pK_a$ values were determined in each of these solutions, and plotted against ionic strength. The final $pK_a$ value is obtained by extrapolating back to zero ionic strength.

In a series of optical density measurements, the "blank" cell
always contained solvent only, i.e. water or 20% dioxan. The absorptions of solutions of buffer, hydrochloric acid, and sodium hydroxide, in the appropriate solvent, were then determined. Finally, the absorptions of amine in solutions of acid, alkali, and buffer were determined, and corrected for the presence of species other than the amine or its conjugate acid. All absorption measurements with buffered solutions were repeated at 10 min intervals until they were constant. It was then assumed that the solutions had attained the same temperature as the housing (25±0.1°C).

Theory of Determining Dissociation Constants Spectrophotometrically.

The dissociation of an acid $HX$ (in this case the buffer acid) in water may be represented thus:

$$HX + H_2O \rightleftharpoons H_3O^+ + X^-$$

The dissociation constant of $HX$ is $K_1 = \frac{a_{H^+} \cdot a_X}{a_{HX}}$.

Therefore $pK_1 = -\log \frac{a_{H^+} \cdot a_X}{a_{HX}}$

where $a$ is the activity and $K_1$ is the acid dissociation constant.

Now $a_X = [X^-] \cdot f_X$, $f$ being the activity coefficient.

$a_{HX} = [HX] \cdot f_{HX}$ and $f_{HX} = 1$ because $HX$ is not charged.

Therefore, $pK_1 = pH - \log \frac{[X^-]}{[HX]} - \log f_X$ ........................ (1)

For a solution of the conjugate acid $HB^+$ of the amine $B$, a
similar expression may be derived:

\[ pK_a = pH - \log \frac{[B]}{[HB^+]} + \log f_{HB^+} \]  \( \text{......... (2)} \)

If \( pK_1 \) is known, \( pK_a \) may be evaluated by eliminating \( pH \) between (1) and (2).

\[ pK_a = pK_1 + \log \frac{[x^-]}{[HX]} - \log \frac{[B]}{[HB^+]} + \log f_{HB^+} f_{x^-} \]  \( \text{......... (3)} \)

The activity coefficient term may be evaluated from the Guggenheim extension of the Debye-Hückel equation

\[- \log f = A \frac{\sqrt{I}}{1 + \sqrt{I}} + b I\]

where \( A \) is a constant (=0.5175 for water at 25°C), \( b \) is an adjustable parameter, and \( I \) is the ionic strength.

Hence

\[- \log f_{HB^+} f_{x^-} = \frac{2A \sqrt{I}}{1 + \sqrt{I}} - (b_{HB^+} + b_{x^-}) I\]

\[= \frac{2A \sqrt{I}}{1 + \sqrt{I}} + b^1 I \]

Substituting in (3) and rearranging

\[ pK_a + b^1 I = pK_1 + \log \frac{[x^-]}{[HX]} - \log \frac{[B]}{[HB^+]} - \frac{2A \sqrt{I}}{1 + \sqrt{I}} \]  \( \text{......... (4)} \)

\( b^1 \) is an adjustable parameter found from the slope of the graph of \( I \) versus the right hand side of (4). The parameter \( b^1 \) should be constant for a series of similar compounds.

The ratio \( \frac{[x^-]}{[HX]} \) is obtained from the concentrations of sodium hydroxide, \( [Na^+] \)_s, and acid, \( [HX]_s \), used in preparing the buffer. The subscript \( s \) denotes the concentration before reaction between alkali and acid has occurred. For electrical
neutrality of the buffered amine hydrochloride solution:

$$[BH^{+}] + [Na^{+}]_s + [H^{+}] = [OH^{-}] + [Cl^{-}]_s + [X^{-}]$$

therefore $$[X^{-}] = [BH^{+}] + [Na^{+}]_s + [H^{+}] - [OH^{-}] - [Cl^{-}]_s$$

Now $$[Cl^{-}]_s - [BH^{+}] = [B]$$

therefore $$[X^{-}] = [Na^{+}]_s + [H^{+}] - [OH^{-}] - [B] \quad \ldots \ldots (5)$$

as the total quantity of $X$ must be constant

$$[HX]_s = [HX] + [X^{-}]$$

therefore $$[HX] = [HX]_s - [X^{-}]$$

Substituting for $[X^{-}]$ from (5)

$$[HX] = [HX]_s - [Na^{+}]_s - [H^{+}] + [OH^{-}] + [B] \quad \ldots \ldots (6)$$

Therefore

$$\frac{[X^{-}]}{[HX]} = \frac{[Na^{+}]_s + [H^{+}] - [OH^{-}] - [B]}{[HX]_s - [Na^{+}]_s - [H^{+}] + [OH^{-}] + [B]}$$

Taking logarithms

$$\log \left( \frac{[X^{-}]}{[HX]} \right) = \log \left( \frac{[Na^{+}]_s}{[HX]_s - [Na^{+}]_s} \right) + \log \left( 1 + \frac{[H^{+}] - [OH^{-}] - [B]}{[Na^{+}]_s} \right) - \log \left( 1 - \frac{[H^{+}] - [OH^{-}] - [B]}{[HX]_s - [Na^{+}]_s} \right)$$
Now \([H^+] - [OH^-] - [B]\) is small compared to \([Na^+]_s\) and \([HX]_s - [Na^+]_s\).

Therefore

\[
\log \left( \frac{[X^-]}{[HX]} \right) = \log \left( \frac{[Na^+]_s}{[HX]_s - [Na^+]_s} \right) + \frac{[H^+] - [OH^-] - [B]}{2.3} \times \\
\left( \frac{1}{[Na^+]_s} + \frac{1}{[HX]_s - [Na^+]_s} \right)
\]

Substituting back in (4)

\[
pK_A = pK_1 + \log \left( \frac{[Na^+]_s}{[HX]_s - [Na^+]_s} \right) + \frac{[H^+] - [OH^-] - [B]}{2.3} \times \\
\left( \frac{1}{[Na^+]_s} + \frac{1}{[HX]_s - [Na^+]_s} \right) - \log \frac{[B]}{[HB^+]} - \frac{2A\sqrt{I}}{1 + \sqrt{I}} - b^I \quad I \ldots (7)
\]

Since the term containing \([H^+]\) is small, approximate evaluations of \([H^+], [OH^-]\) and \([B]\) are adequate. \([H^+]\) is found from equation (1)

\[
- \log [H^+] = pK_1 + \log \left( \frac{[X^-]}{[HX]} \right) - \frac{0.5175 \sqrt{I}}{1 + \sqrt{I}}
\]

\([B]\) is found from the spectrophotometric data as described below, and \([OH^-]\) is so small in the acid buffers used that it is negligible. Thus the ratio \([X^-] / [HX]\) may be evaluated.

The ratio \([B] / [HB^+]\) is determined spectrophotometrically.
The Beer-Lambert law for absorption of light by a solution states:

\[ D = \log \frac{I_0}{I} = \epsilon c l \]

where \( D \) is the optical density, \( I_0 \) and \( I \) are the intensities of the emergent and incident rays, \( \epsilon \) is known as the extinction coefficient, \( c \) is the molar concentration, and \( l \) is the length in centimetres of the cell.

In the buffer solution, the optical density is made up of independent contributions from the amine and cation forms so that

\[ D = \epsilon_{\text{HB}^+} [\text{HB}^+] l + \epsilon_B [B] l \]

therefore

\[ \epsilon ([\text{HB}^+] + [B]) l = \epsilon_{\text{HB}^+} [\text{HB}^+] l + \epsilon_B [B] l \]

where \( \epsilon \) is the extinction coefficient of the buffered solution.

\[ [\text{HB}^+] (\epsilon - \epsilon_{\text{HB}^+}) = (\epsilon_B - \epsilon) [B] \]

\[ \frac{[B]}{[\text{HB}^+]} = \frac{\epsilon - \epsilon_{\text{HB}^+}}{\epsilon_B - \epsilon} \]

Since the stoichiometric concentrations of the amine were the same in acid, alkaline and buffered solutions

\[ \frac{[B]}{[\text{HB}^+]} = \frac{D - D_{\text{HB}^+}}{D_B - D} \]

The ratios may be evaluated more accurately if they are nearly unity. Thus a buffer with a pH nearly equal to the \( pK_a \) of the amine must be used, and the wavelength must be chosen so that \( D_{\text{HB}^+} \) and \( D_B \) are substantially different in magnitude.
For $\text{pK}_a$ values determined in 20% dioxan, the Debye-Hückel equation used to evaluate the activity coefficients requires modification. The full Debye-Hückel equation takes the form

$$\ln f_{\pm} = - \frac{|z_1 z_2| e^2}{2\varepsilon k T} \cdot \frac{K}{1 + K a} \quad \text{(8)}$$

where $K = \left( \frac{8 \pi N e^2}{1000 \varepsilon k T} \right)^{1/2}$.

$e$ is the charge on a proton, $\varepsilon$ is the dielectric constant of the solvent, $k$ is Boltzmann's constant, $T$ is the absolute temperature, $N$ is Avogadro's number, $a$ is the mean diameter of the ions involved which have charges of $z_1$ and $z_2$. The equation is usually abbreviated

$$\log f_{\pm} = - \frac{A |z_1 z_2| \sqrt{\gamma}}{1 + B a \sqrt{\gamma}} \quad \text{(9)}$$

where $A$ and $B$ are adjustable parameters. In water at $25^\circ$, for most ions, $A = 0.5115$, and $B a \approx 1$.

In changing the solvent from water to 20% dioxan, the only value in (8) which changes is the dielectric constant $\varepsilon$. It can be seen that

$A \propto \left( \frac{1}{\varepsilon} \right)^{3/2}$ \quad $B \propto \left( \frac{1}{\varepsilon} \right)^{1/2}$

Hence for solutions of univalent ions ($z_1 = -z_2 = 1$) in 20% dioxan, (9) should read

$$- \log f_{\pm} = \frac{0.5115 \left( \frac{E_W}{E_D} \right)^{3/2} I}{1 + \left( \frac{E_W}{E_D} \right)^{1/2} I}$$
where the subscripts W and D refer to solutions in water and 20% dioxan respectively. Since the dielectric constant of water is 78.5 and of 20% dioxan/water is 62 at 25°, the equation becomes

\[- \log f_+ = \frac{0.729 \sqrt{I}}{1 + 1.13 \sqrt{I}}\]
RESULTS

The tables on the following pages show briefly the crucial figures obtained in the calculation of the $pK_a$ values, as well as the final result. For each compound one set of figures is given in some detail, and the remainder are shown only as results. The tables give the wavelength ($\lambda$) in angstroms ($\AA$) at which the determinations were carried out. The type of buffer used (formate or acetate) is shown, followed by its pH calculated from the stoichiometric ratio of buffer acid to its salt (denoted by $P$).

$$P = pK_1 + \log \frac{[Na^+]_s}{[HX]_s[Na^+]_s}$$

The concentration (c) of the amine is given on the molar scale, followed by the absorption densities of the basic and acidic solutions ($D_B$ and $D_{BH^+}$ respectively). The ionic strength (i) of each buffered solution is given, and then the optical density (d) of the amine in it. The next two columns give $Q$ and $\log Q$ respectively where

$$Q = \frac{D - D_{BH^+}}{D_B - D} = \frac{[B]}{[BH^+]}$$

The fifth column gives values of $S$.

$$S = \frac{1.023 \sqrt{I}}{1 + \sqrt{I}} \quad (\text{or} \quad \frac{1.46 \sqrt{I}}{1 + 1.13 \sqrt{I}})$$

for 20% dioxan solutions). The sixth column gives values of $R$ where

$$R = \left[ \frac{[H^+]}{[Na^+]_s} - \frac{[B]}{2.3} \right] \left( \frac{1}{[Na^+]_s} + \frac{1}{[HX]_s - [Na^+]_s} \right)$$
If \( R \) is positive, it must be subtracted from the other terms in equation. The final column lists the \( pK'_a \) values calculated. These have been plotted against ionic strength, but the graphs have not been reproduced in this thesis. The final figure of each series is the thermodynamic \( pK_a \) value obtained by extrapolating the \( pK'_a \) values to zero ionic strength. These values have been averaged for each compound. To give a better idea of the method of calculation used, all the figures used in calculating one set of \( pK'_a \) values for 1-naphthylamine have been reproduced in detail.

\( pK \) values for formic and acetic acid solutions at 25° are as follows:

<table>
<thead>
<tr>
<th></th>
<th>Water</th>
<th>20% Dioxan</th>
</tr>
</thead>
<tbody>
<tr>
<td>Formic acid</td>
<td>3.75297</td>
<td>4.18090</td>
</tr>
<tr>
<td>Acetic acid</td>
<td>4.75698</td>
<td>5.29089</td>
</tr>
</tbody>
</table>

Unless it is stated otherwise, 1 cm cells were used for the optical density measurements.
1-Naphthylamine

\( \lambda = 3250 \ \text{Å} \)

For the buffer solution,

Acetic acid solution used

<table>
<thead>
<tr>
<th>weight</th>
<th>density</th>
<th>volume</th>
<th>normality</th>
</tr>
</thead>
<tbody>
<tr>
<td>200.34 g</td>
<td>1.000</td>
<td>200.34 ml</td>
<td>0.2009</td>
</tr>
</tbody>
</table>

Sodium hydroxide solution used

<table>
<thead>
<tr>
<th>weight</th>
<th>density</th>
<th>volume</th>
<th>normality</th>
</tr>
</thead>
<tbody>
<tr>
<td>49.97 g</td>
<td>1.009</td>
<td>49.52 ml</td>
<td>0.2002</td>
</tr>
</tbody>
</table>

Total volume, 249.9 ml

\[
[\text{HX}]_s = \frac{200.3 \times 0.2009}{249.9} = 0.16108 \text{ moles l}^{-1}
\]

\[
[\text{Na}^+]_s = \frac{49.52 \times 0.2002}{249.9} = 0.03968 \text{ moles l}^{-1}
\]

\[
[\text{HX}]_s - [\text{Na}^+]_s = 0.12140 \text{ moles l}^{-1}
\]

\[
P = pK_1 + \log \frac{[\text{Na}^+]_s}{[\text{HX}]_s - [\text{Na}^+]_s}
\]

\[
P = 4.756 + \log 0.3269
\]

\[
P = 4.270
\]

As the solutions used for spectral measurements contain buffer solution diluted to \( \frac{4}{5}, \frac{3}{5}, \frac{2}{5} \) and \( \frac{1}{5} \) of the original concentration,

\[
\frac{[\text{Na}^+]_s}{[\text{HX}]_s - [\text{Na}^+]_s} = 0.03174 \quad 0.02581 \quad 0.01587 \quad 0.00794
\]

\[
\frac{1}{[\text{Na}^+]_s} = 126 \quad 63 \quad 42 \quad 32
\]

\[
[\text{HX}]_s - [\text{Na}^+]_s = 0.0971 \quad 0.0728 \quad 0.0486 \quad 0.0243
\]

\[
\frac{1}{[\text{HX}]_s - [\text{Na}^+]_s} = 41 \quad 21 \quad 14 \quad 10
\]

\[
\frac{1}{[\text{Na}^+]_s} + \frac{1}{[\text{HX}]_s - [\text{Na}^+]_s} = 167 \quad 84 \quad 56 \quad 42
\]
In this and other lists of figures, those referring to solutions of high ionic strength are on the left.

The ionic strength is calculated from the equation

\[ I = [Na^+]_s + [Cl^-]_s \]

and is calculated from the weight of amine hydrochloride (0.0862 g, molecular weight 179.6) which was dissolved in 500 ml of water and diluted with buffer solution to \( \frac{3}{5} \) of its original concentration.

\[ [Cl^-] = 1.92 \times 10^{-4} \]

\[ I = [Na^+]_s + 0.0019 \]

\[ = 0.03193 \quad 0.02400 \quad 0.01606 \quad 0.00813 \]

\[ S = \frac{1.023 \sqrt{I}}{1 + \frac{I}{4}} = 0.155 \quad 0.137 \quad 0.114 \quad 0.084 \]

To evaluate \( Q = \frac{D - D_{BH^+}}{D_{BH^+} + D} = \frac{[B]}{[BH^+]_s} \)

\[ D_B = 0.821 \quad D_{BH^+} = 0.003 \]

\[ D = 0.505 \quad 0.511 \quad 0.519 \quad 0.530 \]

\[ Q = 1.589 \quad 1.639 \quad 1.709 \quad 1.811 \]

\[ \log Q = 0.201 \quad 0.215 \quad 0.233 \quad 0.258 \]

To evaluate \( R = - \frac{[H^+]_s - [B]}{2.3} \left( \frac{1}{[Na^+]_s} + \frac{1}{[HX]_s - [Na^+]_s} \right) \).

\( H^+ \) is obtained from the pH of the solution

\[ pH = pK_1 + \log \frac{[Na^+]_s}{[HX]_s - [Na^+]_s} - \frac{0.5115 \sqrt{I}}{1 + \sqrt{I}} \]

\[ pH \quad 4.192 \quad 4.201 \quad 4.213 \quad 4.228 \]

\[ [H^+] \times 10^5 \quad 6.43 \quad 6.30 \quad 6.12 \quad 5.92 \]
[B] is calculated from the equation

\[ B = \frac{D - D_{BH^+}}{D_B - D_{BH^+}} \cdot [HB^+] \]

\[ [B] \times 10^5 \]

\[ = \begin{array}{cccc}
11.51 & 11.69 & 11.87 & 12.11 \\
\end{array} \]

\[ ([H^+] - [B]) \times 10^5 \]

\[ = \begin{array}{cccc}
-5.08 & -5.39 & -5.75 & -6.19 \\
\end{array} \]

Therefore

\[ R = \begin{array}{cccc}
0.001 & 0.001 & 0.002 & 0.004 \\
\end{array} \]

Hence the final \( pK'_a \) values are as follows:

(See equation 7)

<table>
<thead>
<tr>
<th>I</th>
<th>P</th>
<th>log ( Q )</th>
<th>B</th>
<th>(-R)</th>
<th>( pK'_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0319</td>
<td>4.270</td>
<td>-0.201</td>
<td>-0.155</td>
<td>-0.001</td>
<td>3.913</td>
</tr>
<tr>
<td>0.0240</td>
<td>4.270</td>
<td>-0.215</td>
<td>-0.137</td>
<td>-0.001</td>
<td>3.917</td>
</tr>
<tr>
<td>0.0161</td>
<td>4.270</td>
<td>-0.233</td>
<td>-0.115</td>
<td>-0.002</td>
<td>3.920</td>
</tr>
<tr>
<td>0.0081</td>
<td>4.270</td>
<td>-0.258</td>
<td>-0.085</td>
<td>-0.004</td>
<td>3.923</td>
</tr>
</tbody>
</table>

The thermodynamic \( pK_a \) is 3.926.

\[ \lambda = 3010 \text{ \AA} \]

Acetate buffer, \( P = 4.270 \)

\[ c = 1.92 \times 10^{-3} \]

\[ D_B = 0.862 \]

\[ D_{BH^+} = 0.000 \]

<table>
<thead>
<tr>
<th>I</th>
<th>( pK'_a )</th>
<th>( pK_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.319</td>
<td>3.920</td>
<td>3.941</td>
</tr>
<tr>
<td>0.240</td>
<td>3.920</td>
<td>3.934</td>
</tr>
<tr>
<td>0.0161</td>
<td>3.920</td>
<td>3.938</td>
</tr>
<tr>
<td>0.0081</td>
<td>3.920</td>
<td>3.941</td>
</tr>
</tbody>
</table>
\[ \lambda = 3250 \quad \text{Formate buffer, } P = 4.051 \]
\[ e = 1.92 \times 10^{-4} \quad D_B = 0.821 \quad D_{BH^+} = 0.003 \]
\[ I = \quad 0.0404 \quad 0.0304 \quad 0.0203 \quad 0.0101 \]
\[ pK'_a = \quad 3.930 \quad 3.934 \quad 3.937 \quad 3.939 \]
\[ pK_a = 3.943 \]

\[ \lambda = 3010 \quad \text{Formate buffer, } P = 4.051 \]
\[ e = 1.92 \times 10^{-4} \quad D_B = 0.862 \quad D_{BH^+} = 0.000 \]
\[ I = \quad 0.0404 \quad 0.0304 \quad 0.0203 \quad 0.0101 \]
\[ pK'_a = \quad 3.946 \quad 3.946 \quad 3.948 \quad 3.950 \]
\[ pK_a = 3.951 \]

Average \( pK_a = 3.940 \)

2-Naphthylamine

\[ \lambda = 3250 \quad \text{Acetate buffer, } P = 4.287 \]
\[ e = 4.42 \times 10^{-4} \quad D_B = 0.680 \quad D_{BH^+} = 0.004 \]
\[ I \quad D \quad Q \quad \log Q \quad S \quad R \quad pK'_a \]
\[ 0.0334 \quad 0.319 \quad 0.873 \quad -0.059 \quad 0.160 \quad 0.003 \quad 4.183 \]
\[ 0.0251 \quad 0.326 \quad 0.910 \quad -0.041 \quad 0.141 \quad 0.004 \quad 4.183 \]
\[ 0.0169 \quad 0.331 \quad 0.937 \quad -0.028 \quad 0.118 \quad 0.006 \quad 4.191 \]
\[ 0.0086 \quad 0.340 \quad 0.988 \quad -0.005 \quad 0.088 \quad 0.012 \quad 4.192 \]
\[ pK_a = 4.198 \]
<table>
<thead>
<tr>
<th></th>
<th>Acetate buffer, $P = 4.287$</th>
<th>Formate buffer, $P = 4.038$</th>
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<tbody>
<tr>
<td>$\lambda$</td>
<td>$3350 , \AA$</td>
<td>$3250 , \AA$</td>
</tr>
<tr>
<td>$c$</td>
<td>$4.42 \times 10^{-4}$</td>
<td>$4.42 \times 10^{-4}$</td>
</tr>
<tr>
<td>$I$</td>
<td>.0334 .0251 .0169 .0086</td>
<td>.0400 .0301 .0202 .0103</td>
</tr>
<tr>
<td>$pK_a$</td>
<td></td>
<td>4.190</td>
</tr>
</tbody>
</table>

$DB = 0.783 \quad DBH^+ = 0.003$

$DB = 0.680 \quad DBH^+ = 0.004$

Average $pK_a$, $4.204$
4-Methyl-1-naphthylamine

\[ \lambda = 3085 \, \AA \]  \hspace{1cm} \text{Acetate buffer, } P = 4.272
\[ c = 1.27 \times 10^{-4} \]  \hspace{1cm} DB = 0.709 \quad DBH^+ = 0.076

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'_{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0319</td>
<td>.306</td>
<td>.571</td>
<td>-.244</td>
<td>.155</td>
<td>-</td>
<td>4.361</td>
</tr>
<tr>
<td>.0240</td>
<td>.311</td>
<td>.590</td>
<td>-.229</td>
<td>.137</td>
<td>-</td>
<td>4.364</td>
</tr>
<tr>
<td>.0160</td>
<td>.317</td>
<td>.615</td>
<td>-.211</td>
<td>.115</td>
<td>-</td>
<td>4.368</td>
</tr>
<tr>
<td>.0081</td>
<td>.327</td>
<td>.657</td>
<td>-.182</td>
<td>.085</td>
<td>.001</td>
<td>4.370</td>
</tr>
</tbody>
</table>

pK'_{a} = 4.373

\[ \lambda = 3230 \, \AA \]  \hspace{1cm} \text{Acetate buffer, } P = 4.272
\[ c = 1.27 \times 10^{-4} \]  \hspace{1cm} DB = 0.704 \quad DBH^+ = 0.009

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'_{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0319</td>
<td>.306</td>
<td>.571</td>
<td>-.244</td>
<td>.155</td>
<td>-</td>
<td>4.341</td>
</tr>
<tr>
<td>.0240</td>
<td>.311</td>
<td>.590</td>
<td>-.229</td>
<td>.137</td>
<td>-</td>
<td>4.343</td>
</tr>
<tr>
<td>.0160</td>
<td>.317</td>
<td>.615</td>
<td>-.211</td>
<td>.115</td>
<td>-</td>
<td>4.346</td>
</tr>
<tr>
<td>.0081</td>
<td>.327</td>
<td>.657</td>
<td>-.182</td>
<td>.085</td>
<td>.001</td>
<td>4.351</td>
</tr>
</tbody>
</table>

pK'_{a} = 4.355

\[ \lambda = 3085 \, \AA \]  \hspace{1cm} \text{Formate buffer, } P = 4.050
\[ c = 1.27 \times 10^{-4} \]  \hspace{1cm} DB = 0.709 \quad DBH^+ = 0.076

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'_{a}</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0398</td>
<td>.0299</td>
<td>.0200</td>
<td>.0100</td>
<td>.0100</td>
<td>-</td>
<td>4.368</td>
</tr>
<tr>
<td>.0398</td>
<td>.0299</td>
<td>.0200</td>
<td>.0100</td>
<td>.0100</td>
<td>-</td>
<td>4.373</td>
</tr>
<tr>
<td>.0398</td>
<td>.0299</td>
<td>.0200</td>
<td>.0100</td>
<td>.0100</td>
<td>-</td>
<td>4.377</td>
</tr>
<tr>
<td>.0398</td>
<td>.0299</td>
<td>.0200</td>
<td>.0100</td>
<td>.0100</td>
<td>-</td>
<td>4.385</td>
</tr>
</tbody>
</table>

pK'_{a} = 4.388
\[ \lambda = 3250 \text{ Å} \quad \text{Formate buffer, } P = 4.050 \]
\[ c = 1.27 \times 10^{-4} \]
\[ I = 0.0398 \quad 0.0299 \quad 0.0200 \quad 0.0100 \]
\[ pK'_a = 4.343 \quad 4.349 \quad 4.359 \quad 4.374 \]
\[ pK_a = 4.379 \]

\[ \lambda = 3270 \text{ Å} \quad \text{Acetate buffer, } P = 4.604 \]
\[ c = 1.45 \times 10^{-4} \]
\[ I = 0.0405 \quad 0.0304 \quad 0.0203 \quad 0.0102 \]
\[ pK'_a = 4.342 \quad 4.344 \quad 4.348 \quad 4.353 \]
\[ pK_a = 4.356 \]

\[ \lambda = 3125 \text{ Å} \quad \text{Acetate buffer, } P = 4.604 \]
\[ c = 1.45 \times 10^{-4} \]
\[ I = 0.0405 \quad 0.0304 \quad 0.0203 \quad 0.0102 \]
\[ pK'_a = 4.351 \quad 4.352 \quad 4.353 \quad 4.356 \]
\[ pK_a = 4.356 \]
\[ \text{Average } pK_a, 4.368 \]
103.

4-Methyl-2-naphthylamine

\[
\begin{align*}
\lambda &= 3370 \text{ nm} \\
\text{Acetate buffer, } P &= 4.612 \\
c &= 4.49 \times 10^{-4} \\
D_B &= 0.841 \\
D_{BH^+} &= 0.001
\end{align*}
\]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>(pK'_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0412</td>
<td>.484</td>
<td>1.353</td>
<td>.131</td>
<td>.173</td>
<td>.004</td>
<td>4.304</td>
</tr>
<tr>
<td>.0310</td>
<td>.493</td>
<td>1.414</td>
<td>.150</td>
<td>.154</td>
<td>.006</td>
<td>4.302</td>
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<tr>
<td>.0208</td>
<td>.504</td>
<td>1.493</td>
<td>.174</td>
<td>.129</td>
<td>.009</td>
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<td>.0106</td>
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<td>1.553</td>
<td>.191</td>
<td>.096</td>
<td>.018</td>
<td>4.307</td>
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</table>

\(pK_a = 4.306\)

\[
\begin{align*}
\lambda &= 3370 \text{ nm} \\
\text{Acetate buffer, } P &= 4.453 \\
c &= 4.49 \times 10^{-4} \\
D_B &= 0.841 \\
D_{BH^+} &= 0.001
\end{align*}
\]

\[pK'_a = 4.301 \quad 4.290 \quad 4.297 \quad 4.301\]

\(pK_a = 4.306\)

\[
\begin{align*}
\lambda &= 3370 \text{ nm} \\
\text{Acetate buffer, } P &= 4.360 \\
c &= 4.28 \times 10^{-4} \\
D_B &= 0.804 \\
D_{BH^+} &= 0.002
\end{align*}
\]

\[pK'_a = 4.309 \quad 4.310 \quad 4.310 \quad 4.313\]

\(pK_a = 4.313\)
\[ \lambda = 3270 \text{ Å} \quad \text{Acetate buffer, } P = 4.453 \]
\[ c = 4.28 \times 10^{-4} \quad \text{DB} = 0.697 \quad \text{DBH}^+ = 0.005 \]
\[ I = .0363 \quad .0273 \quad .0184 \quad .0094 \]
\[ pK'_a = 4.282 \quad 4.288 \quad 4.295 \quad 4.302 \]
\[ pK_a = 4.309 \]

\[ \lambda = 3370 \text{ Å} \quad \text{Acetate buffer, } P = 4.472 \]
\[ c = 4.29 \times 10^{-4} \quad \text{DB} = 0.736 \quad \text{DBH}^+ = 0.003 \]
\[ I = .0411 \quad .0310 \quad .0208 \quad .0106 \]
\[ pK'_a = 4.311 \quad 4.310 \quad 4.313 \quad 4.312 \]
\[ pK_a = 4.315 \]

Average pK\(_a\), 4.309

4,5-Dimethyl-1-naphthylamine

\[ \lambda = 3320 \text{ Å} \quad \text{Acetate buffer, } P = 4.509 \]
\[ c = 1.01 \times 10^{-4} \quad \text{DB} = 0.580 \quad \text{DBH}^+ = 0.007 \]
\[ I \quad D \quad Q \quad \log Q \quad S \quad R \quad pK'_a \]
\[ .0402 \quad .275 \quad .875 \quad -.058 \quad .171 \quad - \quad 4.396 \]
\[ .0302 \quad .279 \quad .900 \quad -.046 \quad .152 \quad - \quad 4.403 \]
\[ .0202 \quad .286 \quad .949 \quad -.023 \quad .128 \quad - \quad 4.404 \]
\[ .0101 \quad .294 \quad 1.004 \quad .002 \quad .094 \quad .001 \quad 4.416 \]

pK\(_a\) = 4.420
\[ \lambda = 3320 \, \text{Å} \quad \text{Acetate buffer, } p = 4.322 \]
\[ c = 1.01 \times 10^{-4} \quad D_B = 0.580 \quad D_{BH}^+ = 0.007 \]
\[ I = 0.0343 \quad 0.0257 \quad 0.0172 \quad 0.0086 \]
\[ pK'_a = 4.392 \quad 4.397 \quad 4.402 \quad 4.404 \]
\[ \text{pK}_a = 4.410 \]

\[ \lambda = 3330 \, \text{Å} \quad \text{Acetate buffer, } p = 4.604 \]
\[ c = 1.16 \times 10^{-4} \quad D_B = 0.659 \quad D_{BH}^+ = 0.005 \]
\[ I = 0.0405 \quad 0.0304 \quad 0.0203 \quad 0.0102 \]
\[ pK'_a = 4.405 \quad 4.408 \quad 4.408 \quad 4.412 \]
\[ \text{pK}_a = 4.416 \]

\[ \lambda = 3170 \, \text{Å} \quad \text{Acetate buffer, } p = 4.604 \]
\[ c = 1.16 \times 10^{-4} \quad D_B = 0.765 \quad D_{BH}^+ = 0.106 \]
\[ I = 0.0405 \quad 0.0304 \quad 0.0203 \quad 0.0102 \]
\[ pK'_a = 4.405 \quad 4.407 \quad 4.410 \quad 4.414 \]
\[ \text{pK}_a = 4.418 \]

Average \text{pK}_a, 4.416
The measurements were conducted in 4 cm cells.

### 4,5-Dimethyl-2-naphthyamine

<table>
<thead>
<tr>
<th>λ</th>
<th>Acetate buffer, P = 4.472</th>
</tr>
</thead>
<tbody>
<tr>
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<table>
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</thead>
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<table>
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<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pk'a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0408</td>
<td>0.422</td>
<td>1.084</td>
<td>0.035</td>
<td>0.172</td>
<td>-</td>
<td>4.265</td>
</tr>
<tr>
<td>0.0307</td>
<td>0.430</td>
<td>1.0128</td>
<td>0.052</td>
<td>0.153</td>
<td>-0.001</td>
<td>4.266</td>
</tr>
<tr>
<td>0.0205</td>
<td>0.440</td>
<td>1.186</td>
<td>0.074</td>
<td>0.128</td>
<td>-0.001</td>
<td>4.269</td>
</tr>
<tr>
<td>0.0103</td>
<td>0.453</td>
<td>1.267</td>
<td>0.103</td>
<td>0.094</td>
<td>-0.002</td>
<td>4.273</td>
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</table>

pk'a = 4.275

### 4,5-Dimethyl-2-naphthyamine

<table>
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</thead>
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<table>
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</table>

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<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pk'a</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0394</td>
<td>0.0295</td>
<td>0.0197</td>
<td>0.0099</td>
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<td></td>
<td></td>
</tr>
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</table>

pk'a = 4.281

pk'a = 4.276

### 4,5-Dimethyl-2-naphthyamine

<table>
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<tr>
<th>λ</th>
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</thead>
<tbody>
<tr>
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</table>

<table>
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<tr>
<th>c</th>
<th>1.07 x 10^{-4}</th>
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<table>
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<tr>
<th>I</th>
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<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pk'a</th>
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<tbody>
<tr>
<td>0.0321</td>
<td>0.0241</td>
<td>0.0161</td>
<td>0.0081</td>
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pk'a = 4.277

pk'a = 4.274

Average pk'a, 4.274
5-Acenaphthalamine

<table>
<thead>
<tr>
<th>λ</th>
<th>Acetate buffer, P = 4.815</th>
</tr>
</thead>
<tbody>
<tr>
<td>c = 1.19 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>I</td>
<td>D</td>
</tr>
<tr>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>.0408</td>
<td>.509</td>
</tr>
<tr>
<td>.0307</td>
<td>.515</td>
</tr>
<tr>
<td>.0205</td>
<td>.523</td>
</tr>
<tr>
<td>.0103</td>
<td>.533</td>
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</table>

pK_a = 4.584

<table>
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<th>λ</th>
<th>Acetate buffer, P = 4.815</th>
</tr>
</thead>
<tbody>
<tr>
<td>c = 1.19 \times 10^{-4}</td>
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</tr>
<tr>
<td>I = 4.580</td>
<td></td>
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</tbody>
</table>

pK_a = 4.580

<table>
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<th>λ</th>
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</thead>
<tbody>
<tr>
<td>c = 1.19 \times 10^{-4}</td>
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</tr>
<tr>
<td>I = 4.583</td>
<td></td>
</tr>
</tbody>
</table>

pK_a = 4.583

<table>
<thead>
<tr>
<th>λ</th>
<th>Acetate buffer, P = 4.645</th>
</tr>
</thead>
<tbody>
<tr>
<td>c = 1.19 \times 10^{-4}</td>
<td></td>
</tr>
<tr>
<td>I = 4.582</td>
<td></td>
</tr>
</tbody>
</table>

Average pK_a, 4.582
\[ \lambda = 3380 \text{ nm} \]

\[ c = 4.28 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0407</td>
<td>.322</td>
<td>.739</td>
<td>-.131</td>
<td>.172</td>
<td>.002</td>
<td>4.465</td>
</tr>
<tr>
<td>.0306</td>
<td>.336</td>
<td>.755</td>
<td>-.121</td>
<td>.155</td>
<td>.004</td>
<td>4.473</td>
</tr>
<tr>
<td>.0206</td>
<td>.342</td>
<td>.780</td>
<td>-.108</td>
<td>.129</td>
<td>.005</td>
<td>4.482</td>
</tr>
<tr>
<td>.0105</td>
<td>.351</td>
<td>.818</td>
<td>-.087</td>
<td>.096</td>
<td>.011</td>
<td>4.488</td>
</tr>
</tbody>
</table>

\[ \text{Acetate buffer, } P = 4.508 \]

\[ D_B = 0.773 \quad D_{BH^+} = 0.006 \]

\[ \lambda = 3380 \text{ nm} \]

\[ c = 4.28 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0407</td>
<td>.322</td>
<td>.739</td>
<td>-.131</td>
<td>.172</td>
<td>.002</td>
<td>4.465</td>
</tr>
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<td>.0306</td>
<td>.336</td>
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<td>-.121</td>
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</tr>
<tr>
<td>.0206</td>
<td>.342</td>
<td>.780</td>
<td>-.108</td>
<td>.129</td>
<td>.005</td>
<td>4.482</td>
</tr>
<tr>
<td>.0105</td>
<td>.351</td>
<td>.818</td>
<td>-.087</td>
<td>.096</td>
<td>.011</td>
<td>4.488</td>
</tr>
</tbody>
</table>

\[ \text{Acetate buffer, } P = 4.830 \]

\[ D_B = 0.773 \quad D_{BH^+} = 0.006 \]

\[ pK_a = 4.497 \]

\[ \lambda = 3320 \text{ nm} \]

\[ c = 4.28 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK_a</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0407</td>
<td>.322</td>
<td>.739</td>
<td>-.131</td>
<td>.172</td>
<td>.002</td>
<td>4.465</td>
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<tr>
<td>.0306</td>
<td>.336</td>
<td>.755</td>
<td>-.121</td>
<td>.155</td>
<td>.004</td>
<td>4.473</td>
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<td>.005</td>
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</tr>
<tr>
<td>.0105</td>
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<td>.818</td>
<td>-.087</td>
<td>.096</td>
<td>.011</td>
<td>4.488</td>
</tr>
</tbody>
</table>

\[ \text{Acetate buffer, } P = 4.508 \]

\[ D_B = 0.711 \quad D_{BH^+} = 0.013 \]

\[ pK_a = 4.496 \]

\[ \text{Average } pK_a, 4.497 \]
1-Dimethylaminonaphthalene

\[ \lambda = 3100 \text{ } \AA \]

Acetate buffer, \( P = 4.787 \)

\[ c = 1.92 \times 10^{-4} \]

\[
\begin{array}{cccccc}
I & D & \log Q & S & R & \text{pK}_a' \\
0.0325 & 0.505 & 1.413 & 0.150 & 0.219 & 0.002 & 4.415 \\
0.0245 & 0.511 & 1.461 & 0.165 & 0.195 & 0.002 & 4.425 \\
0.0164 & 0.521 & 1.544 & 0.189 & 0.164 & 0.003 & 4.431 \\
0.0083 & 0.536 & 1.681 & 0.226 & 0.121 & 0.007 & 4.433 \\
\end{array}
\]

\[ \text{pK}_a = 4.440 \]

\[ \lambda = 3100 \text{ } \AA \]

Formate buffer, \( P = 4.622 \)

\[ c = 1.62 \times 10^{-4} \]

\[
\begin{array}{cccccc}
I & D & \log Q & S & R & \text{pK}_a' \\
0.0401 & 0.0301 & 0.0202 & 0.0102 \\
\end{array}
\]

\[ \text{pK}_a' = 4.408 \]

\[ \text{pK}_a = 4.414 \]

Average \( \text{pK}_a = 4.422 \)
2-Dimethylaminonaphthalene

\[ \lambda = 3380 \, \text{Å} \]

\[ c = 4.79 \times 10^{-4} \]

\[
\begin{array}{ccccccc}
\text{I} & \text{D} & \text{Q} & \text{log Q} & S & R & \text{pK}_a' \\
0.0328 & 0.483 & 1.601 & 0.204 & 0.220 & 0.005 & 4.358 \\
0.0247 & 0.492 & 1.691 & 0.228 & 0.196 & 0.007 & 4.356 \\
0.0166 & 0.504 & 1.807 & 0.257 & 0.165 & 0.010 & 4.355 \\
0.0086 & 0.515 & 1.922 & 0.284 & 0.123 & 0.021 & 4.359 \\
\end{array}
\]

\[ \text{pK}_a = 4.358 \]

\[ \lambda = 3380 \, \text{Å} \]

\[ c = 4.26 \times 10^{-4} \]

\[
\begin{array}{cccc}
\text{pK}_a' = 4.355 & 4.354 & 4.351 & 4.355 \\
\end{array}
\]

\[ \text{pK}_a = 4.355 \]

\[ \text{formate buffer, } p = 4.622 \]

\[ \text{acetate buffer, } p = 4.787 \]

\[ D_B = 0.774 \quad D_{BH^+} = 0.000 \]

\[ D_B = 0.699 \quad D_{BH^+} = 0.001 \]

\[ \text{Average } \text{pK}_a, 4.355 \]
4-Methyl-1-dimethylaminonaphthalene

\[
\lambda = 3150 \, \AA \\
c = 1.61 \times 10^{-4}
\]

Acetate buffer, \( \rho = 4.821 \)

\[
\begin{array}{cccccc}
I & D & Q & \log Q & S & R \\
0.0341 & 0.391 & 0.755 & -0.122 & 0.224 & - \\
0.0253 & 0.400 & 0.794 & -0.100 & 0.198 & - \\
0.0172 & 0.412 & 0.850 & -0.071 & 0.167 & 0.001 \\
0.0086 & 0.429 & 0.935 & -0.029 & 0.122 & 0.001 \\
\end{array}
\]

\( \rho_{Ka} = 4.730 \)

\[
\lambda = 3150 \, \AA \\
c = 1.61 \times 10^{-4}
\]

Acetate buffer, \( \rho = 4.963 \)

\[
\begin{array}{cccccc}
I & D & Q & \log Q & S & R \\
0.0341 & 0.0253 & 0.0172 & 0.0086 \\
\end{array}
\]

\( \rho_{Ka} = 4.720 \)

\[
\rho_{Ka} = 4.729 \quad 4.731
\]

\( \rho_{Ka} = 4.736 \)

\[
\lambda = 3150 \, \AA \\
c = 1.63 \times 10^{-4}
\]

Acetate buffer, \( \rho = 4.843 \)

\[
\begin{array}{cccccc}
I & D & Q & \log Q & S & R \\
0.0416 & 0.0313 & 0.0209 & 0.0105 \\
\end{array}
\]

\( \rho_{Ka} = 4.708 \)

\[
\rho_{Ka} = 4.711 \quad 4.716 \quad 4.720
\]

\( \rho_{Ka} = 4.725 \)

Average \( \rho_{Ka} = 4.730 \)
4-Methyl-2-dimethylaminonaphthalene

$\lambda = 3410 \AA$
$c = 3.64 \times 10^{-4}$

<table>
<thead>
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<th>$I$</th>
<th>$D$</th>
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<th>log $Q$</th>
<th>$S$</th>
<th>$R$</th>
<th>$pK'_a$</th>
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<td>.122</td>
<td>.010</td>
<td>4.570</td>
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$pK'_a = 4.572$

$\lambda = 3410 \AA$
$c = 3.59 \times 10^{-4}$

$D_B = 0.606 \quad D_{BH^+} = 0.018$

<table>
<thead>
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<th>$D$</th>
<th>$Q$</th>
<th>log $Q$</th>
<th>$S$</th>
<th>$R$</th>
<th>$pK'_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0412</td>
<td>.0310</td>
<td>.0310</td>
<td>.0203</td>
<td>.0106</td>
<td>4.566</td>
<td>4.565</td>
</tr>
</tbody>
</table>

$pK'_a = 4.567$

$\lambda = 3410 \AA$
$c = 1.17 \times 10^{-4}$

$D_B = 0.720 \quad D_{BH^+} = 0.023$

$4 \text{ cm cells.}$

<table>
<thead>
<tr>
<th>$I$</th>
<th>$D$</th>
<th>$Q$</th>
<th>log $Q$</th>
<th>$S$</th>
<th>$R$</th>
<th>$pK'_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0360</td>
<td>.0271</td>
<td>.0271</td>
<td>.0181</td>
<td>.0091</td>
<td>4.572</td>
<td>4.576</td>
</tr>
</tbody>
</table>

$pK'_a = 4.572$

Average $pK'_a$, 4.574
### 4,5-Dimethyl-1-dimethylaminonaphthalene

\[
\lambda = 3150 \ \AA
\]

\[
\varepsilon = 1.34 \times 10^{-4}
\]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>\log Q</th>
<th>S</th>
<th>N</th>
<th>(pK'_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0413</td>
<td>0.387</td>
<td>0.988</td>
<td>-0.005</td>
<td>0.243</td>
<td>0.001</td>
<td>4.731</td>
</tr>
<tr>
<td>0.0310</td>
<td>0.394</td>
<td>1.044</td>
<td>0.019</td>
<td>0.215</td>
<td>0.001</td>
<td>4.735</td>
</tr>
<tr>
<td>0.0207</td>
<td>0.399</td>
<td>1.113</td>
<td>0.046</td>
<td>0.183</td>
<td>0.002</td>
<td>4.470</td>
</tr>
<tr>
<td>0.0104</td>
<td>0.414</td>
<td>1.224</td>
<td>0.088</td>
<td>0.135</td>
<td>0.004</td>
<td>4.744</td>
</tr>
</tbody>
</table>

\(pK_a = 4.748\)

\[
\lambda = 3150 \ \AA
\]

\[
\varepsilon = 1.34 \times 10^{-4}
\]

<table>
<thead>
<tr>
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<th>\log Q</th>
<th>S</th>
<th>N</th>
<th>(pK'_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0331</td>
<td>0.0249</td>
<td>0.0166</td>
<td>0.0084</td>
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<td></td>
<td></td>
</tr>
</tbody>
</table>

\(pK_a = 4.731\)

\[
\lambda = 3150 \ \AA
\]

\[
\varepsilon = 1.41 \times 10^{-4}
\]

<table>
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<th>S</th>
<th>N</th>
<th>(pK'_a)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0416</td>
<td>0.0313</td>
<td>0.0209</td>
<td>0.0105</td>
<td></td>
<td></td>
<td></td>
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</table>

\(pK_a = 4.743\)

Average \(pK_a\), \(4.741\)
4 cm cells were used.

<table>
<thead>
<tr>
<th>I</th>
<th>U</th>
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<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0365</td>
<td>.389</td>
<td>0.997</td>
<td>-0.001</td>
<td>.231</td>
<td>.001</td>
<td>5.518</td>
</tr>
<tr>
<td>.0274</td>
<td>.399</td>
<td>1.051</td>
<td>0.002</td>
<td>.205</td>
<td>.001</td>
<td>5.521</td>
</tr>
<tr>
<td>.0183</td>
<td>.415</td>
<td>1.143</td>
<td>0.058</td>
<td>.172</td>
<td>.002</td>
<td>5.517</td>
</tr>
<tr>
<td>.0092</td>
<td>.431</td>
<td>1.244</td>
<td>0.095</td>
<td>.127</td>
<td>.004</td>
<td>5.523</td>
</tr>
</tbody>
</table>

$pK_a = 4.520$

<table>
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<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0451</td>
<td>.0338</td>
<td></td>
<td></td>
<td>.0226</td>
<td>.0114</td>
<td></td>
</tr>
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</table>

$pK_a = 4.533$

<table>
<thead>
<tr>
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<th>log Q</th>
<th>S</th>
<th>R</th>
<th>pK'</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0360</td>
<td>.0271</td>
<td></td>
<td></td>
<td>.0181</td>
<td>.0091</td>
<td></td>
</tr>
</tbody>
</table>

$pK_a = 4.526$

Average $pK_a$, 4.526
5-Dimethylaminonaphthene

\[ \lambda = 3270 \text{ Å} \]
\[ c = 1.49 \times 10^{-4} \]

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>( pK'_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.0408</td>
<td>0.344</td>
<td>0.690</td>
<td>-1.161</td>
<td>0.241</td>
<td>0.001</td>
<td>5.057</td>
</tr>
<tr>
<td>0.0307</td>
<td>0.354</td>
<td>0.729</td>
<td>-1.137</td>
<td>0.214</td>
<td>0.001</td>
<td>5.060</td>
</tr>
<tr>
<td>0.0205</td>
<td>0.367</td>
<td>0.783</td>
<td>-1.106</td>
<td>0.180</td>
<td>0.002</td>
<td>5.062</td>
</tr>
<tr>
<td>0.0103</td>
<td>0.384</td>
<td>0.859</td>
<td>-0.966</td>
<td>0.134</td>
<td>0.004</td>
<td>5.067</td>
</tr>
</tbody>
</table>

\[ pK'_a = 5.069 \]

\[ \lambda = 3270 \text{ Å} \]
\[ c = 1.49 \times 10^{-4} \]

\[ I = 0.0417 \]
\[ \begin{array}{c}
\text{DB} = 0.782 \\
\text{DBH}^+ = 0.042
\end{array} \]

\[ \begin{array}{c}
\text{DB} = 0.782 \\
\text{DBH}^+ = 0.042
\end{array} \]

\[ pK'_a = 5.057 \]
\[ pK'_a = 5.055 \]
\[ pK'_a = 5.064 \]
\[ pK'_a = 5.065 \]

\[ pK'_a = 5.072 \]

\[ \lambda = 2800 \text{ Å} \]
\[ c = 1.49 \times 10^{-4} \]

\[ I = 0.0417 \]
\[ \begin{array}{c}
\text{DB} = 0.438 \\
\text{DBH}^+ = 0.714
\end{array} \]

\[ \begin{array}{c}
\text{DB} = 0.438 \\
\text{DBH}^+ = 0.714
\end{array} \]

\[ pK'_a = 5.051 \]
\[ pK'_a = 5.051 \]
\[ pK'_a = 5.058 \]
\[ pK'_a = 5.054 \]

\[ pK'_a = 5.060 \]

Average \( pK'_a \), 5.067
4 cm cells were used.

\[ \lambda = 3410 \, \Omega \]  
\[ c = 1.10 \times 10^{-4} \]

Acetate buffer, \( p = 4.827 \)

<table>
<thead>
<tr>
<th>I</th>
<th>D</th>
<th>Q</th>
<th>log Q</th>
<th>S</th>
<th>R</th>
<th>( pK'_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0408</td>
<td>.194</td>
<td>.468</td>
<td>-.330</td>
<td>.241</td>
<td>-</td>
<td>4.916</td>
</tr>
<tr>
<td>.0306</td>
<td>.202</td>
<td>.497</td>
<td>-.303</td>
<td>.214</td>
<td>-</td>
<td>4.916</td>
</tr>
<tr>
<td>.0205</td>
<td>.211</td>
<td>.532</td>
<td>-.274</td>
<td>.180</td>
<td>.001</td>
<td>4.920</td>
</tr>
<tr>
<td>.0103</td>
<td>.224</td>
<td>.585</td>
<td>-.233</td>
<td>.133</td>
<td>.001</td>
<td>4.926</td>
</tr>
</tbody>
</table>

\( pK_a = 4.928 \)

\[ \lambda = 3410 \, \Omega \]  
\[ c = 1.24 \times 10^{-4} \]

Acetate buffer, \( p = 5.006 \)

\( \nu_B = 0.681 \)  
\( D_{BH^+} = 0.000 \)

<table>
<thead>
<tr>
<th>I</th>
<th>( pK'_a )</th>
</tr>
</thead>
<tbody>
<tr>
<td>.0407</td>
<td>4.899</td>
</tr>
<tr>
<td>.0306</td>
<td>4.906</td>
</tr>
<tr>
<td>.0204</td>
<td>4.911</td>
</tr>
<tr>
<td>.0103</td>
<td>4.915</td>
</tr>
</tbody>
</table>

\( pK_a = 4.919 \)

Average \( pK_a = 4.924 \)
In water at $25^\circ$

<table>
<thead>
<tr>
<th>Compound</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Naphthylamine</td>
<td>3.94</td>
</tr>
<tr>
<td>2-Naphthylamine</td>
<td>4.20</td>
</tr>
<tr>
<td>4-Methyl-1-naphthylamine</td>
<td>4.37</td>
</tr>
<tr>
<td>4-Methyl-2-naphthylamine</td>
<td>4.31</td>
</tr>
<tr>
<td>4,5-Dimethyl-1-naphthylamine</td>
<td>4.42</td>
</tr>
<tr>
<td>4,5-Dimethyl-2-naphthylamine</td>
<td>4.27</td>
</tr>
<tr>
<td>5-Acenaphthenamine</td>
<td>4.58</td>
</tr>
<tr>
<td>4-Acenaphthenamine</td>
<td>4.50</td>
</tr>
</tbody>
</table>

In 20% w/w dioxan/water

<table>
<thead>
<tr>
<th>Compound</th>
<th>pK$_a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Dimethylaminonaphthalene</td>
<td>4.43</td>
</tr>
<tr>
<td>2-Dimethylaminonaphthalene</td>
<td>4.36</td>
</tr>
<tr>
<td>4-Methyl-1-dimethylaminonaphthalene</td>
<td>4.73</td>
</tr>
<tr>
<td>4-Methyl-2-dimethylaminonaphthalene</td>
<td>4.57</td>
</tr>
<tr>
<td>4,5-Dimethyl-1-dimethylaminonaphthalene</td>
<td>4.74</td>
</tr>
<tr>
<td>4,5-Dimethyl-2-dimethylaminonaphthalene</td>
<td>4.53</td>
</tr>
<tr>
<td>5-Dimethylaminoacenaphthene</td>
<td>5.07</td>
</tr>
<tr>
<td>4-Dimethylaminoacenaphthene</td>
<td>4.92</td>
</tr>
</tbody>
</table>
Accuracy of the Amino Base Strengths

The method for determining the base strengths depends on the differences in the spectra of the amines and their conjugate acids. The differences are quite large in the compounds studied, the most unfavourable case being 4,5-dimethyl-1-dimethylaminonaphthalene for which the ratio of the absorptions of the base to conjugate acid was 3:1. The ratios for other compounds varied from 10:1 to infinity.

The main errors arise from uncertainties associated with the ultraviolet absorption measurements. Optical densities were accurate to ±0.002 or fewer density units. An error of 0.002 units in the optical densities of the alkaline, acidic, and buffered solutions, taken in the least favourable combination, results in an error of ±0.010 pK units in the final pKₐ value.

The errors in the dissociation constants of the buffer acids vary from 0.7% (for acetic acid in 20% dioxan) to 0.2% (for acetic acid in water) which correspond to 0.003 and 0.001 pK units respectively in the present work. The normalities of the acids and sodium hydroxide used in making up the buffers are accurate to ±0.3% and 0.2% respectively. In addition an error is introduced in making up the buffer solutions, mostly because of the uncertainty in the densities of the constituent solutions, and this is estimated as being ±0.2% for each solution. The total error in making up the buffer solutions should therefore not exceed 0.7% or
0.003 pK units. Hence, the total error in the final results is 
+0.06 pK units. In duplicate pKₐ determinations in different 
buffers at the same wavelength, the difference in fact never exceeds 
twice this value, and it therefore appears to be a realistic error 
to attach to the results. However, a less easily assessable 
error arises because the pKₐ value appears to be slightly dependent 
on the wavelength at which it is measured. Variations of up to 
0.02 pK units were observed at wavelengths differing by 150 Å, but 
the spectra would unfortunately not allow accurate determinations 
to be made at wavelengths differing by more than this amount. 
However, there is not obvious reason for a variation of pKₐ with 
Wavelength, and the error arising from this variation is taken as 
+0.01 pK units, which is the maximum error required to cover all 
the results obtained at different wavelengths.

All the base strengths have been measured in at least two 
different buffer solutions, and the final results are obtained 
by averaging from two to six pKₐ values. The total range of 
results for one compound never exceeds 0.035 pK units; a range 
which is adequately covered by the sum of all the errors mentioned 
above, i.e. +0.03 pK units. However, since each pKₐ value is a 
mean of several results, an error of +0.02 pK units in the mean 
results seems reasonable.
DISCUSSION OF RESULTS

In comparing the $pK_a$ values for the amino and the dimethylamino compounds, it must be remembered that the former were determined in water, and the latter in 20% dioxan-water. Therefore comparisons within each series are valid, but comparisons between the series must be made with extreme caution. However, solvent effects should be small enough to allow differences in one series to be compared with differences in the other.

The general points to be considered for all comparisons of amine $pK_a$s are briefly noted below.

1) Polar effects may stabilize the cation by spreading the ionic charge, or they may destabilize it by inhibiting charge spreading.

2) Resonance effects are important only in the base. They result in aromatic amines being much less basic than aliphatic ones.

3) Solvation stabilizes protonated primary amines by helping to distribute the cationic charge. It is less important in tertiary amines.

4) Steric strain may occur in the amine or its conjugate acid. In an N-substituted amine steric strain may result in rotation of the amino group from the plane of the aromatic ring and consequently in reduced resonance. The amino group rotates until the steric strain is equal to the loss of resonance energy. In the conjugate acid steric strain reduces solvation until the loss of solvation energy balances the consequent reduction in steric strain.
$\mathrm{pK}_a$ of $X$-substituted napthalenes.

$X = \text{NMe}_2$

$X = \text{NH}_2$
In the discussion following, an attempt has been made to assess the importance of each of these effects in relation to the $pK_a$ values obtained.

In the diagram opposite, the $pK_a$ values of the amino compounds have been plotted against the $pK_a$ values of the dimethylamino compounds. The points for the "meta" compounds lie on a straight line, which indicates that the substituent effects on their $pK_a$ values are purely electronic as expected. However, no straight line can be drawn through the points for the "para" compounds, and this points to the importance of steric factors in determining the $pK_a$ values of 1-amino naphthalenes. The nature of these steric factors will be brought out in the discussion.

**The Unsubstituted Amines**

The table below shows the $pK_a$ values for the unsubstituted amines as well as some other data which may be useful in interpreting the results in the present work.
<table>
<thead>
<tr>
<th>Compound</th>
<th>$pK_a$</th>
<th>$pK_a$ (literature)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1-Naphthylamine</td>
<td>3.94</td>
<td>3.92$^{16}$, 94, 95</td>
</tr>
<tr>
<td>2-Naphthylamine</td>
<td>4.20</td>
<td>4.11$^{16}$, 4.16$^{94}$, 4.27$^{95}$</td>
</tr>
<tr>
<td>1-Dimethylaminonaphthalene</td>
<td>4.43</td>
<td>4.88$^{16}$</td>
</tr>
<tr>
<td>2-Dimethylaminonaphthalene</td>
<td>4.36</td>
<td>4.57$^{37}$</td>
</tr>
<tr>
<td>Aniline</td>
<td></td>
<td>4.58$^{38}$</td>
</tr>
<tr>
<td>o-Toluidine</td>
<td></td>
<td>4.42$^{38}$</td>
</tr>
<tr>
<td>N,N-Dimethylaniline</td>
<td></td>
<td>$^{+}4.26^{19}$</td>
</tr>
<tr>
<td>o-Methyl-N,N-dimethylaniline</td>
<td></td>
<td>$^{+}5.07^{19}$</td>
</tr>
<tr>
<td>1-Naphthoic acid</td>
<td></td>
<td>3.70$^{36}$, $^{*}4.53^{1}$</td>
</tr>
<tr>
<td>2-Naphthoic acid</td>
<td></td>
<td>$^{*}4.89^{1}$</td>
</tr>
</tbody>
</table>

* Measured in 20% dioxan/water.

† Measured in 50% v/v aqueous ethanol.

Agreement between the values determined in this work and the literature values is very satisfactory. The difference in the $pK_a$ values of the dimethylaminonaphthalenes in water and in 20% dioxan-water is not unreasonable.

The relative polar effects of the 2,3-benzo and the 3,4-benzo substituents are relevant to a discussion of the relative basicities of 1- and 2-naphthylamines. The $\sigma^*$ values, a measure of the polar effect of a substituent are $^{*}0.026^{3}$ and $^{*}0.042^{7}$ for the 2,3-benzo group and the 3,4-benzo group respectively. As a positive value of $\sigma^*$ indicates an electron attracting group, the 2,3-benzo substituent is a more effective electron donor than the 3,4- group by $^{*}0.07$ sigma units. Thus the 1-naphthylammonium
ion should be more stable than the 2-naphthylammonium ion, and the difference in $pK_a$ values should be about 0.2 (since $\epsilon$ for the $pK_a$'s of aromatic amines is 2.77$^{37}$). In fact the $pK_a$ difference is 0.27 $pK$ units in the opposite direction thus demonstrating the importance of non-polar factors.

Resonance stabilization in 1-naphthylamine is expected to be greater than that in 2-naphthylamine. This follows from the observation that a substituent in the 1-position of naphthalene must be conjugated with the ring system to a greater extent than the same substituent in the 2-position$^{99}$. This is reasonable, as seven resonance structures showing conjugation may be written for 1-substituted naphthalenes, and only six for 2-substituted naphthalenes. There is also experimental evidence for this phenomenon, but it will not be reproduced here. Thus the effect of resonance in the free bases is to make 2-naphthylamine more basic than 1-naphthylamine. Any steric inhibition of resonance would tend to reverse this order of basicities, but as will be pointed out later, such inhibition is at the most of minor importance.

In discussing the relative basicities of 1- and 2-naphthylamines, consideration of the steric requirements of the peri-hydrogen atom of the naphthalene nucleus is relevant. Packer, Vaughan and Wong$^5$ have deduced that the peri-hydrogen atom has greater steric requirements than an ortho methyl group. They attribute this to the fact that unlike a methyl group, the peri-CH group cannot rotate to relieve steric strains.
Steric inhibition of mesomerism has been demonstrated to be negligible in ortho-substituted anilines even with two very large ortho groups (see p. 13) but there is some conflict as to whether or not it exists in 1-naphthylamine. For example dipole moment measurements on a series of aromatic primary amines yielded no evidence for inhibition of mesomerism in 1-naphthylamine, but the infra-red spectroscopic data reported by Krueger does\textsuperscript{22,27}. The spectral measurements are used to calculate the H-N-H bond angles, which are related to the type of hybridization exhibited by the nitrogen orbitals, and consequently to the extent of participation of the nitrogen lone pair of electrons in the C-N bond. Thus the greater the bond angle the more mesomerism is implied. Not only is the extent of mesomerism deduced by a devious process, but the H-N-H bond angle varies in a rather unpredictable manner in the presence of many ortho substituents. Data from this source must therefore be interpreted with extreme caution.

Although the primary amino group appears to be too small to exhibit appreciable interaction with the peri-CH group, the primary ammonium cation, by virtue of its solvation shell, is large enough to do so. Steric inhibition of solvation in the 1-naphthylammonium cation destabilizes it relative to the 2-naphthylammonium ion, and consequently 2-naphthylamine is the stronger base. The effect is similar to that observed in o-toluidine which has a $pK_a$ value 0.16 $pK$ units lower than that of aniline (see table on p. 122) in spite
of the fact that the electronic effect of added methyl group tends to raise the \( pK_a \). Steric inhibition of solvation in the 1-naphthylammonium ion therefore appears to be the major effect making 2-naphthylamine the stronger of the two bases.

Because they have been determined in 20\% dioxan-water, the \( pK_a \) values of the dimethylaminonaphthalenes cannot be directly compared with those found in the literature, which are in water. It will be noted that while the \( pK_a \) values of the dimethylaminonaphthalenes are lower in the less polar solvent, those of the carboxylic acids are greater. On dissociation of a substituted ammonium ion, the ionic concentration remains constant, whereas dissociation of a carboxylic acid yields two ions from a neutral molecule. A change in solvent to one of lower dielectric constant will therefore depress dissociation of the carboxylic acids compared with ammonium ions, as observed.

While 2-naphthylamine is a stronger base than 1-naphthylamine, the order of basicities is reversed in the dimethylaminonaphthalenes. This may readily be explained on the basis of steric effects. Steric effects of ortho groups on mesomerism in dimethylamino compounds have been observed by their influence on dipole moments\(^{26}\), ultraviolet spectra\(^{29}\), reaction rates\(^{30,31}\), and equilibria\(^{14}\). All these have been discussed at some length in the introduction. In the present work it is suggested that the peri-hydrogen atom causes the dimethylamino group in 1-dimethylaminonaphthalene to take up a rotational conformation such that its conjugation with
the aromatic nucleus is impaired. The base is therefore less stable (stronger) relative to 1-naphthylamine than is the base 2-dimethylyaminonaphthalene relative to 2-naphthylamine. The effect is observed throughout the whole series of amines studied, although its magnitude appears to be diminished by substitution in the naphthalene nucleus.

Evidence from dipole moment, reaction rate and ultraviolet spectral studies also suggest that steric inhibition of mesomerism occurs in 1-dimethylaminonaphthalene. The dipole moments of aniline, o-toluidine and 1-naphthylamine are almost the same, but in the corresponding dimethyl amines they are in the approximate ratio of \(3:2:2\)\(^{26}\). The actual figures are shown on page 18. The decrease in dipole moment when dimethylaniline is substituted with an ortho-methyl group or a 2,3-benzo group is attributed to steric inhibition of mesomerism. It has been found that the rate constant for the alkaline hydrolysis of ethyl 4-dimethylamino-1-naphthoate indicates that the \(\sigma\) values of the dimethylamino group is -0.23 instead of its usual value of -0.83\(^6\). The increase is consistent with a loss of more than one half of the usual electron donating power of the dimethylamino group; a result of steric inhibition of mesomerism by the peri-hydrogen atom. In studying the first ultraviolet absorption band at about 310 m\(\mu\) of 1-naphthylamine and its dimethyl derivative, Mataga\(^{100}\) found that in a series of non-polar solvents the wavelengths of the absorption maxima were always greater for the former compound than for the
latter. This was considered to indicate greater mesomeric stabilization in 1-naphthylamine. Moreover the extinction coefficient of 1-dimethylaminonaphthalene (4,700) at the wavelength of maximum absorption was considerably less than that for 1-naphthylamine (6,900). The reduction in extinction coefficient is again indicative of inhibition of mesomerism in the dimethyl amine. It should be mentioned that this substantial difference in extinction coefficients has not been observed either by Steck and Ewing \(^{101}\) or in the present work. However it is thought that the apparent conflict is a result of the different solvents used for the spectral measurements. Steck and Ewing used ethanol, and in the present work water and 20\% dioxan-water were used. Hataga used a series of non-polar solvents, and he has noted a marked solvent effect on the first absorption band of 1-naphthylamine but not on the corresponding band of 1-dimethylaminonaphthalene.

The other factors which might conceivably influence the relative \(pK_a\) values of 1- and 2-dimethylaminonaphthalenes are probably of less importance than the steric strain (resulting inhibition of resonance) already discussed. As has been shown in the introduction, solvation, and therefore steric inhibition of solvation, in tertiary amines is of minor importance. Also the polar effects on the \(pK_a\) values of the \(N\)-dimethylated naphthylamines will be very much the same as those present in the naphthylamines and discussed previously.
The Methyl Substituted Amines

A table of $pK_a$ values used in the discussion is shown below.

<table>
<thead>
<tr>
<th>Compound</th>
<th>$X = \text{NH}_2$</th>
<th>$\text{NMe}_2$</th>
<th>$\text{CO}_2\text{H}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Naphthalenes</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - $X$</td>
<td>3.94</td>
<td>4.43</td>
<td>4.53$^1$</td>
</tr>
<tr>
<td>2 - $X$</td>
<td>4.20</td>
<td>4.36</td>
<td>4.89$^1$</td>
</tr>
<tr>
<td>4 - $\text{Me}-1-X$</td>
<td>4.37</td>
<td>4.73</td>
<td>4.81$^1$</td>
</tr>
<tr>
<td>4 - $\text{Me}-2-X$</td>
<td>4.31</td>
<td>4.57</td>
<td>4.98$^1$</td>
</tr>
<tr>
<td>Benzene:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1 - $X$</td>
<td>4.58$^38$</td>
<td>5.07$^37$, $^4$4.26$^19$</td>
<td></td>
</tr>
<tr>
<td>4 - $\text{Me}-1-X$</td>
<td>5.08$^38$</td>
<td>5.63$^37$, $^4$4.77$^32$</td>
<td></td>
</tr>
<tr>
<td>3 - $\text{Me}-1-X$</td>
<td>4.73$^38$</td>
<td>5.34$^37$</td>
<td></td>
</tr>
<tr>
<td>2 - $\text{Me}-1-X$</td>
<td></td>
<td>$^5$5.07$^19$</td>
<td></td>
</tr>
<tr>
<td>2,4-$\text{diMe}-1-X$</td>
<td></td>
<td>$^5$5.28$^19$</td>
<td></td>
</tr>
</tbody>
</table>

* Determined in 50% v/v aqueous ethanol at 25°C

† Determined in 50% v/v aqueous ethanol at 20°C

Introduction of 4-methyl substituents into 2-amino- and
2-dimethylaminonaphthalene result in the $pK_a$ values increasing by
0.11 and 0.21 $pK$ units respectively, both of which effects are
complicable to the $pK_a$ elevations observed when a meta-methyl
group is introduced into the corresponding benzene amines
(0.15 and 0.27 $pK$ units respectively). It is quite general that
the $pK_a$ values of aromatic dimethylamines are more sensitive than
those of aromatic primary amines to substituents in the aromatic
nucleus. This is reflected in the $\eta$ values for dissociation
of anilinium ions \( (2.77)^{106} \) and of dimethylanilinium ions \( (3.34)^{37} \). The larger \( pK_a \) value of the dimethylanilinium dissociation may reasonably be attributed to the greater positive charge on the nitrogen atom as a consequence of the diminished importance of solvation. The elevation of the \( pK_a \) value of an aryl amine by the introduction of a methyl substituent into the aromatic ring is a general effect, caused by the electron donating properties of the methyl group which results in increased relative stability of the ammonium cation through charge spreading.

Para-methyl groups introduced into 1-naphthylamine and 1-dimethylaminonaphthalene cause increases in \( pK_a \) values of 0.43 and 0.30 \( pK \) units respectively. However, para-methyl groups in aniline and dimethylaniline elevate the \( pK_a \) values by 0.50 and 0.56 \( pK_a \) units respectively. Thus the effect of the methyl substituent in 4-methyl-1-dimethylaminonaphthalene appears to be damped.

A study of some of the \( pK_a \) values of dimethylanilines given in the literature reveals that this case is not unique (see table p. 128). All the relevant \( pK_a \'s have been determined in 50\% v/v ethanol at 25\(^\circ\)C except that for dimethyl-p-toluidine which was determined in the same solvent at 20\(^\circ\)C. No temperature correction is applied to this value because the change is very small. The results to be noted are that while introduction of a para-methyl group in dimethylaniline results in an elevation of base strength
of 0.56 pK units, the same group introduced into dimethyl-o-
toluidine causes a rise of only 0.21 pK units. Even allowing
for the fact that data for this comparison came from two different
sources the difference is quite striking. Moreover the occurrence
of the effect in the benzene series shows by analogy that the
damping of the effectiveness of the 4-methyl group in the
corresponding naphthalene amines is a result of an "ortho" effect
on the dimethylamino group or its cation, and not on the methyl
substituent.

An explanation of this "ortho" effect is offered as follows.
In an unsubstituted aromatic dimethylaniline, the base is considerably
stabilized by conjugation between the lone pair of electrons on
the nitrogen atom and the aromatic \( \pi \) electrons as shown below.

\[
\begin{aligned}
\text{(a)} & \quad \text{(b)} \\
\begin{array}{c}
\text{NMe}_2 \\
\text{NMe}_2
\end{array} & \quad \begin{array}{c}
\text{NMe}_2 \\
\text{NMe}_2
\end{array}
\end{aligned}
\]

If we now add an electron donating substituent, such as a methyl
group, to the meta or para positions of the aromatic ring, the
importance of structures such as (b) is diminished, and the base
becomes less stable. The electron donor, is, of course, much
more effective acting from the para position and its effect may be
barely noticed when it is located meta to the amino group. If the
amino group is unable to conjugate effectively with the aromatic
ring (such as when it is ortho substituted) structures like (b) become unimportant and the base is strengthened. When an electron donor is added to the aromatic ring of this system it has little effect on the now unimportant structures represented by (b), and it therefore destabilizes the base only slightly. The effects of the electron donor on the cations of the hindered and unhindered amines will probably be comparable. It follows then that the overall effect of a *para* electron donating substituent is greater in unhindered amines than in hindered ones.

The $pK_a$ change caused by a 4-methyl substituent in the 2-amine naphthalenes is less than that resulting from similar substitution in the 1-amine naphthalenes. This is a reflection of the general observation that a methyl group donates electrons more effectively to the *para* position of an aromatic ring than to the *meta* position.

**The Dimethyl Substituted Amines**

<table>
<thead>
<tr>
<th>Naphthalenes</th>
<th>$X = \text{NH}_2$</th>
<th>$\text{NMe}_2$</th>
<th>$\text{CO}_2\text{H}^+$</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-Me-1-X</td>
<td>4.37</td>
<td>4.73</td>
<td>4.81</td>
</tr>
<tr>
<td>4-Me-2-X</td>
<td>4.31</td>
<td>4.57</td>
<td>4.98</td>
</tr>
<tr>
<td>4,5-dime-1-X</td>
<td>4.42</td>
<td>4.74</td>
<td>4.61</td>
</tr>
<tr>
<td>4,5-dime-2-X</td>
<td>4.27</td>
<td>4.53</td>
<td>5.00</td>
</tr>
</tbody>
</table>
2-BROMO-4,5-DIMETHYLNAPHTHALENE

Distances in Å

Angles in Degrees

NAPHTHALENE
4,5-Dimethyl-1-naphthylamine is a stronger base than 4-methyl-1-naphthylamine by 0.05 pK units. At first sight this may seem surprising when it is considered that the addition of a 5-methyl group to 4-methyl-1-naphthoic acid increases the acid strength by 0.20 pK units. The acid strengthening effect in the acids has been explained on the basis of the 5-methyl group inhibiting the hyperconjugation of the 4-methyl group. Hyperconjugation is an acid weakening effect, and if it is inhibited the acid will become stronger. However, since the work on naphthoic acids was completed, the crystallographic structure of 2-bromo-4,5-dimethyl-naphthalene has been determined, and the molecular dimensions are shown opposite as well as those of naphthalene. It was found that the 2-bromo-4,5-dimethyl-naphthalene molecule is not perfectly planar, the main distortion being a rotation of 2° about the C₅-C₆ bond. This results in the 5-methyl group being below the general plane of the molecule and in C₆ being above. The effect of this non-planarity on the reactivity of 1,8-dimethyl-naphthalene derivatives is difficult to assess, but it is probably small. Also, the non-planarity may be a specific effect in the compound studied, and other substituted 1,8-dimethyl-naphthalenes may be quite planar. However, it is reasonable to assume that the distance between the methyl groups and the principal in-plane distortions of the naphthalene nucleus will be of comparable magnitude in all 1,8-dimethylnaphthalenes. The main distortions to be noted are the "bending out" of the methyl
groups, and the closing of the gap between C₁ and C₈ from 2.50° in naphthalene to 2.44° in 2-bromo-4,5-dimethylnaphthalene. The steric effect of the peri-hydrogen will therefore be greater in the 4,5-dimethylnaphthalenes* than in the naphthalenes. Ortho groups strengthen aryl carboxylic acids by inhibiting conjugation of the carboxyl groups with the aromatic ring, and the greater "ortho effect" of the peri-hydrogen is a more substantial reason for the greater acidic strength of 4,5-dimethyl-1-naphthoic acid than of 4-methyl-1-naphthoic acid, than the one previously advanced. Steric inhibition of hyperconjugation alone is probably too small an effect to serve as a basis for an increase in acid strength of 0.20 pK units.

The steric effects of the peri-hydrogen may influence the equilibrium between 4,5-dimethyl-1-naphthylamine and its conjugate acid. In the case of 1-naphthylamine it was pointed out that steric inhibition of resonance (a base strengthening effect) was insignificant whereas steric inhibition of solvation (a base weakening effect) was a major effect. The increased steric requirements of the peri-hydrogen atom in 4,5-dimethyl-1-naphthylamine can make little difference to steric inhibition of resonance.

* Following normal nomenclature we should refer to these derivatives as 1,8-dimethylnaphthalenes, in which case the peri-hydrogen is attached to the 4- or 5- position.
and even steric inhibition of solvation cannot be significantly increased, because the effect of the 5-methyl group is to increase the $pK_a$ value.

The fact then that 4,5-dimethyl-1-naphthylamine is a slightly stronger base than 4-methyl-1-naphthylamine must be ascribed to the added inductive effect of the 5-methyl group. As methyl groups exert only a weak hyperconjugative influence on amine-ammonium ion equilibria, their inductive effects should be predominant. The inductive effect of the 5-methyl group may even be enhanced by the presence of the 4-methyl group, because its electric vector is oriented along a line passing much closer to the reaction site than that produced by an isolated 5-methyl group. However it must be realized that the electric vector of the 4-methyl group is similarly deflected away from the reaction site because of the presence of the 5-methyl group, and the two effects may cancel. The effect of an electric vector deflected by a peri-hydrogen atom is used by Bryson to explain the low inductive effects observed in 4-substituted-2-naphthylamines.

Solvating molecules are held by hydrogen bonds which have very little directional character, and small changes in groups inhibiting solvation will have little effect because the solvating molecules are free to move to a position where strain is slight.
4,5-Dimethyl-1-dimethylaminonaphthalene has almost the same $pK_a$ as 4-methyl-1-dimethylaminonaphthalene (see p. 131). The difference is less than the experimental error. In this case the added inductive effect of the 5-methyl group on the $pK_a$ value is opposed by increased steric interaction of the peri-hydrogen with the dimethylamino group, with consequent loss of resonance in the base. These small opposing effects cancel out so that the introduction of the 5-methyl substituent has no effect on the $pK_a$ value.

Substitution of a 5-methyl group into 4-methyl-2-naphthylamine and into 4-methyl-2-dimethylaminonaphthalene results in similar $pK_a$ changes; i.e. in decreases of 0.04 $pK$ units. The differences are almost within the limits of experimental error, but they are probably real because the $pK_a$ values for the two partners of each pair were measured in the same buffer. The direction of the change is unexpected. Introduction of a 5-methyl group increases the basic strength of 4-methyl-1-naphthylamine and of the 4-methyl-2-naphthoate anion by virtue of its positive inductive effect. In both cases (4-methyl-1-dimethylaminonaphthalene and 4-methyl-1-naphthoate anion) where the 5-methyl group does not result in an appreciable increase in basicity, the $+I$ effect has been opposed by increased steric inhibition of mesomerism. However there can be no significant steric effect at the 2-position in naphthalene. The only plausible explanation for the decrease in $pK_a$ observed
ACENAPHTHENE

Distances in Å

Angles in Degrees

NAPHTHALENE
when a 5-methyl group is introduced into the 4-methyl-2-amino-naphthalenes appears to lie in the fact that the 5-methyl group deflects the electric vector of the 4-methyl group away from the amino group, and therefore makes the cations less stable than they otherwise would be. The changes in pK are very small and a minor effect such as that described above might be large enough to explain them.

The Acenaphthenamines

Some pKₐ values to be used in the discussion are shown below.

Both 4- and 5-acenaphthenamine are considerably stronger bases than the corresponding naphthylamines and 4,5-dimethylnaphthylamines. 5-Aacenaphthenamine is 0.64 pK units stronger than 1-naphthylamine and 4-acenaphthenamine is 0.30 pK units stronger than 2-naphthylamine. The corresponding figures for the naphthoic acids are 0.77 and 0.19 pK units respectively.

Reference to the crystal structure of acenaphthene may be useful in interpreting the pKₐ data obtained. Some of the more important distances and angles are shown opposite and compared with those of naphthalene.
There is no obvious reason for the inductive effect of the dimethylene bridge being much different to that of the 4,5-dimethyl "substituent". However, the greater basic strength of the acenaphthenamines than of the corresponding 4,5-dimethylnaphthylamines suggests that the inductive effect of the acenaphthene bridge is indeed rather larger than expected.

The low acid strengths of the acenaphthoic acids have been explained on the basis of the enhanced hyperconjugative power of the dimethylene bridge (relative to two methyl groups) due to the ideal placement of the C-H bonds for maximum overlap with the \( \pi \) electron shell of the aromatic nucleus. Hyperconjugation is an acid weakening effect, because the resulting mesomerism may be extended through the aromatic nucleus and into the undissociated carboxyl group. So far in the discussion of the amine pK\( _a \)s hyperconjugation has been avoided because it will obviously be much less important in influencing the pK\( _a \)s of amines than in influencing the pK\( _a \)s of carboxylic acids. The relative hyperconjugative stabilizations effected in the two series can be estimated from the diagrams below.

![Diagrams showing hyperconjugation](image)

However, it appears that the high basicities of the acenaphthenamines must be due in part to hyperconjugative stabilization of the...
ammonium ions, because the inductive effect of the dimethylene bridge is apparently insufficient alone. Of course hyperconjugation occurs in addition to the normal inductive cation stabilizing effect of the bridge.

Superimposed on the electronic effects is the steric effect of the peri-hydrogen atom on the $pK_a$ of 5-acenaphthenamine. As the effect of the peri-hydrogen in 1-naphthylamine is base weakening because it inhibits solvation of the 1-naphthylammonium ion, and because it is more distant from the amino group in 5-acenaphthenamine, steric inhibition of solvation will be slightly less in the 5-acenaphthenammonium ion than in the 1-naphthylammonium ion. The effect is quite small, and is base strengthening.

In considering the dimethylaminoacenaphthenes, steric effects are superimposed on the electronic effects already mentioned. It is to be noted that the difference in the $\Delta pK_a$ values ($\Delta pK_a = pK_a$ for the substituted naphthalene amine minus $pK_a$ for the unsubstituted naphthalene amine) for the dimethylaminoacenaphthenes ("para", 0.64; "meta", 0.56) is much less than the similar differences for the amino acenaphthenes ("para", 0.64; "meta", 0.30). It will be recalled that a similar situation arose in the corresponding 4-methyl "meta" and "para" naphthalene amines, and the explanation offered on page 130 can be also applied to the acenaphthene case. However, there is an additional factor contributing to the relatively small $\Delta pK$ difference for the
The reduced peri-hydrogen atom interaction in 5-dimethylaminoacenaphthene compared with 1-dimethylaminonaphthalene permits the dimethylamino group to conjugate slightly more efficiently with the aromatic nucleus in the former compound. The effect is base weakening and is probably small.

From the above discussion and from the $pK_a$ values of a series of appropriately substituted naphthoic acids, the relative inductive and hyperconjugative effects of some alkyl substituents in naphthalene may be deduced. It appears that the order of inductive electron release is acenaphthene bridge $>$ 4,5-dimethyl $\geq$ 4-methyl. The order of hyperconjugative electron release is acenaphthene bridge $>$ 4-methyl $\geq$ 4,5-dimethyl.

The Ultraviolet Spectra

The ultraviolet spectra of substituted dimethylanilines have been used to determine the steric inhibition of resonance when these compounds are ortho substituted. The band used was the first absorption band occurring at about 250$\mu m$. For example dimethylaniline and dimethyl-ortho-toluidine have extinction coefficients of 15,500 and 6,400 respectively at the wavelength of maximum absorption. It was thought that useful information on the relative effects of the peri-hydrogen in naphthalene, acenaphthene and 1,8-dimethylnaphthalene may have been gained by comparing the
intensities of ultraviolet absorption in the corresponding bands of appropriate dimethylaminonaphthalenes. Unfortunately this was not possible because the second absorption band in 1-naphthylamines undergoes a substantial bathochromic shift relative to its position in naphthalene and therefore obscures the more interesting first absorption band, making it a dubious source of information on mesomerism in the molecules. In the 2-naphthylamines the first absorption band is quite accessible, but because there can be no steric inhibition of mesomerism in these compounds, it yields no useful information.

In the 1-dimethylaminonaphthalenes an attempt was made to relate the differences in absorption of the acid and base forms to the probable degree of conjugation in the amines. However these values varied along the series in a random manner, and in addition the differences were so small that interpretation was not possible.
Discussion

During the course of this work it was necessary to dimethylate all the naphthylamines, and trimethyl phosphate was chosen as the methylating agent. It is more suitable for this purpose than methyl iodide because it does not give rise to appreciable quantities of tertiary ammonium salts, and it is easier to work with than dimethyl sulphate because it is not as toxic. The technique used in the methylations was based on that of Billman, Radike and Mundy. The amine was heated with trimethyl phosphate at about 250° for some time, and then the complex formed was hydrolysed by boiling with aqueous sodium hydroxide. The organic product was extracted, treated with acetic anhydride to remove primary and secondary amines as their acetyl derivatives, and distilled.

Although the methylation procedure was quite satisfactory for preparing naphthalene compounds with the dimethylamino group in the 1-position, methylation of 4-methyl-2-naphthylamine and 4-acenaphth-enamine gave two products in each case. This was shown by vapour phase chromatography, and the products were separated by
chromatography on alumina. Elemental analysis of the products of methylation of 4-acenaphthenamine showed that they were a dimethylated acenaphthenamine and a trimethylated acenaphthenamine respectively, and similar results were obtained for the products of methylation of 4-methyl-2-naphthylamine. None of these compounds showed infra-red absorption peaks characteristic of an N-H bond, and they must all therefore be tertiary amines. It appeared probable that whereas the dimethylated products were the expected dimethylamino compounds, the trimethylated products were 5-methyl-4-dimethylaminoacenaphthene and 1,4-dimethyl-2-dimethylaminonaphthalene.

![Diagram of chemical structures](image)

**Fig. XII**

In order to test this hypothesis, attempts were made to produce 1-methyl-2-dimethylaminonaphthalene by reacting trimethyl phosphate with 2-naphthylamine. By varying the proportions of the two reactants, and the time and temperature of reaction, this compound was indeed obtained, and the conditions were established under which it can be conveniently synthesized. It was identified by its melting-point, and by its ultraviolet spectrum which was identical with that recorded by Mitchell\(^{107}\) for 1-methyl-2-dimethylaminonaphthalene. By analogy it therefore appears certain that the
### Reaction of 2-Naphthylamine with Trimethyl Phosphate

<table>
<thead>
<tr>
<th>2-NH₂·C₁₀H₇</th>
<th>CH₃PO₄</th>
<th>Temperature</th>
<th>Time</th>
<th>1-CH₂-2-N(CH₃)₂·C₁₀H₆</th>
<th>2-N(CH₃)₂·C₁₀H₇</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
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<td>6.0</td>
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<td>3.25</td>
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<tr>
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<td>63</td>
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<td>10</td>
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<tr>
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<tr>
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<tr>
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<td>15</td>
<td>3.0</td>
<td>240-310</td>
<td>3.5</td>
<td>10*</td>
</tr>
<tr>
<td>50</td>
<td>45</td>
<td>2.7</td>
<td>220</td>
<td>0.7</td>
<td>-</td>
</tr>
</tbody>
</table>

* Relative percentages only.

† Ratio of methyl groups to amine groups.

‡ Heated with a microburner. Heating was otherwise on an oil bath.
trimethylated 4-acenaphthenamine and the trimethylated 4-methyl-2-naphthylamine were in fact the compounds shown in fig. XII (a) and XII (b) respectively.

Investigation of the methylation of 4-methyl-2-naphthylamine and 4-acenaphthene was discontinued at this point because the amines are not easily synthesized. However, 2-naphthylamine and trimethyl phosphate were heated together under a wide variety of conditions to establish the optimum conditions for the preparation of 1-methyl-2-dimethylaminonaphthalene. Some of the relevant data from these experiments is shown in the table opposite. The yields shown were obtained by distilling the product, weighing it, and determining its composition from the areas under the peaks of the vapour phase chromatogram.

It was found that 2-naphthylamine was more difficult to methylate in the aromatic nucleus than either 4-acenaphthenamine or 4-methyl-2-naphthylamine. This is not an unexpected result, as in the latter two cases the carbon atom substituted is activated not only by the "ortho" amino group, but by a "para" alkyl group as well.

It can be seen from the table that the maximum yield of 1-methyl-2-dimethylaminonaphthalene is obtained when 2-naphthylamine is heated with twice the theoretical quantity of trimethyl phosphate at 250-276° for three hours. Under these conditions the reaction may be formulated thus:
\[
2-C_{10}H_7\cdot NH_2 + 2(CH_3)_3PO_4 \rightarrow 1-CH_3-2-N(CH_3)_2-C_{10}H_6
\]

+ \(H_2CH_3PO_4\) + \(H(CH_3)_2PO_4\)

When less trimethyl phosphate is used the yield of C-methylated product falls off, and this may be interpreted as indicating that the methylating agent loses successive methyl groups with increasing reluctance; i.e., the first methyl group to be lost is the strongest methylating agent. Hence high molar ratios of phosphate to amine should favour polyalkylation.

However, it can also be seen from the table that high ratios of phosphate to amine do not give a high yield of C-methylated product. This is probably a temperature effect, and it appears that temperatures above 250° are necessary to obtain a high yield of the 1-methyl amine. Now the product of reaction of an amine with trimethyl phosphate is phosphoric acid or an acid methyl phosphate, and these compounds should form high-boiling salts with the amines present. Hence the reaction temperature may be quite high. However, when an excess of trimethyl phosphate is present, the reaction temperature is largely determined by its boiling-point (193°)\(^1\), and is evidently too low to allow efficient carbon methylation.

It is apparent that the C-methylation reaction may be a result of rearrangement of an ammonium salt, or it may be a result of a direct reaction of a methyl phosphate with the amine. To try to distinguish between these two possibilities, an attempt was made to rearrange
2-dimethyaminonaphthalene by heating it with orthophosphoric acid. When equal weights of the two reactants were heated together at 240-280⁰ for 20 min, 36% of 2-dimethyaminonaphthalene (90% pure by V.P.C.) was obtained, and the infrared spectrum of it showed only a vestige of a peak corresponding to an N-H bond. The rest of the organic product was a high-boiling resin. When the reaction was carried out for a longer period of time, no products boiling in the temperature range expected for simple substituted naphthylamines were isolated. At lower temperatures, the reaction yielded only slightly impure starting material. It was therefore concluded that rearrangement of a 2-dimethyaminonaphthalene phosphate is not a step in the production of 1-methyl-2-dimethyaminonaphthalene. The experiment does not, however, rule out the possibility that the C-methylated product is a result of rearrangement of the 2-trimethylnaphthylammonium ion.

Trimethyl phosphate was also heated with 1-naphthylamine under a variety of conditions to determine whether or not it would methyleate one of the carbon atoms in this compound. Once again the products were isolated by distillation, and the composition of the weighed distillate was determined by vapour phase chromatography. It was found that although 4-methyl-1-dimethyaminonaphthalene was one of the products, it was never produced in high yield, and its formation necessitated using reaction conditions which also gave rise to extensive decomposition of the mixture. Thus the maximum yield of 4-methyl-1-dimethyaminonaphthalene was about 15%, and the volatile product in this case contained five other
major compounds, one of which was probably 1-dimethylamino-2-methylnaphthalene. The infrared spectrum of the mixture showed no peak characteristic of the N-H bond, and all the amine products must therefore be tertiary amines. An attempt to separate them by chromatography on alumina was unsuccessful. The reaction was also carried out in the presence of phosphorus pentoxide, but the products differed little from those produced in the absence of this reagent. It therefore appears that the procedure is not suitable for synthesis of ring-methylated 1-dimethylaminonaphthalenes.

The mechanism of the reaction is not resolved, as it is difficult to devise experiments to differentiate between direct carbon methylation and rearrangement of an ammonium salt. The latter reaction is analogous with the Hoffmann-Martius rearrangement, which has recently been investigated for N-methylated naphthylamines$^{109}$. However, since no appreciable amount of 1-methyl-2-methylaminonaphthalene was produced when 2-dimethylaminonaphthalene was heated with orthophosphoric acid, it appears unlikely, that the C-methylated products are formed by rearrangement of an N-methylated amine. More data is necessary before a definite conclusion can be reached.

No examples of C-alkylation reactions involving trialkyl phosphates were found in the literature. However, there are some reactions which might be considered related; among them, the well-known reaction of acid anhydrides with various aromatic substrates, in the presence of polyphosphoric acid, to give aromatic ketones$^{75,110}$. 

Although this method has been widely used in the C-acylation of phenols, phenolic ethers, and other activated aromatic compounds, it has only recently been used in the C-acylation of aromatic amines. Thus Denton and Suschitsky\textsuperscript{111} heated a series of anilines or benzanilides with some carboxylic acid anhydrides in polyphosphoric acid at 150-155\degree, and obtained a series of ortho- and para- acyl anilines in good yields.

A few alkylations using polyphosphoric acid as a catalyst have also been recorded. For example anisole reacts with iso-propanol at 85\degree in the presence of this reagent to give p-iso-propylanisole, and phenol reacts with cyclohexanol to give ortho- and para- cyclohexylphenols\textsuperscript{37}. Similarly 2-naphthol yields 6-(1-methylcyclohexyl)-2-naphthol when it is heated with polyphosphoric acid and 1-methylcyclohexanol\textsuperscript{79}. However, the only alkylation reaction found in the literature involving amines comes from the work of Chambers\textsuperscript{65}. Esters of polyphosphoric acid (prepared from polyphosphoric acid and an alcohol) were used to alkylate aromatic amines at the nitrogen atoms, and it was found that above 200\degree some C-alkylation occurred. This aspect of the reaction does not appear to have been investigated further. These reactions involving polyphosphoric acid and its esters may in fact be analogous to the reactions discovered in this work, because at high temperatures trimethyl phosphate may lose methanol and form a methyl polyphosphate. There is a precedent for this suggestion in the synthesis of polyphosphoric acid by heating orthophosphoric acid\textsuperscript{75}. Methanol did in fact appear to be produced in the methylation
reactions involving trimethyl phosphate.

Further work is obviously necessary to determine the scope and mechanism of the reaction. Thus it would be interesting to find out if it could be applied to anilines and substituted anilines, and to identify the products when different alkyl phosphates are used as alkylating agents.
Experimental Details

Reagents.

Fluka practical grade trimethyl phosphate was fractionated through a 30 cm Vigreux column, and the middle 70%, b.p. 106-108°/30 mm (193°)108, was collected.

Commercial grades of 1- and 2- naphthylamine were used without further purification. 4-Acenaphthenamine and 4-methyl-2-naphthylamine were prepared as described earlier in this thesis, and were of high purity.

Gas chromatography was carried out at 200° on a column of 10% apiezon L on alkali-washed celite.

Reactions of various compounds with trimethyl phosphate are described below, the headings indicating the amine involved only.

4-Acenaphthenamine

4-Acenaphthenamine (5.4 g) and trimethyl phosphate (5.5 g) were carefully heated together in a 50 ml flask fitted with a vertical air condenser. When the initial exothermic reaction had been controlled by partly immersing the flask in cold water, the two-layered mixture was gently refluxed over a microburner for 30 min. Sodium hydroxide solution (25% w/w, 30 ml) was added to the cooled mixture, and the resinous bottom layer was dissolved by carefully heating it with a microburner. Hydrolysis was completed by heating the mixture on a boiling water-bath for 1 hr. It was
added to water (150 ml), and the mixture was extracted with ether (150 ml, 2 x 50 ml). The ethereal extract was washed with water (100 ml), dried over anhydrous magnesium sulphate, filtered, and the ether was distilled off. Acetic anhydride (6 ml) was added to the residual oil, and the solution was left for 14 hr before it was warmed to 100° for 5 min. It was poured into aqueous sodium hydroxide (10% w/w, 50 ml). The mixture was extracted with ether (40 ml, 2 x 25 ml), and the ether solution was washed with water (30 ml), dried over anhydrous magnesium sulphate, and filtered. Evaporation of the ether left a residue which was distilled to give 4.10 g of oil, b.p. 148-162°/1 mm, smelling of blackberries.

It was chromatographed on activated alumina (200 g), the progress of the bands being followed with the aid of an ultraviolet light.

Elution with petroleum ether (b.p. 55-65°, 1300 ml) yielded 2.47 g of crystals, m.p. 46-48°. Recrystallization from methanol gave 1.84 g (27%) of 5-methyl-4-dimethylaminoacenaphthene, m.p. 62-63°, shown to be pure by vapour phase chromatography. (Found: C, 85.45; H, 8.25; N, 6.45. C_{15}H_{17}N requires C, 85.25; H, 8.1; N, 6.65%).

Elution with a further 2 l of solvent, gradually changing from petroleum ether to benzene, gave 1.63 g of a brown liquid.

Distillation yielded 1.51 g of crystals, m.p. 35-42°, b.p. 154-158°/1 mm. Recrystallization from aqueous methanol yielded 1.16 g (18%) of 4-dimethylaminoacenaphthene, m.p. 53-54°. (Found: C, 85.35; H, 7.6; N, 7.5. C_{14}H_{15}N requires C, 85.25; H, 7.65; N, 7.1%).
4-Methyl-2-naphthylamine

4-Methyl-2-naphthylamine (2.4 g) and trimethyl phosphate (2.4 g), in an apparatus similar to that described above, were refluxed for 35 min after the initial vigorous reaction had subsided. The product was isolated and treated with acetic anhydride as described above. Distillation of the material obtained gave 2.26 g of oil, b.p. 120-132°/1 mm, which was shown by vapour phase chromatography to be composed of two compounds. It was chromatographed on activated alumina (100 g) and an ultraviolet light source was used to illuminate the bands. Elution with petroleum ether (b.p. 55-65°) gave 1.41 g of yellow oil which was shown by vapour phase chromatography to contain two compounds in the ratio 1:9. It was therefore chromatographed again, and distilled to give 0.96 g (34%) of 1,4-dimethyl-2-dimethylamino-naphthalene, b.p. 127-129°/1 mm. (Found: C, 84.1; H, 8.9. C14H17N requires C, 84.35; H, 8.6%).

Elution of both columns with petroleum ether and then with mixtures of petroleum ether and benzene afforded 0.67 g of another oil. Distillation yielded 0.50 g (17%) of 4-methyl-2-dimethylamino-naphthalene, b.p. 136-138°/1 mm (ca. 98% pure by V.P.C.). (Found: C, 84.3; H, 8.25; C13H15N requires C, 84.3; H, 8.15%).

2-Naphthylamine

1. 2-Naphthylamine (50 g) and trimethy phosphate (45 g) were heated together in a 500 ml flask fitted with a vertical air condenser, and a thermometer was partly immersed in the reactants.
(For a reaction on this scale, some caution is necessary when the reactants are initially heated). After the initial reaction, the mixture was heated at 220° for 40 min, and cooled. The amine product was isolated, treated with acetic anhydride, and recovered as usual. The distilled product was 45 g (75%) of 2-dimethylaminonaphthalene, shown by vapour phase chromatography to be 99% pure. It was recrystallized from aqueous distilled methanol to give 32.2 g (65%) of pure product, m.p. 46-47° (46°).

2. 2-Naphthylamine (10 g) and trimethyl phosphate (20 g) were heated together in a 100 ml flask. After the initial exothermic reaction had ceased, the flask was heated for 2.75 hr in an oil bath maintained at 315-325°. The reaction mixture refluxed, and the internal temperature rose from 230° to 275° during the first hour, and then stayed constant. The cooled mixture was hydrolysed with aqueous sodium hydroxide (25% w/w, 60 ml) as usual, and extracted with ether. A solid hindered separation of the organic and aqueous layers, and centrifuging was necessary. The organic product was isolated without being treated with acetic anhydride. It was distilled through a small Vigreux column to give 8.90 g of product, m.p. 32-35°. It was analysed by vapour phase chromatography, and the overall yields were found to be 65% of 1-methyl-2-dimethylaminonaphthalene, and 2% of 2-dimethylamino-naphthalene. Recrystallization of the product from aqueous redistilled methanol gave 5.36 g of 1-methyl-2-dimethylaminonaphthalene, m.p. 36-37° (35-35.5°)112, and a further 1.27 g (m.p. 34-35°)
was recovered from the residues. The ultraviolet spectrum in the region 360-230 μ was identical with the previously reported by Mitchell.  

1-Naphthylamine

1-Naphthylamine (10 g) and trimethyl phosphate were allowed to react together under the usual conditions. The mixture was heated on an oil-bath at 320° for 1.5 hr, during which time the internal temperature rose from 240° to 320°. The mixture was worked up as usual, omitting the acetic anhydride treatment, and distilled to give 4.51 g of oil, b.p. 107-137°/760 mm. The vapour phase chromatogram showed that it contained six major products. These included 4-methyl-1-dimethylaminonaphthalene (ca. 40%) and 1-dimethylaminonaphthalene (ca. 10%). Hence the total yield of 4-methyl-1-dimethylaminonaphthalene was approximately 15%, and this was the highest yield of this compound obtained in several methyllations.

An attempt was made to separate the product mixture into its constituent compounds by chromatography on activated alumina, but it was not successful.

Two methylations were carried out, under the conditions similar to those described above, using solutions of phosphorus pentoxide in trimethyl phosphate, but they failed to give an enhanced yield of 4-methyl-1-dimethylaminonaphthalene.
Attempted Rearrangement of 2-Dimethylaminonaphthalene in Orthophosphoric Acid.

1 2-Dimethylaminonaphthalene (5.0 g) and orthophosphoric acid (90%, 6.0 g) were carefully heated with a microburner, but no reaction was evident. Some water boiled off, and the flask was partly immersed in an oil bath at 305° for 5 min. Two layers formed, and the internal temperature rose to 280°. The cooled product was stirred with aqueous sodium hydroxide (25% w/w, 18 ml) until no further reaction was evident, and was then refluxed for 1 hr. The bright red mixture was poured into water (200 ml) and this was extracted with ether (200 ml, 2 x 100 ml). The ethereal solution was washed with water (100 ml), dried over anhydrous magnesium sulphate, and the ether was evaporated. The residue was distilled through a short Vigreux column, and fractions weighing 0.45 g (b.p. 100-118°/1 mm) and 1.37 g (b.p. 118-126°/1 mm) were collected. Infrared spectra of both were almost identical with that of 2-dimethylaminonaphthalene, although both had small peaks at 2.9 μ corresponding to small amounts of primary or secondary amine. Both contained about 90% 2-dimethylaminonaphthalene (V.P.C.). The remainder of the product was a high-boiling resin.

2 A similar reaction kept at 250-270° for 1.5 hr gave a negligible amount of product boiling in the range expected for simple naphthylamines.

3 A further reaction was carried out, with 5 g of amine and 6 g of orthophosphoric acid, for 1.25 hr on an oil bath at 275°. The "reaction" temperature was 220-240°. When the mixture was
worked up, products weighing 3.06 g (b.p. 116-128°/1 mm) and 0.20 g (b.p. 128-150°/1 mm) were collected. The first was a solid. Both had infrared spectra closely similar to that of 2-dimethylaminonaphthalene except for very small peaks at 2.9 μ. Vapour phase chromatography showed the larger fraction to be 96% starting material, and the smaller fraction to be 95% starting material.
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